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ECOS 2012

The 25th International Conference on Efficiency, Cost,
Optimization and Simulation of Energy Conversion
Systems and Processes

(Perugia, June 26th-June 29th, 2012)

edited by

Umberto Desideri, Giampaolo Manfrida,
Enrico Sciubba

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ECOS 2012

The 25th International Conference on

Efficiency, Cost, Optimization and Simulation
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The 25th ECOS Conference 1987-2012: leaving a mark

The introduction to the ECOS series of Conferences states that “ECOS is a series of international conferences that focus on all aspects of Thermal Sciences, with particular emphasis on Thermodynamics and its applications in energy conversion systems and processes”. Well, ECOS is much more than that, and its history proves it!

The idea of starting a series of such conferences was put forth at an informal meeting of the Advanced Energy Systems Division of the American Society of Mechanical Engineers (ASME) at the November 1985 Winter Annual Meeting (WAM), in Miami Beach, Florida, then chaired by Richard Gaggioli. The resolution was to organize an annual Symposium on the Analysis and Design of Thermal Systems at each ASME WAM, and to try to involve a larger number of scientists and engineers worldwide by organizing conferences outside of the United States. Besides Rich other participants were Ozer Arnas, Adrian Bejan, Yehia El-Sayed, Robert Evans, Francis Huang, Mike Moran, Gordon Reistad, Enrico Sciubba and George Tsatsaronis.

Ever since 1985, a Symposium of 8-16 sessions has been organized by the Systems Analysis Technical Committee every year, at the ASME Winter Annual Meeting (now ASME-IMECE). The first overseas conference took place in Rome, twenty-five years ago (in July 1987), with the support of the U.S. National Science Foundation and of the Italian National Research Council. In that occasion, Christos Frangopoulos, Yalcin Gogus, Elias Gyftopoulos, Dominick Sama, Sergio Stecco, Antonio Valero, and many others, already active at the ASME meetings, joined the core-group.

The name ECOS was used for the first time in Zaragoza, in 1992: it is an acronym for Efficiency, Cost, Optimization and Simulation (of energy conversion systems and processes), keywords that best describe the contents of the presentations and discussions taking place in these conferences. Some years ago, Christos Frangopoulos inserted in the official website the note that “ècos” (’ółkoç) means “home” in Greek and it ought to be attributed the very same meaning as the prefix “Eco-“ in environmental sciences.

The last 25 years have witnessed an almost incredible growth of the ECOS community: more and more Colleagues are actively participating in our meetings, several international Journals routinely publish selected papers from our Proceedings, fruitful interdisciplinary and international cooperation projects have blossomed from our meetings. Meetings that have spanned three continents (Africa and Australia ought to be our next targets, perhaps!) and influenced in a way or another much of modern Engineering Thermodynamics.

After 25 years, if we do not want to become embalmed in our own success and lose momentum, it is mandatory to aim our efforts in two directions: first, encourage the participation of younger academicians to our meetings, and second, stimulate creative and useful discussions in our sessions. Looking at this years’ registration roster (250 papers of which 50 authored or co-authored by junior Authors), the first objective seems to have been attained, and thus we have just to continue in that direction; the second one involves allowing space to “voices that sing out of the choir”, fostering new methods and approaches, and establishing or reinforcing connections to other scientific communities. It is important that our technical sessions represent a place of active confrontation, rather than academic “lecturing”.

In this spirit, we welcome you in Perugia, and wish you a scientifically stimulating, touristically interesting, and culinarily rewarding experience. In line with our 25 years old scientific excellency and friendship!

*Umberto Desideri, Giampaolo Manfrida, Enrico Sciubba*
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VOLUME II
A comparative analysis of cryogenic recuperative heat exchangers based on exergy destruction

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Abstract:
The paper deals with the possibility of optimizing the recuperative heat exchanger for a cryogenic system. The effect of the pressure drop, the heat transfer across a finite temperature difference and the imperfect insulation of the cryogenic recuperative heat exchanger is estimated by a unique measure, which is the exergy destruction. The analysis takes into account the heat exchanger and heat transfer surface type, the flow velocity of the cryogenic agent, the value of the state parameters of the working agent and the outside size of the heat exchanger insulation. The different types of recuperative heat exchangers have equipped a cryogenic refrigeration plant working with air. The simulation program developed for this case calculates for each type of cryogenic recuperative heat exchanger the size of the heat transfer surfaces, the volume, weight and cool-down time. Two different types of heat exchangers, a helically coiled heat exchanger and a plate-fin heat exchanger were analysed considering exergy destruction.

Keywords:
Exergy destruction, Recuperative heat exchanger, Optimization.

1. Introduction

Exergy analysis is an essential tool in technical and economical optimization of thermal systems, during both operation and design phase.

Thermal equipment most frequently used in industrial applications are heat exchangers. A heat exchanger is the typical example of exergy destruction due to heat exchange at finite difference of temperature and pressure drop. A significant number of studies can be found in literature attempting optimization of various types of heat exchangers through minimization of entropy generation.

Ogulata and Doba [1] carried out and experimental and analytical investigation attempting to minimize the entropy generation in a recuperative cross-flow air-air heat exchanger. The concept of path flow length given by the ratio $4L/D$ was introduced and its influence on the exergy efficiency of the heat exchanger was assessed. The optimum value of the path flow length resulting in the lowest value of the number of entropy generation units was determined analytically. The existence of an optimum value for the flow path length is intuitively explained by the two contradictory effects resulting from its increase: the positive effect is the increase in the heat exchanger efficiency, while the negative effect is an increase in the irreversibility due to friction.

Narayan et al [2] investigated analytically the entropy generation optimization for devices with heat and mass transfer (air dehumidifiers, cooling towers, etc.). A non-dimensional parameter was defined as the ratio between maximum enthalpy increase of the cold fluid and maximum decrease of enthalpy of the hot fluid (considering also enthalpy variation due to mass transfer). It was shown...
that an optimum value of this parameter exists for which entropy generation in devices with combined heat and mass transfer exists and its value was determined analytically.

Lerou et al [3] carried out a study attempting to optimize the geometry of a counter-flow heat exchanger using the entropy generation minimization criteria. Unlike conventional design approaches, which take into account estimations of various losses, resulting in a geometry with a certain degree of arbitrary, the analytical study carried out by Lerou et al considered all losses as entropy generation sources. Such an approach made possible to compare and to sum up various types of losses (thermal and friction). By modifying some geometrical parameters of the heat exchangers it was possible to identify those values for which entropy generation reaches the minimum value.

The number of entropy generation units is a fundamental concept in exergy analysis of thermal systems introduced by Bejan [4]. Based on the number of entropy generation units, Sarangi and Chowdhury [5] carried out an analytical investigation of entropy generation in a counter-flow heat exchanger. It was shown that a critical value of the heat exchanger efficiency exists for which the number of entropy generation units reaches a maximum value. The effect of the heat capacity ratio on the critical value of the heat exchanger efficiency was also assessed.

Cornelissen and Hirz [6] integrated life cycle analysis study in the design of a heat exchanger. The concept of life cycle irreversibility was introduced and a design approach was presented, in the aim of using with the highest possible efficiency the exergy of natural resources.

2. The schematic of the gaseous cryogenic refrigeration cycle

The analysis is focused on the recuperative heat exchanger of a gaseous cryogenic refrigeration system. The cryogenic system operates under the following conditions: the temperature level of the cold chamber is $T_c = 180$ K; the minimum temperature difference between the refrigerant (air) and the cold chamber is $\Delta T_c = 3$ K; the temperature of the environment is $T_0 = 300$ K; the temperature difference at the warm end of the recuperative heat exchanger is $\Delta T_h = 6$ K; the pressure of the forward gas stream is $p_2 = 4$ MPa; the pressure of the return gas stream is $p_4 = 0.15$ MPa; the pressure drop in the low temperature chamber (LTC) is $\Delta p_{LTC} = 0.1$ MPa; the isentropic efficiency of the expander is $\eta_s = 0.8$; the mechanical efficiency of the expander (the fraction of the compression work returned to the cycle) is $\eta_m = 0.8$ and the isothermal efficiency of the compressor is $\eta_T = 0.6$; the heat insulation of the recuperative heat exchanger has a medium thermal conductivity $\lambda = 0.033$ W/(m$^2$K), the convective heat transfer coefficient on the external side of the insulation is $h = 10.5$ W/(m$^2$K).

The flow chart and the representation of the cycle in the T-S diagram are presented in Fig. 1. A simple gas expander cycle includes the refrigeration cycles or systems in which expanders are located at the lower temperature level. The refrigerant used in this cycle is air. On being compressed in a compressor $K$, the gas is cooled in a cooler $C$ to a temperature $T_2$ and admitted to a heat exchanger $HX$. The work performed by the compressor is $w_k$ and the heat rejected is $q_k'$. The heat absorbed in the cooler is $q_k''$. After the heat exchanger, the gas is admitted to an expander, $E$, where it expands to a low pressure and goes to a low temperature chamber, $LTC$. In the low temperature chamber, the gas absorbs the heat $q_c$, and is raised in temperature from $T_4$ to $T_5$. Then, the return stream is heated in the heat exchanger by absorbing the heat from the compressed gas (the forward stream). At the warm (high temperature) end of the heat exchanger, the difference in temperature between the forward and return gas streams is $\Delta T_h$. The heat exchanger, expander, and low temperature chamber are insulated from the surroundings.

Different types of heat transfer surfaces have been compared from the point of view of conceiving the available energy during the working processes.
The heat transfer process that occurs in the recuperative heat exchanger of a cryogenic system is accompanied by losses due to gas dynamic resistance at the passing of the forward and return flow gas, heat transfer at variable finite difference of temperature and imperfect thermal insulation.

Noticing that the pressure drops, the destructions due to heat transfer at a variable finite difference of temperature and imperfect thermal insulation are brought about by internal and external irreversibility, the performance of the recuperative heat exchanger has been estimated by a unique amount – the growth rate of the whole exergy loss and destruction of the working processes, \( I_{HX} \).

The heat transfer surface types analyzed and compared from the point of view of conserving the available energy during the working processes have equipped a gaseous air refrigeration plant.

For studying a various number of cryogenic heat exchanger types, a computer program has been conceived, which also calculates the heat transfer surfaces size, volume, weight and cool-down time of these devices based on the Fourier equation [7].

The analysis has been performed under real conditions on a computer program based on the state equation developed by Baehr and Schwier [12] and the thermal and caloric properties of the working agent [8].

![Fig. 1 Refrigeration cycle: (a) flow diagram; (b) T-s diagram.](image)

### 3. Exergy Analysis

In general, in the case of a surface heat exchanger, if the heat flux and the inlet states of the two agents are specified, an increase in the heat transfer surface obviously leads not only to a reduction in the temperature difference between the two fluids, but also to a corresponding growth of the pressure drops and heat leaks due to imperfect thermal insulation. In cryogenic systems, on the other hand, due to the functional interdependence between the different parts, the working parameters of recuperative heat exchangers depend on their own design and conduct.

For cryogenic heat exchangers, the demand for high-level performance from the point of view of efficiency, compactness and heat transfer coefficients together with the concern for low pressure drops has determined their large number of design solutions and analyzing methods.

The great variety of heat transfer augmentation techniques used in the aim of reducing the apparatus size causes the rise in friction coefficients.

At the design stage, it is important to be able to predict if, by using a certain heat transfer augmentation technique, the overall effectiveness of the heat exchanger will be improved or not.
The overall exergy destruction and loss due to the internal and external irreversibility of the working processes in the recuperative heat exchanger is:

$$\dot{I}_{HX} = \dot{I}_{\Delta T} + \dot{I}_{\Delta p_f} + \dot{I}_{\Delta p_r} + \dot{I}_{qs},$$  \hspace{1cm} (1)

where the terms from the right side represent, in order, the destruction exergy rates due to the irreversibility of the heat transfer at a finite difference of temperature - $\dot{I}_{\Delta T}$, throttling corresponding to the pressure drops of the forward - $\dot{I}_{\Delta p_f}$ and return flow - $\dot{I}_{\Delta p_r}$, and the exergy loss due to the imperfect thermal insulation - $\dot{I}_{qs}$.

These destructions and losses are not independent, there is a straight connection between the resistance to flow, the temperature difference between the forward and return streams, the heat exchanger type, the heat transfer surface geometry, the flow velocity and the value of the state parameters of the working agent.

Taking into account the Gouy-Stodola theorem, the exergy destruction due to internal irreversibility in the recuperative heat exchanger may be calculated such as:

$$\dot{I}_{\Delta T} = T_0 \cdot \dot{S}_{\Delta T}^{\text{gen}} = T_0 \cdot Q \left( \frac{1}{T_{m_f}} - \frac{1}{T_{m_f}} \right),$$  \hspace{1cm} (2)

$$\dot{I}_{\Delta p_f} = T_0 \cdot \dot{S}_{\Delta p_f}^{\text{gen}} = T_0 \cdot \frac{\dot{Q}_{ff}}{T_{m_f}},$$  \hspace{1cm} (3)

where $\dot{Q}_{ff}$ represents the thermal effect due to friction in the forward gas stream; considering that the specific shaft work wasted to overcome the friction forces is entirely transformed into thermal energy, namely $d_{ff} = \left| w_{ff} \right|$, (3) becomes:

$$\dot{I}_{\Delta p_f} = T_0 \cdot \dot{m} \frac{w_{ff}}{T_{m_f}},$$  \hspace{1cm} (4)

and finally

$$\dot{I}_{\Delta p_f} = T_0 \cdot \dot{m} \frac{\Delta p_f}{T_{m_f}}.$$  \hspace{1cm} (5)

The loss from imperfect insulation is equal to the absolute value of the heat exergy income from the surroundings:

$$\dot{I}_{qs} = \left| \dot{E}_{x_q} \right|.$$  \hspace{1cm} (6)

Depending on the gas dynamic and heat transfer characteristics, the pressure drops in the forward and return flow may be calculated, for instance, using the following relationship [9]:

$$\Delta p = \frac{\mu^2}{2 v_i} \left( K_e + 1 - \sigma^2 \right) + 2 \left( \frac{v_o}{v_i} - 1 \right) + f A_c A \left( \frac{v_m}{v_i} - \left( 1 - \sigma^2 - K_e \right) \frac{v_o}{v_i} \right),$$  \hspace{1cm} (7)

where the terms in brackets take into account, in order: the heat exchanger entrance effect, the flow acceleration, the core friction and the leaving effect.
In order to avoid the difficulties coming out at the calculation of the medium difference of temperature between the forward and return streams, the heat transfer study is accomplished by the NTU - ε approach [9].

The total heat transfer area on one side of the heat exchanger may be calculated using the following relationship:

\[ A = \frac{NTU \cdot C_{\text{min}}}{k_i}. \]  

(8)

Considering a uniform distribution of the fluid stream on the free flow area, it results:

\[ A = \frac{m}{u}. \]  

(9)

Taking into account (8) and (9), (7) becomes:

\[ \Delta\rho = \frac{u^2}{2} \left[ \left( K_e + 1 - \sigma^2 \right) + 2\left( \frac{v_o}{v_i} - 1 \right) + f \frac{NTU \cdot C_{\text{min}} \cdot u}{k_i} \cdot \frac{v_m}{v_i} \cdot \left( 1 - \sigma^2 - K_e \frac{v_o}{v_i} \right) \right]. \]  

(10)

The determination of the friction factors and the heat transfer convective coefficients on the forward or return flow side is performed on the basis of the heat transfer surfaces criterial equations.

### 4. A comparative analysis of the heat exchanger surfaces performance

Two heat transfer surfaces corresponding to two different types of heat exchangers have been analyzed from the point of view of the overall exergy destruction.

In Fig. 2 a copper coiled tubular heat exchanger with smooth inside surface, characterized by the following design and operating parameters [10,11] is presented: smooth outside surface, compact winding, diameter of the mandrel (central body), \( d_c = 150 \text{ mm} \), transverse tube spacing \( x_1 = 11.5 \text{ mm} \), longitudinal tube spacing \( x_2 = 10 \text{ mm} \), tube outside diameter \( d_o = 10 \text{ mm} \), tube inside diameter \( d_i = 6 \text{ mm} \), the heat transfer and pressure drops are given by the criterial relationships \( Nu_r = 0.0185 \text{Re}_r^{0.99} \) and \( (Eu \cdot n)_r = 8.1 \text{Re}_r^{-0.21} \) [10].

![Fig. 2 Coiled tubular heat exchanger with smooth outside surface.](image)
It has been noticed that, in the specified study conditions, at the variation of the flowing pattern from the forward and return streams, the overall loss $\dot{I}_{HX}$ is practically influenced only by the irreversibility of throttling at the gas passing through the heat exchanger and the incoming heat from imperfect insulation.

Obviously, the rise in $Re_r$ and $Re_f$ leads to a rapid decrease of the heat transfer surface and the cool down time of the heat exchanger (Figs 3. b, 3. c).

At the increase of $Re_r$, the rising effect of both friction factor and mass velocity, from the return stream, more important than the heat transfer surface reduction, involves a quick increase in the overall loss $\dot{I}_{HX}$ (Fig. 3. a).

![Fig. 3. a Variation of exergy destruction rate at the increase of Re_s with Re_p as curve parameter.](image)

![Fig. 3. b Variation of heat transfer surface area at the increase of Re_s with Re_p as curve parameter.](image)
Fig. 3. c Variation of cooling down time at the increase of $Re_s$ with $Re_p$ as curve parameter.

From a certain flow pattern of the return stream, the increase in $Re_f$ leads to a reduction of the heat transfer surface at a higher rate than that of the forward stream friction factor rising, finally involving the decrease in $I_{HX}$.

In Fig. 4 is presented the conduct, at the variation of the flowing pattern from the forward and return streams of a plate-fin heat transfer surface defined by the following design and operating parameters: the heat transfer surface on the forward stream side has lowered plate-fin being of 3/16-11.1 [9] type for which the heat transfer and the resistance to flow are described by relationships $j_f = St_f \cdot Pr_f^{2/3} = 0.1922 Re_f^{0.383}$ and respectively $f_f = 1.03 Re_f^{-0.3968}$; the heat transfer surface on the return gas flow has wavy-fin plate-fin being of 11.44-3/8w [9] type for which $j_r = 0.2285 Re_r^{-0.387}$ and $f_r = 1.197 Re_r^{-0.389}$.

Fig. 4 Plate-fin heat exchanger.
Fig. 5. a Variation of exergy destruction rate at the increase of $Re_s$ with $Re_p$ as curve parameter.

Fig. 5. b Variation of heat transfer surface area at the increase of $Re_s$ with $Re_p$ as curve parameter.
It can be noticed for the plate-fin type heat exchanger has the smallest surface and much reduced thermal inertia. The lowest exergy destruction and losses are registered for the copper coiled tubular heat exchanger with smooth outside surface case, phenomena accompanied by the largest heat transfer surface and longest cool down times (Figs 2 and 4).

Obviously, beside this thermodynamic analysis, a thermo-economic one will provide more information concerning the proper choose of the cryogenic heat exchanger.

5. Conclusions

The large variety of heat transfer surfaces and types of heat exchangers require a procedure for rating their performance.

Noticing that the pressure drops, losses due to heat transfer across a finite temperature difference and heat inlets from the surroundings are due to internal and external irreversibility, in this paper is evaluated the thermodynamic performance of the heat exchanger based on a unique measure – the total exergy destruction and loss.

The heat exchanger has been analyzed operating in a gaseous cryogenic refrigeration system.

For identical values of $Re_s$ and constant values of $Re_p$, $I_{HX}$ value for the plate-fin heat exchanger (fig. 5. a) is higher than the one for the coiled tubular heat exchanger (fig. 3. a).

The situation is reversed for the parameter $A_p/Q$, in the sense that the specific area requirements for the plate-fin heat exchanger (fig. 5. b) is lower than for the coiled tubular heat exchanger (fig. 3. b).

From the stationary operating point of view, the coiled tubular heat exchanger with smooth inside and outside surfaces is the most economic one, being characterized by the smallest exergy destruction.

The plate heat exchanger is the most compact one, with the lowest time to get into a stationary regime.
The exergoeconomic analysis, which takes into account both the operating cost and the capital amortization rate, will offer more information concerning the proper choice of the cryogenic heat exchanger.

**Acknowledgments**

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**Nomenclature**

**Latin symbols**

- $A$: exchanger total heat transfer area on one side, $m^2$
- $A_C$: exchanger minimum free-flow area, $m^2$
- $A_{fr}$: exchanger total frontal area, $m^2$
- $C$: cooler
- $C_{\text{min}}$: minimum flow stream capacity rate, $W/K$
- $c_{\text{min}}$: minimum specific heat, $J/(kgK)$
- $d_c$: heat exchanger’s central body diameter, $m$
- $D_f$: outside fin diameter, $m$
- $d_i$: tube inside diameter, $m$
- $d_o$: tube outside diameter, $m$
- $f$: friction factor
- $E$: expander
- $\dot{E}x$: exergy flux, $W$
- $Eu$: Euler number
- $HX$: heat exchanger
- $j = St \cdot Pr^{2/3}$: generalized heat transfer grouping
- $K$: compressor
- $K_c$: contraction coefficient
- $K_e$: expansion coefficient
- $k_i$: overall heat transfer coefficient, $W/(m^2K)$
- $LTC$: low-temperature chamber
- $\dot{m}$: mass flow, $kg/s$
- $NTU$: number of heat transfer units
- $Pr$: Prandlt number
- $p$: pressure $N/m^2$, fin pitch
- $Q$: heat, $J$
- $\dot{Q}$: heat flux, $W$
- $q$: heat per unit mass, $J/kg$
Friction heat flux, $\dot{Q}_f$

heat inleak from the surroundings, $q_i$, J/kg

Reynolds number

Stanton number

entropy, J/K

entropy rise rate, W/K

absolute temperature, K

mean thermodynamic temperature, K

mass velocity, kg/(m$^2$s)

specific volume, m$^3$/kg

specific shaft work, J/kg

transverse tube spacing, m

longitudinal tube spacing, m

convective heat transfer coefficient, W/(m$^2$K)

fin thickness, m

intermediate shell thickness, m

exchanger effectiveness

mechanical efficiency of the expander (the fraction of the compression work returned to the cycle)

isentropic efficiency of the expander

isothermal efficiency of the compressor

thermal conductivity, W/(mK)

loss due to irreversibility, J

specific exergetic loss, J/kg

exergetic loss flux, W

ratio of free-flow area to frontal area

cool down time, s

ratio of the outside heat transfer area to inside area

cold

external

forward gas stream, friction

generated

hot

heat exchanger

inlet, insulation
\( m \) medium
\( \text{min} \) minimum
\( o \) outlet
\( p \) high pressure gas
\( r \) return gas stream
\( 0 \) environment
\( \Delta p \) pressure drop
\( q_s \) heat inleak
\( s \) low pressure gas
\( \Delta T \) temperature difference

**References**


A Critical Exploration of the Usefulness of Rational Efficiency as a Performance Parameter for Heat Exchangers

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Abstract:
This paper examines and critically explores the possible usefulness of rational efficiencies of heat exchangers, based on the theoretical principles of exergy analysis. The rational efficiency is described first for the simplest possible heat exchanger, consisting of a flat conducting layer between two isothermal reservoirs. Secondly, a rational efficiency is defined for a simple compound heat exchanger with multiple isothermal heat sources and sinks. The concept is then expanded to include heat exchangers wherein heat transfer occurs from one fluid stream to another through a separating wall, with each stream experiencing a pressure loss due to fluid friction that depends on the flow rate of the fluid. The mathematical form of the rational efficiency in terms of the temperatures at which heat transfer occurs and of the environment is investigated. The manner of involvement of heat transfer and fluid friction effects in the rational efficiency is critically examined. Lastly, the relationship of the rational efficiency of a heat exchanger to the overall rational efficiency of a complete plant is considered. Based on the critical and analytical exploration, the authors conclude that rational efficiency is a useful performance parameter for heat exchangers that do not exchange heat directly with the exergetic reference environment.

Keywords:

1. Introduction

It is not common practice for engineers to make use of a rational or exergetic efficiency of heat exchangers for design or performance characterization purposes. For instance, heat transfer textbooks [1] and [2] make no reference to such an efficiency. However, the concept of exergetic or rational efficiency for heat exchangers is not new and [3] provides some useful insights, as well as referring to a definition from Andreev and Kostenko (paper in Russian), 1965, in which the exergetic input and output are based on the exergy changes of the hot and cold streams respectively. The work described in the present paper was undertaken to explore and clarify the possible usefulness of the concept of heat exchanger rational efficiency.

2. Rational Efficiency of Steady State Systems

The rational efficiency of a steady state system with exergy flows in and out, based on the boundary that encloses it, can be defined as the rate of exergy output divided by the rate of exergy input, (1).

\[
\psi = \frac{\dot{E}_\text{out}}{\dot{E}_\text{in}}
\]  

(1)

Certain exergetic inputs or outputs are constrained in such a way that a net exergy input cannot be represented as separate input and output components. For example, the pumping work for a flow...
stream cannot be represented as an exergy input associated with flow work and an exergy output associated with flow work because of a flow constraint. Conceptual devices that can be used to explain and visualize such flow constraints are provided in [4]. A flow constraint arises because a stream of fluid that passes through, for example, one side of a heat exchanger is contained by an impermeable, rigid boundary that ensures the fluid’s separation from the remainder of the system and, in steady state, that there is no net mass or substance transfer to the system from the stream. For fixed entry and exit states of the flow stream, the net flow work transfer (which has a corresponding net exergy transfer) is fully determined. An approach to applying (1) to a heat exchanger is included in [5,6]. The nature of irreversibility and entropy generation within a heat exchanger has been understood for a long time, e.g. [7,8], and it is straightforward to express the rational efficiency in terms of these quantities and the rate of exergy input, as in (2).

\[
\psi = \frac{\dot{e}_{in} - I}{\dot{e}_{in}} = \frac{\dot{e}_{in} - T_0 \dot{S}_{gen}}{\dot{e}_{in}}
\]

(2)

3. The Simplest Heat Exchanger

The simplest heat exchanger might be a flat conducting layer of uniform thickness that separates a thermal reservoir at a constant temperature \( T_H \) from a thermal reservoir at a lower constant temperature \( T_L \). The heat transfer within the plate is assumed to be one-dimensional and so the heat flux is given by (3).

\[
\phi = \frac{\dot{Q}}{A} = \frac{k(T_H - T_L)}{l} = U(T_H - T_L)
\]

(3)

3.1. Description of the simplest heat exchanger in exergetic terms

For the purposes of exergy analysis the heat exchanger is assumed to exist in the context of an all-enclosing infinite environment that has a uniform temperature \( T_0 \), as shown in Fig. 1. For compactness in some of the expressions that follow, it is convenient to define the dimensionless temperature ratios \( \theta_H = T_H / T_0 \) and \( \theta_L = T_L / T_0 \).

![Fig. 1. Schematic representation of the simplest heat exchanger for exergy analysis purposes. The perfect thermal insulation shown is for the exclusion of any incidental heat losses or gains.](image)

By imagining a boundary around the heat exchanger, the exergy flows into and out of the ‘system’ are easily identified as
\[ \dot{e}_H = \dot{Q} \frac{T_H - T_0}{T_H} = \phi A \frac{T_H - T_0}{T_H} \]
\[ = \phi A (\theta_H - 1) / \theta_H \]  
and
\[ \dot{e}_L = \dot{Q} \frac{T_L - T_0}{T_L} = \phi A \frac{T_L - T_0}{T_L} \]
\[ = \phi A (\theta_L - 1) / \theta_L. \]

In exergetic terms, the simplest heat exchanger can be described as a system that accepts heat transfer at temperature \( T_H \) and provides the same amount of heat transfer at temperature \( T_L \). The heat transfer at \( T_H \) is associated with an exergy input if \( T_H > T_0 \), while the heat rejection at \( T_L \) is associated with an exergy output if \( T_L > T_0 \). From (4) and (5), if either \( T_H \) or \( T_L \) equals \( T_0 \) then the corresponding exergy flow is zero. The rate of exergy destruction in the simple heat exchanger is given by (6) and the rate of entropy generation by (7).

\[ i = \dot{e}_H - \dot{e}_L = \dot{Q} \frac{T_H - T_L}{T_H T_L} \]
\[ = \phi A \frac{\theta_H - \theta_L}{\theta_H \theta_L} \]  
\[ \dot{S}_{\text{gen}} = \frac{i}{T_0} = \dot{Q} \frac{T_H - T_L}{T_H T_L} \]
\[ = \phi A \frac{(\theta_H - \theta_L)}{T_0} \frac{1}{\theta_H \theta_L} \]  

3.2. The rational efficiency of the simplest heat exchanger

Equation (1) can be applied to the simplest steady state heat exchanger, yielding (8) to (10).

\[ \psi = \frac{(T_L - T_0)/T_L}{(T_H - T_0)/T_H} \bigg|_{T_L > T_0} \]
\[ = \frac{(\theta_L - 1)/\theta_L}{(\theta_H - 1)/\theta_H} \bigg|_{\theta_L > 1} \]  
\[ \psi = \frac{(T_H - T_0)/T_H}{(T_L - T_0)/T_L} \bigg|_{T_H < T_0} \]
\[ = \frac{(\theta_H - 1)/\theta_H}{(\theta_L - 1)/\theta_L} \bigg|_{\theta_H < 1} \]  
\[ \psi = 0 \bigg|_{T_L < T_0 < T_H} \]
\[ = 0 \bigg|_{\theta_L < 1 < \theta_H} \]  

Given that \( T_L < T_H \), there is a range of values of \( T_L \), defined by the inequality \( T_L < T_0 < T_H \), for which the rate of exergy output is zero while there is a positive rate of exergy input. Of particular note are the cases where either \( T_H \) or \( T_L \) equals \( T_0 \), where there is one exergy input only. It is important to
note too that, in accordance with (5), the rate of exergy output at $T_L$ is negative when $T_L$ is less than $T_0$, i.e. the direction of the exergy flow associated with the heat rejection is into the simple heat exchanger. Similarly, the rate of exergy input at $T_H$ is negative if $T_H$ is less than $T_0$. Where both $T_H$ and $T_L$ are below $T_0$, there is a flow of exergy from the heat sink to the heat source and the rates of exergy transfer at both $T_H$ and $T_L$ have the opposite direction to the heat transfer rate.

### 3.2.1. Dependence of rational efficiency on $T_0$ for the simplest heat exchanger

Perhaps the strongest objection to the use of rational efficiency as a performance parameter for heat exchangers is the dependence of the rational efficiency on the temperature of the all-enclosing equilibrium environment. As illustrated by (8) to (10), for a given heat exchanger operating between given constant temperature thermal reservoirs with a given rate of heat transfer there are two distinct ranges of $T_0$ for which the rational efficiency has positive values and one range of values of $T_0$ for which the rational efficiency is zero. However, as has been shown in these equations, a certain simplification can be achieved by using dimensionless temperatures in place of the actual temperatures. In exergetic terms, the dependence of the performance of the simple heat exchanger on the reference temperature is inescapable.

### 3.2.2. Usefulness of $\psi$ as a performance parameter for the simplest heat exchanger

The simplest heat exchanger, as described thus far, can be regarded as having an energy-based efficiency of 100%, as the energy input from the source thermal reservoir at $T_H$ equals the energy output to the sink thermal reservoir at $T_L$. For simplicity, any incidental heat losses or gains are excluded here. The commonly-used concept of heat exchanger effectiveness is not directly applicable to the simple heat exchanger, as neither thermal reservoir involves a temperature glide. In contrast, the rational efficiency is a meaningful performance parameter. In ‘pure’ thermodynamics an ideal heat exchanger would be a compound heat engine, requiring access to the reference environment, but in finite dimensional thermodynamics the rational efficiency quantifies the goodness of a compromise device, not requiring access to the reference environment, for which the irreversibility rate, or the rate of entropy generation, can be minimized or optimized. The economic optimum may not correspond to the thermodynamic goal of irreversibility rate minimization.

![Fig. 2. Schematic representation of a simple compound heat exchanger for exergy analysis purposes.](image-url)
4. Simple Compound Heat Exchanger

Fig. 2 represents a simple compound heat exchanger consisting of $n$ simple heat exchangers. There are multiple heat source thermal reservoirs at temperatures $T_{H,i}$ and each of these has a corresponding heat sink thermal reservoir at temperatures $T_{L,i}$. Fig. 3 is a diagram of temperature versus cumulative heat transfer rate for this simple compound heat exchanger.

![Diagram of temperature versus cumulative heat transfer rate for a simple compound heat exchanger](image)

**Fig. 3.** Plot of temperature versus cumulative heat transfer rate for a simple compound heat exchanger.

4.1. Rational efficiency of the simple compound heat exchanger

The rational efficiency of the simple compound heat exchanger can be expressed by inserting the appropriate expressions for $\dot{Q}_{in}$ and $\dot{Q}_{out}$ into (1), yielding (11), which contains four conditional summation terms.

$$\psi = \frac{\sum_{i, \text{diff } \theta_{L,i} > 1} \dot{Q}_i \frac{\theta_{H,i} - 1}{\theta_{L,i}} + \sum_{i, \text{diff } \theta_{L,i} < 1} \dot{Q}_h \frac{\theta_{L,i} - 1}{\theta_{H,i}}}{\sum_{i, \text{diff } \theta_{L,i} < 1} \dot{Q}_i \frac{\theta_{H,i} - 1}{\theta_{L,i}} + \sum_{i, \text{diff } \theta_{L,i} > 1} \dot{Q}_h \frac{\theta_{L,i} - 1}{\theta_{H,i}}} \tag{11}$$

By way of clarifying the notation for $\dot{Q}_i$ in (11) and $\dot{Q}_h$ in (12), these terms are all positive in the direction from higher to lower temperature.

5. Simple Heat Exchangers with a Temperature Glide

By extension of the concept represented in Fig. 2 it is possible to imagine a composite heat source and a composite heat sink that each involve a continuous temperature range. A heat exchanger consisting of a conducting medium is envisaged. A diagram of temperature versus cumulative heat transfer rate for this type of simple heat exchanger is represented in Fig. 4. The corresponding expression for rational efficiency is (12).

$$\psi = \frac{\int_{\forall \theta_{L} > 1} \frac{\theta_{L} - 1}{\theta_{H}} dQ + \int_{\forall \theta_{H} < 1} \frac{\theta_{H} - 1}{\theta_{L}} d\dot{Q}}{\int_{\forall \theta_{L} < 1} \frac{\theta_{L} - 1}{\theta_{H}} dQ + \int_{\forall \theta_{H} > 1} \frac{\theta_{H} - 1}{\theta_{L}} d\dot{Q}} \tag{12}$$
6. Heat Exchangers with Two Fluid Streams

Actual heat exchangers with two fluid streams are usually insulated externally so that extraneous heat losses or heat gains are kept small or negligible. These effects can be accounted for readily in the rational efficiency, but, for brevity are not addressed in the present paper.

The principal causes of irreversibility are the heat transfer that occurs from one fluid to the other over finite temperature differences and fluid friction within each fluid stream within the heat exchanger. Another, usually relatively minor, mechanism of irreversibility is due to heat fluxes within the fluid streams or within the material of the heat exchanger that are not part of the overall heat transfer from one stream to the other. In traditional calculations for heat exchangers a continuously varying quasi-equilibrium state is assumed for the bulk fluid of each stream as it moves through the heat exchanger. The use of this same assumed quasi-equilibrium state is also useful, as a practical approximation, in exergy analysis.

Fig. 4. Plot of temperature versus cumulative heat transfer rate for a simple heat exchanger wherein there is a temperature glide within the heat source and within the heat sink. In this particular case $T_0$, the temperature of the environment, happens to lie between the maximum temperature of the heat source and the minimum temperature of the heat sink.

6.1. Incorporating convective heat transfer irreversibility into the rational efficiency

Fig. 5 illustrates how the convection temperature differences for heat transfer within a two-fluid counter flow heat exchanger can be represented on a diagram of the same type as Figs 3 and 4. The temperature curves can be established from the standard techniques for heat exchanger analysis and a rational efficiency for convection and conduction between the fluid streams can be calculated using (12).
6.2. Incorporating fluid friction irreversibility into the rational efficiency

Traditional approaches can be used to establish the quasi-equilibrium thermodynamic states at the positions where each fluid stream enters or leaves a heat exchanger, e.g. positions 2, 7, 4 and 8 for recuperator R in Fig. 6, allowing for the pressure losses within each fluid stream. The net rate of exergy input to a heat exchanger from a flow stream that passes through it is

\[
\dot{E}_{\text{in}} = m\left(\beta_i - \beta_o\right) = m\left[(h_i - T_0s_i) - (h_o - T_0s_o)\right].
\]

If the rate of exergy input (13) is negative then the exergetic interaction is an output. Thus (13) can be used to evaluate the numerator and the denominator for (1) to calculate the overall rational efficiency of the heat exchanger to include all irreversibilities.

7. Numerical Example

In order to better illustrate the usefulness of the rational efficiency, the case of a gas turbine with recuperation of heat will be analysed, Fig. 6. The heat exchanger of the system is a gas-to-gas plate and fin heat exchanger, Fig. 7, and its purpose is to preheat the compressed air before it enters the combustion chamber using the residual heat of the exhaust gases from the turbine.
In order to analyse the system, fixed parameters for the environment were chosen, namely $T_0 = 300 \text{ K}$ and $p_0 = 1.013 \text{ bar}$. The maximum temperature of the cycle was set at $T_3 = 1,500 \text{ K}$. The pressure ratio was taken as $r_p = 10$. Table 1 shows the main imposed parameters for the analysis. The simulation was performed using Engineering Equation Solver.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isentropic efficiency of the compressor</td>
<td>$\eta_C = 86%$</td>
</tr>
<tr>
<td>Isentropic efficiency of the turbine</td>
<td>$\eta_T = 87%$</td>
</tr>
<tr>
<td>Combustion efficiency</td>
<td>$\eta_{\text{comb}} = 98%$</td>
</tr>
<tr>
<td>Mechanical efficiency of the system</td>
<td>$\eta_M = 99.8%$</td>
</tr>
<tr>
<td>Flow stream mass velocity on the air side of the heat exchanger</td>
<td>$G_a = 25 \text{ kg/(m}^2\text{s)}$</td>
</tr>
<tr>
<td>Flow stream mass velocity on the gas side of the heat exchanger</td>
<td>$G_g = 12 \text{ kg/(m}^2\text{s)}$</td>
</tr>
</tbody>
</table>

The calculated thermal efficiency of the entire plant, taking into account all the irreversibilities due to pressure losses and temperature differences, is $\eta = 38.19\%$.

Using (1), the rational efficiency of the plant is:

$$\psi = \frac{\dot{E}_{\text{out}}}{\dot{E}_{\text{in}}} = \frac{\dot{E}_6}{\dot{E}_{\text{fuel}}} = 31.8\%.$$  

According to (13) and (1), the rational efficiency of heat exchanger R is 78.1%. The dependence of this rational efficiency on the ambient temperature is plotted in Fig. 8 for values of $T_0$ from 273 K to 313 K.

![Fig. 8. Heat exchanger rational efficiency as a function of the ambient temperature $T_0$.](image)

The approach of [6] for evaluating sub-rational efficiency values for heat transfer and fluid friction yields the following:

$$\psi_Q = 87.2\% \quad \text{Rational efficiency value for heat transfer}$$

$$\psi_{F,A} = 95.8\% \quad \text{Rational efficiency values for fluid friction}$$

$$\psi_{F,B} = 93.5\%$$

$$\psi = 78.1\%.$$  

8. Heat Exchanger Rational Efficiency in the Overall Context
Using the approach of [9,10], the exergy interaction rate diagram, Fig. 9, is drawn. Without regenerator R the exergy input with the fuel $\dot{E}_{\text{fuel}}$ would be increased significantly and the exergy destruction in the exhaust discharge region $\dot{E}_{0,\text{EXH}}$ would be greater. Thus, the regenerator allows recovery of part of the exergy that would be wasted with the exhaust. A high rational efficiency $\psi_R$ for the regenerator has a calculable influence on the rational efficiency of the entire plant. It can be seen from Fig. 9 that this is somewhat analogous to the way in which the rational efficiency of the turbine or that of the compressor has a calculable influence on the overall rational efficiency.

**Fig. 9. Exergy interaction diagram for the gas turbine plant.**

**Conclusions**

On the basis of the considerations presented in this paper the authors believe that rational efficiency has a useful role as a performance parameter for heat exchangers wherever they do not interact directly with the exergetic reference environment. This performance parameter can be useful in the process of design optimization in the same way as the efficiency of an electric motor or generator can be useful: in the optimum design the efficiency will be maximized subject to constraints. The rational efficiency of a heat exchanger (provided it is non-zero) has a calculable influence on the rational efficiency of the entire plant. Thus, the heat exchanger rational efficiency can also be useful in following the trail of exergy currents in exergoeconomics. Where a heat exchanger interacts directly with the environment, to reject or accept heat, it is an exergy destruction sink and has a rational efficiency of zero.

**Acknowledgments**

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**Nomenclature**

- $A$ area, $m^2$
- C compressor
- CC combustion chamber
- EXH exhaust discharge region
- FCS flow constraint system
- $G$ mass velocity, $kg/(m^2s)$
specific enthalpy, J/kg
irreversibility rate, W
thermal conductivity, W/(mK)
length, m
number of heat exchanger elements
pressure, Pa
rate of heat transfer, W
regenerator
reversible heat engine
reversible node
pressure ratio
specific entropy, J/(kgK)
rate of entropy generation, W/K
turbine
absolute temperature, K
absolute temperature, lower than $T_H$, K
absolute temperature of the environment, K
overall heat transfer coefficient, W/(m$^2$K)
rate of work, W
Greek symbols
specific flow exergy function, J/kg
temperature ratio
rate of exergy transfer, W
heat flux, W/m$^2$
efficiency
rational efficiency
Subscripts and superscripts
reference environment
fluid streams
air
combustion
fluid friction
associated with the fuel
gas
generation
high
into a specified system
inlet
index of a heat exchanger element
low
mechanical
outlet
out of a specified system

$Q$ relates to heat transfer

References


A new procedure for the design of LNG processes by combining Exergy and Pinch Analyses

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Abstract:
This paper presents an alternative design procedure for LNG processes. The procedure combines Pinch and Exergy Analyses and uses a new graphical representation of exergy. In the literature, there are several approaches using the pinch method and exergy analysis in combination for process design; however, most of them use exergy analysis as a post design tool. One goal of this work is to illustrate the inclusion of exergy calculations in the early stages of design, such as in energy (and exergy) targeting. The paper introduces a novel diagram for exergy and energy targeting which utilizes a new energy quality parameter called exergetic temperature. This quality parameter can be used to manipulate exergy changes caused by pressure adjustments. The main objective of the pressure manipulations is to reduce both heat and power requirements. The Reverse Brayton process is used as a case study for illustrating both the novel diagram and the proposed methodology.

Keywords:
Exergy Analysis, LNG, Low Temperature Processes, Pinch Analysis, Process Design.

1. Introduction
The simultaneous use of Pinch Analysis (PA) and Exergy Analysis (EA) is not a new idea. Actually, PA is based on the Second Law of Thermodynamics [1] (by matching hot and cold streams with corresponding level of energy; highest hot stream temperature with highest cold stream temperature and vice versa for the cold end). PA has proven to be a powerful tool for designing Heat Recovery Systems (HRSs). By decomposing an HRS into two independent systems, one above pinch and the other below pinch, the PA method provides a set of designs with minimum heating and cooling requirements. However, PA is rather limited in the sense that it only uses temperature as the main design variable. For an HRS operating below ambient temperature ($T_0$), where expansion and/or compression of streams are required, pressure is also an important variable. Moreover in HRSs, if pressure is manipulated, the utility requirements may be reduced in comparison to those obtained with the traditional PA. Exergy Analysis (EA) is a good alternative for measuring the minimum exergy required or rejected by the HRS. Conveniently, temperature, pressure and composition are the main process variables utilized in the calculation of exergy content in process streams. However, EA can be used only to evaluate design decisions but not to guide them, thus it does not give conclusive information with respect to the design [2]. For process analysis of HRSs operating below or across ambient temperature, using PA and EA in combination can be beneficial due to the large amount of energy in form of shaftwork required for compression in the utility system (refrigeration cycles). In addition, for processes operating below ambient temperature where external cooling is provided by compression, there is an intimate relationship between thermal energy and mechanical energy, thus both temperature and pressure are important design variables. In this paper, the Reverse Brayton process for the liquefaction of natural gas is used as a case study to illustrate the use of the new energy quality parameter and the new graphical diagram.

Typically for processes with operating conditions below ambient temperature, the most important objective is to supply the cooling demand i.e. refrigeration load. Because refrigeration is expensive
and its demand increases significantly as temperature is reduced, such processes tend to become rather complicated. The temperature differences inside heat exchangers can be very small, (i.e. less than 5 K) hence the heat transfer area is quite large causing other problems related to material stresses and two-phase flow distribution. In conclusion, the design of such processes is not a simple task and should be done in a systematic way by utilizing the energy resources available in the best possible way.

1.1 Background

Many attempts have been made for combining PA and EA [1, 3-10]. In 1979, Umeda et al. [3] presented the so-called energy availability diagram where the Carnot factor is used as ordinate and enthalpy as abscissa. Here, the hot and cold streams of an HRS are plotted in a composite manner generating two curves: a total hot curve and a total cold curve. Later, Linnhoff [1] and Linnhoff and Dhole [4] re-named this diagram as the Exergy Composite Curves (ECCs). An example diagram of the ECCs is shown in Fig. 1a. The area between the hot and the cold ECC provides a quantitative measure of the exergy losses due to heat transfer since the axes are enthalpy and Carnot factor. There is also a corresponding Exergy Grand Composite Curve (EGCC) that shows the exergy loses related to the heat transfer between the process and the utility system. The EGCC can be used for appropriate placement of heat engines, heat pumps and refrigeration cycles (load, level and number of cycles).

In 1993, Staine and Favrat [5] extended the ECCs diagram for representing the exergy losses not only due to process-to-process heat transfer (exergy destruction), but also those caused by dissipation (pressure drop) and the losses during the fabrication of the heat exchanger. In addition, they introduced an alternative diagram for representing exergy losses in mechanical equipment (pumps, fans, compressors). Later, Sorin and Paris [6, 8] used the so-called exergy load distribution approach (introduced by Sorin and Brodyansky [11]) and minimum energy requirements obtained from the traditional PA. They used their approach for improving a hydrogen production process [6] and found that the number of unit operations was reduced and the yield increased by 2%. In 1997, Feng and Zhu [7] presented the referred to as energy level – enthalpy diagram where they combined the exergy loss representations of HRSs and mechanical equipment. The energy level concept was first suggested by Rant [12] with his Exergy/Energy ratio which can be directly applied to energy streams. For material streams with change in state conditions from state 1 to state 2, Ishida and Kawamura [13] introduced the energy level factor (A) as shown in Eq. (1).

\[ A = \frac{\dot{E}_2 - \dot{E}_1}{H_2 - H_1} = \frac{\Delta \dot{E}}{\Delta H} \]  \hspace{1cm} (1)

![Fig. 1](image-url)
The Energy Utilization Diagram (EUD) was also introduced by Ishida and Kawamura [13]. Fig. 1b shows the EUD for three unit operations: $U_1$ (first heat exchanger), $U_2$ (compressor) and $U_3$ (second heat exchanger). Here, the so-called energy donors (top curves) and energy acceptors (bottom curves) are plotted for all unit operations, not only the HRS. The energy level is plotted on the $y$ axis while enthalpy is plotted on the $x$ axis. Both the EUD and the diagram presented by Feng and Zhu [7] illustrate the irreversibilities in all unit operations. The difference between these two diagrams is that the first (EUD) plots the energy donors and acceptors of all unit operations in a consecutive manner according to the process flow. Intermediate state conditions are calculated for a more accurate shape of the energy donor and acceptor curves. In contrast, the diagram developed by Feng and Zhu [7] is focused on illustrating the exergy losses without considering the order in which the unit operations are plotted, and without calculating intermediate states for other units than heat exchangers.

In our research group, efforts have been placed on developing new process design methodologies that combine PA and EA. Anantharaman et al. [9] used the energy level parameter in the construction of a set of energy donor and energy acceptor composite curves for complete processes. In contrast to the EUD and the diagram proposed by Feng and Zhu [7], Anantharaman et al. [9] constructed the so-called energy level composite curves by sorting, in descending order, the energy level of the streams without taking into consideration the order in which the streams appear in the process flow diagram or the corresponding unit operations. Thus, with the energy level composite curves, one can clearly visualize where in the process the most energy demanding streams are. However, in terms of process integration, this diagram does not indicate which streams should be coupled. Aspelund et al. [10] proposed the Extended Pinch Analysis and Design (ExPAnD) procedure. One objective of the ExPAnD methodology is to maximize the utilization of the exergy obtained by pressure changes and to minimize work consumption (or maximize work production) while maximizing heat recovery. The ExPAnD method utilizes ten heuristic rules to achieve this goal. At present, the ExPAnD method has only been applied in processes operating below ambient.

1.2 Scope

This paper is focused on demonstrating the use of a new representation of exergy for the design of Heat Recovery Systems where both temperature and pressure are important design variables. A extended problem definition for such systems has been proposed by Aspelund et al. [10].

“Given a set of process streams with a supply state (temperature, pressure, and resulting phase) and a target state, as well as utilities for power, heating, and cooling; design a system of heat exchangers, expanders, compressors, pumps and valves in such a way that the irreversibilities are minimized”

Examples of such systems are low temperature processes e.g. refrigeration and liquefaction processes. The graphical representation described here fits very well in HRSs where the streams have near-constant heat capacity and that may or not require a change in pressure from their supply to target conditions. In the case that process streams require pressure modifications; these streams should be preferable in gas phase and with a behavior close to an ideal gas. One could use this graphical representation for real gases for a first and quick estimation; however, the results should be contrasted with those from rigorous calculations.

For the design of the extended HRSs, a similar procedure to the one described by Linhoff et al. [14] for the design of HRS is proposed. The extended procedure is decomposed into several stages: Data Extraction, Exergy Calculations, Exergy Targeting, Process Modifications, Design and Optimization. The new diagram is proposed to be used for exergy targeting e.g. for obtaining the minimum exergy requirement (minimum theoretical work required) in HRSs, as well as in the process modification stage. This diagram can be used as alternative to the ECCs introduced by Linhoff and Dhole [4].

2. Exergy Analysis of Heat Recovery Systems
In HRSs, two classes of exergy are included for EA calculations: the thermo-mechanical exergy of process streams and the exergy of heat. In the literature, the thermo-mechanical exergy [15] is also referred to as physical exergy [16] and its components are also known as thermal and mechanical exergies [17, 18]. In other publications [19, 20], the sum of the thermo-mechanical (physical) and chemical exergy is referred to as thermal exergy. Petela [20] calls mechanical exergy to the sum of the potential and thermo-mechanical (physical) exergy. Thus, in order to have a homogeneous nomenclature in this paper, the authors decided to use self-explanatory names for the exergy of material streams and its components. Thus for a material stream, the exergy content given by its temperature and pressure is referred to as thermo-mechanical exergy and its components are named as temperature based exergy and pressure based exergy.

2.1 Exergy of process streams

The exergy of process streams is equal to the sum of thermo-mechanical and chemical exergies. If the process stream is under a change of state from \((T_1, p_1)\) to \((T_2, p_2)\) and there is no chemical reaction, separation or mixing, then the chemical exergy of the stream can be omitted in the exergy calculations. The thermo-mechanical exergy is given by (2).

\[
\dot{E}_{TM}^{\text{ex}}(T, p) = \dot{H}(T, p) - \dot{H}(T_0, p_0) - T_0 \left[ \dot{S}(T, p) - \dot{S}(T_0, p_0) \right]
\]

(2)

\[
\dot{E}^T(T, p) = \dot{H}(T, p) - \dot{H}(T_0, p_0) - T_0 \left[ \dot{S}(T, p) - \dot{S}(T_0, p) \right]
\]

(3)

\[
\dot{E}^p(T, p) = \dot{H}(T_0, p_0) - \dot{H}(T_0, p_0) - T_0 \left[ \dot{S}(T_0, p) - \dot{S}(T_0, p_0) \right]
\]

(4)

The thermo-mechanical exergy \((\dot{E}_{TM}^{\text{ex}})\) can be further decomposed into temperature based exergy \(\dot{E}^T\) and pressure based exergy \(\dot{E}^p\). While this decomposition is not unique and thus has no fundamental meaning, commonly accepted definitions for \(\dot{E}^T\) and \(\dot{E}^p\) are given in (3) and (4). Fig. 2a shows this exergy decomposition graphically. Despite the arbitrariness of this decomposition, it is used for a better understanding of the temperature and pressure based exergy contributions in various processes.

2.2 Exergy of heat

The exergy accompanying heat also depends on temperature. In Fig. 2b, it is shown that the exergy of heat (energy stream) above \(T_0\) is horizontally asymptotic to \(\dot{Q}\) (5); the maximum work produced
even by an ideal (reversible) heat engine will always be less than the energy supplied by the heat reservoir ($Q$). Below $T_0$, the exergy of heat is vertically asymptotic to zero (6); the minimum work required to take $Q$ from $T_0$ to lower temperatures can be equal or larger than $Q$ (at $T = 0$ K, an infinite amount of work is required). Actually, for temperatures below half of $T_0$, the ratio between $E^o$ and $Q$ is larger than one (see Fig. 1b), meaning that heat (cooling) is more valuable than work.

$$\dot{E}^o = \dot{Q} \left(1 - \frac{T_0}{T}\right) \quad \text{for} \quad T \geq T_0$$  \hspace{1cm} (5)

$$\dot{E}^o = \dot{Q} \left(\frac{T_0}{T} - 1\right) \quad \text{for} \quad T \leq T_0$$  \hspace{1cm} (6)

### 3. A novel energy quality parameter

As discussed earlier in the paper, the established energy quality parameters such as Carnot factor and the so-called energy level introduced in different forms have limitations when used in graphical representations and for exergy targeting. This section introduces a new energy quality parameter that enables new graphical diagrams that are easy to construct and that can be used explicitly for exergy targeting.

#### 3.1 Exergetic temperatures

If the specific heat capacity is assumed constant with respect to temperature in the range from $T$ to $T_0$, Equation (3) can be rewritten as (7). In addition, if ideal gas conditions are valid, then (4) can be simplified as shown in (8). Notice that in (7) and (8), the factors inside the square brackets have temperature dimension and absolute temperature units (K). These factors are the so-called exergetic temperatures. For $\dot{E}^r$, the exergetic temperature ($T^E^r$) is only a function of temperature, and for $\dot{E}^p$, the corresponding exergetic temperature ($T^E^p$) is only a function of pressure. The procedure for obtaining (7) and (8) from (3) and (4) is straightforward using the correct thermodynamic relations for the abovementioned assumptions. Several textbooks have derived (7) and (8) in a very comprehensive manner [15, 16, 19, 21], thus the mathematical development for these equations is left to the reader. One should notice that the assumption of ideal gas conditions only has an effect in (8) and not in (7).

$$\dot{E}^r = \dot{m}c_p \left[T_0 \left(\frac{T}{T_0} - \ln\left(\frac{T}{T_0}\right) - 1\right)\right] - \dot{m}c_p T^E^r$$  \hspace{1cm} (7)

$$\dot{E}^p = \dot{m}c_p \left[T_0 \ln\left(\frac{p}{p_0}\right)\right] = \dot{m}c_p T^E^p$$  \hspace{1cm} (8)

Notice that the simplified equations for $\dot{E}^r$ and $\dot{E}^p$ in (7) and (8) exhibit a linear relation between the exergetic temperatures and the corresponding exergy components. This linear relationship is of course also present between the changes in exergetic temperatures and the corresponding changes in exergy components as shown in (9) and (10).

$$\Delta \dot{E}^r_{1 \rightarrow 2} = \dot{m}c_p \left[T_0 \left(\frac{T_2 - T_1}{T_0} - \ln\left(\frac{T_2}{T_1}\right)\right)\right] = \dot{m}c_p \Delta T^E^r_{1 \rightarrow 2}$$  \hspace{1cm} (9)

$$\Delta \dot{E}^p_{1 \rightarrow 2} = \dot{m}c_p \left[T_0 \ln\left(\frac{p_2}{p_1}\right)\right] = \dot{m}c_p \Delta T^E^p_{1 \rightarrow 2}$$  \hspace{1cm} (10)
3.2 Relationship between $\Delta T^{ET}$ and $\Delta T^{EP}$

For a given state $(T, p)$, $T^{ET}$ and $T^{EP}$ are independent variables (the first is only a function of temperature and the second is only a function of pressure). For a process where the pressure of a stream changes from $p_1$ to $p_2$ (i.e., compression or expansion), there will be a corresponding change in temperature from $T_1$ to $T_2^{ise}$ unless an isothermal process is assumed. While the pressure $p_2$ after the process can be regarded as a specification (fixed by some process needs), the corresponding temperature $T_2^{ise}$ is a function of the initial temperature $T_1$ and the pressure ratio ($p_2/p_1$). Considering the definitions of the changes in exergetic temperatures in (9) and (10), it is clear that for such processes, while $T_2^{EP}$ only depends on $p_2$ which is specified, $T_2^{ET}$ depends on $T_2^{ise}$, which in turn depends on $T_1$ and the ratio $p_2/p_1$. This means that $T_2^{ET}$ depends on both $T_1^{ET}$ and $p_2/p_1$ (or $\Delta T^{ET}_{1 \rightarrow 2}$). If the change in pressure follows an isentropic path, Equations (11) and (12) are valid for ideal gases. If (11) is substituted into (10), then the change in pressure based exergy for an isentropic operation is shown in (13). The resulting change in temperature based exergy is given by (14). Thus, the change in $T^{ET}$ is defined as in (15).

\[
\frac{T_2^{ise}}{T_1} = \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}}
\]

(11)

\[-\dot{W}^{ise} = \dot{m} c_p \left( T_2^{ise} - T_1 \right)\]

(12)

\[
\Delta \dot{E}^{EP}_{ise} = \dot{m} c_p \left[ T_0 \ln \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right] = \dot{m} c_p \left[ T_0 \ln \left( \frac{T_2^{ise}}{T_1} \right) \right]_{p_1 \rightarrow p_2} = \dot{m} c_p \Delta T^{EP}_{lse} \left|_{p_1 \rightarrow p_2} \right.
\]

(13)

\[
\Delta \dot{E}^{ET}_{ise} = \dot{m} c_p \left[ \frac{T_2^{ise} - T_1}{T_1} - T_0 \ln \left( \frac{T_2^{ise}}{T_1} \right) \right]_{p_1 \rightarrow p_2} = \dot{m} c_p \Delta T^{ET}_{lse} \left|_{p_1 \rightarrow p_2} \right.
\]

(14)

\[
\Delta T^{ET}_{lse} = T_1 \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} - T_0 \ln \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}}
\]

(15)

By substituting (13) into (14) and realizing that $T_2^{ise} - T_1 = \Delta T^{ise}$, the relationship between the changes in exergetic temperatures reduces to the very simple form given in (16). Equation (17) is the equivalent relation for exergy components and shaft-work for isentropic changes of pressure.

\[
\Delta T^{ise} = \Delta T^{ET}_{lse} + \Delta T^{EP}_{lse}
\]

(16)

\[
-\dot{W}^{ise} = \dot{E}^{ET}_{lse} + \dot{E}^{EP}_{lse}
\]

(17)

Notice that the changes for the variables in (16) and (17) can be positive or negative. The sign of the changes is determined by two things: (i) the temperature level of the streams (i.e., whether the operation is carried out above or below ambient temperature), and (ii) the type of operation.
performed (i.e. compression or expansion). Here, the sign convention adopted is the one used by Moran and Shapiro [22]; for a control volume, all heat flow inlets and generated work are positive entities while heat outlets and consumed work are negative. Table 1 shows the combinatorial scenarios for (16) and (17).

Table 1. Combinatorial scenarios for the relationship between $\Delta T^{E_T}$ and $\Delta T^{E_P}$

<table>
<thead>
<tr>
<th>Above $T_0$</th>
<th>Compression</th>
<th>+</th>
<th>+</th>
<th>+</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expansion</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>The shaftwork input increases both exergy components. Reductions in both exergy components contribute to generate shaftwork.</td>
</tr>
<tr>
<td>Below $T_0$</td>
<td>Compression</td>
<td>−</td>
<td>+</td>
<td>+</td>
<td>Both shaftwork input and reduction in $\dot{E}_T$ increases $\dot{E}_P$.</td>
</tr>
<tr>
<td></td>
<td>Expansion</td>
<td>+</td>
<td>−</td>
<td>−</td>
<td>The reduction in $\dot{E}_P$ generates both shaftwork and an increase in $\dot{E}_T$.</td>
</tr>
</tbody>
</table>

If the changes in pressure are performed with an isentropic efficiency ($\eta$) less than unity, then (18a) and (18b) need to be introduced in the analysis. The isentropic efficiency factor ($f_{\text{is-eff}}$) is equal to the inverse of the isentropic efficiency for compressors ($1/\eta_{\text{compressor}}$) while for expanders it is equal to the isentropic efficiency ($\eta_{\text{expander}}$). Thus, the corresponding power and the changes in pressure and temperature based exergies are calculated with (19), (20) and (21). The change in pressure based exergy is not affected by the isentropic efficiency as shown in (20). Equation (22a) shows in a similar way to which it was demonstrated in (15), that the change in $T^{E_T}$ is a function of $T_1$, pressure ratio and, in this case, also of $f_{\text{is-eff}}$. The relation between the changes in exergetic temperatures shown in (23) is observed after (22a) is rearranged into (22b). Notice that the exergy balance shown in (17) has now changed into (24) by including the exergy destruction rate ($\dot{D}_E$).

$$T_2^{\eta=1} - T_1 = f_{\text{is-eff}} \left( T_2^{\text{is}} - T_1 \right)$$

$$\frac{T_2^{\eta=1}}{T_1} - 1 = f_{\text{is-eff}} \left( \frac{P_2}{P_1} \right)^{\frac{1}{\kappa-1}} - 1$$

$$-\dot{W}_{\eta=1} = mc_p f_{\text{is-eff}} \left( T_2^{\text{is}} - T_1 \right)$$

$$\Delta \dot{E}_{\eta=1} = mc_p \left[ I_0 \ln \left( \frac{P_2}{P_1} \right)^{\frac{1}{\kappa-1}} \right] = mc_p \left[ I_0 \ln \left( \frac{T_2^{\text{is}}}{T_1} \right) \right]_{P_1 \rightarrow P_2}$$

$$\text{(18a)}$$

$$\text{(18b)}$$

$$\text{(19)}$$

$$\text{(20)}$$
4. A novel diagram for exergy targeting

In the Composite Curves of Pinch Analysis, due to the assumption of constant \( m_c \) or piecewise linear enthalpy/temperature relationship, the construction of the diagram is very simple and only needs the supply and target temperatures of the streams. In exergy based diagrams (such as ECCs and EGCC), there is a non-linearity introduced since exergy is a non-linear function of temperature even when the heat capacity flowrate is constant (e.g. through the Carnot factor). The introduction of exergetic temperatures is motivated by the resulting linear behavior, which again means that by only using the supply and target conditions of the streams, in the form of exergetic temperatures one does not have to do multiple simulations/calculation to get points along a non-linear curve. The proposed diagram plots exergy sources and exergy sinks as linear composite curves in a \( T^E - \bar{E}^F \) diagram (Figs 3a and 3b). For HRSs above \( T_0 \), the exergy sources are the hot streams and the exergy sinks are the cold streams, while for HRSs below \( T_0 \) the hot streams are the exergy sources and the cold streams are the exergy sinks. It is important to notice that below \( T_0 \), exergy and heat flows have opposite directions.

Some characteristics of the new diagram are:

- The minimum value of \( T^E \) (zero) is at ambient temperature. Thus, \( T^E \) is positive for the complete temperature range, which is in contrast to the Carnot factor in the ECCs. The stream with the condition that has the highest exergy value is always placed at the top of the curves while the lowest (closest to \( T_0 \)) is at the bottom. Notice that for streams below \( T_0 \), the coldest temperature corresponds to the highest exergy content and the largest exergetic temperature.

- When the minimum approach temperature (\( \Delta T_{min} \)) between the CCs is fixed, then a corresponding minimum exergetic approach temperature (\( \Delta T_{min}^{E^T} \)) is obtained. As a consequence:
  - The exergy deficit and surplus are calculated ahead of any design actions from the exergy cascade by only using the stream data, similar to how minimum external heating and cooling demands are obtained from the traditional heat cascade. The exergy cascade is described in Section 5.
  - The heat pinch and exergy pinch are placed in corresponding enthalpy and exergy intervals, thus if the pinch rules are followed, exergy is neither imported below pinch nor exported above pinch, and exergy is not transferred across pinch.
The exergy destruction is graphically shown by transforming the boundary temperatures of the overlapping region obtained in the traditional CCs into exergetic temperatures (squares and circles in Figs. 3a and 3b).

**Fig. 3** $T^{E_f} - E^{T}$ diagram (a) above $T_0$, and (b) below $T_0$

- The maximum exergy recovery for a given $\Delta T_{min}$ is the maximum amount of exergy that the exergy sink curve can accept in the overlapping region, and the minimum process-to-process exergy destruction is the difference between the process-to-process exergy transferred from the exergy source curve and the maximum exergy recovered. The calculation of exergy targets is given by (25) and (26).

  Above exergy pinch:  
  \[ \dot{E}_{\text{Requirement, min}} = \dot{E}_{\text{Deficit, min}} + \dot{E}_{\text{Destruction, min}} \]  
  (25)

  Below exergy pinch:  
  \[ \dot{E}_{\text{Rejection, min}} = \dot{E}_{\text{Surplus, min}} - \dot{E}_{\text{Destruction, min}} \]  
  (26)

**5. Heat and Exergy cascades**

The algorithm used for the calculation of the minimum exergy deficit and surplus is similar to the one used for obtaining the minimum heat deficit and surplus. Following the analogy made by Papoulias and Grossmann [23] with the transshipment model for heat recovery problems, one could represent the transportation of exergy from exergy sources to exergy sinks. Fig. 4a shows the heat and exergy patterns for the $k^{th}$ temperature interval both heat and exergy cascades. The regular temperature intervals are calculated using the method proposed by Linnhoff and Flowers [24] for a given minimum temperature difference $\Delta T_{min}$. The exergetic temperature intervals can be calculated from the regular temperature intervals or by means of the corresponding minimum exergetic temperature difference $\Delta T^{E_f}_{min,k}$ described in (27a) and (27b).

\[ \Delta T^{E_f}_{min,k} = \Delta T_{min} - T_0 \ln \left( \frac{T_{i,k}}{T_{j,k}} \right) \]  
(27a)

\[ \Delta T^{E_f}_{min,k} = -\Delta T_{min} + T_0 \ln \left( \frac{T_{j,k}}{T_{i,k}} \right) \]  
(27b)

It should be mentioned that Fig 4a and (27a) are valid for HRSSs operating above ambient temperature. For systems operating below $T_0$, the heat sources are exergy sinks and vice versa, thus the corresponding identification of the streams identity should be made and (27b) be used instead of (27a).
Fig. 4 (a) Heat and exergy flow pattern in each Temperature Interval (TI) and (b) heat flow pattern in each Enthalpy Interval (EI)

Notice that the exergy destruction of the \( k \)th Temperature Interval (TI) is lumped in the exergy sinks. Then, it is obvious that the heat cascade fails in illustrating clearly the exergy destruction in each TI, however, the information given by the exergy cascade is valuable. The obtained exergy deficit or exergy surplus in each TI assumes that all the exergy from the exergy sources is transferred to the exergy sinks without exergy losses. In order to calculate the minimum exergy destruction (irreversibilities) one should shift from TI to Enthalpy Intervals (EI) by means of vertical heat exchange. In practice, a strict vertical exchange will lead to the so-called Spaghetti design which should not be used in actual HEN designs (i.e. it will need a large number of units), however, for targeting purposes, vertical heat exchange may aid in the calculation of the HEN minimum area [25]. Pure countercurrent (strict vertical) heat exchange will indubitably be using the driving forces more efficiently than any other heat exchange arrangement i.e. concurrent or criss-cross; even when it cannot always ensure the HEN minimum area. Exergy destruction due to heat exchange on the other hand, is only a function of the temperature differences of the streams, thus vertical heat exchange will always lead to the minimum exergy destruction of the HEN. Fig. 4a illustrates the heat flow pattern in each \( \lambda \)th EI where \( \Delta H_{i,\lambda} \equiv \Delta \dot{H}_{j,\lambda} \).

Fig. 5 Exergy flow patterns for HRSs with \( L+M \) EIs in (a) discontinuous and (b) continuous exergy exchange representations.
Gundersen and Grossman [26] proposed the vertical transshipment model as an extension of the heat cascade. In their analysis, they combined the vertical heat exchange with the heat cascade in a transshipment model with the intention of automatizing the Heat Exchange Network Synthesis (HENS). For calculating the exergy targets, the coupling of these two models is not needed. Figs 5a and 5b show the exergy flow pattern for vertical heat exchange in a balanced HRS. If the pinch rules abovementioned are followed, then utility streams can only supply exergy in the above pinch EIs (λ) and exergy can only be rejected from below pinch EIs (m). Fig. 5a shows the actual exergy balance of each (L+M) EIs including the exergy destruction. Because the CCs and the curves in the $T^{Ef} - E^T$ diagram are continuous, Fig. 5b shows a better representation of the exergy exchange in HRS. The exergetic temperature intervals in Figs. 5a and 5b are calculated from the regular temperatures.

6. Case study: Design of an LNG process

The liquefaction of natural gas is used as case study. The main purpose of this example is to illustrate the application of the new thermodynamic diagram by providing the information when changes in pressure are introduced.

6.1 Stream data for the process

The design starts with basic stream data only. Table 2 shows the stream data for 2 hot streams (natural gas and nitrogen) and one cold stream (nitrogen). The natural gas is mainly composed by methane (> 85% mole) and has an average compressibility factor of 0.8 from 25°C to its dew point (~50°C) at 65 bar. At supply conditions, the natural gas can be regarded as close to ideal gas while at target conditions is in liquid state. On the other hand, both nitrogen streams can be considered as ideal gases at both supply and target conditions, even at very high pressure. The heat capacity flowrate of the natural gas stream is varying with temperature, and this is also the case with the value of $\kappa$. The natural gas stream is divided into segments with constant heat capacity flowrates.

Table 2. Initial stream data

<table>
<thead>
<tr>
<th></th>
<th>$T_s$ (°C)</th>
<th>$T_t$ (°C)</th>
<th>$P_s$ (bar)</th>
<th>$P_t$ (bar)</th>
<th>$\dot{m}c_p$ (kW/°C)</th>
<th>$\kappa$</th>
<th>$\Delta H$ (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG</td>
<td>25.0</td>
<td>-168.0</td>
<td>65.0</td>
<td>1.0</td>
<td>varying</td>
<td>varying</td>
<td>-13.84</td>
</tr>
<tr>
<td>N2$_a$</td>
<td>25.0</td>
<td>-168.0</td>
<td>120.0</td>
<td>6.3</td>
<td>121.6</td>
<td>1.48</td>
<td>23.46</td>
</tr>
<tr>
<td>N2$_b$</td>
<td>-168.0</td>
<td>25.0</td>
<td>6.3</td>
<td>120.0</td>
<td>121.6</td>
<td>1.48</td>
<td>23.46</td>
</tr>
</tbody>
</table>

6.2 Changes in exergy components and construction of diagrams

Table 3 shows the exergetic temperatures and the changes in the exergy components. The calculations have been carried out with (9) and (10). The ambient conditions are 25°C and 1 bar. Notice that the pressure based exergy of the natural gas is decreased to zero from supply to target pressure (1 bar), and therefore $\Delta \hat{E}_p = E^p_s$.

Table 3. Exergetic temperatures and changes in exergy components

<table>
<thead>
<tr>
<th></th>
<th>$T^E_s$ (K)</th>
<th>$T^E_t$ (K)</th>
<th>$T^{Ep}_s$ (K)</th>
<th>$T^{Ep}_t$ (K)</th>
<th>$\Delta \hat{E}_p$ (MW)</th>
<th>$\Delta E^p$ (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG</td>
<td>0.00</td>
<td>117.73</td>
<td>555.33</td>
<td>0.00</td>
<td>8.13</td>
<td>-27.21</td>
</tr>
<tr>
<td>N2$_a$</td>
<td>0.00</td>
<td>117.73</td>
<td>462.94</td>
<td>177.98</td>
<td>14.32</td>
<td>-34.65</td>
</tr>
<tr>
<td>N2$_b$</td>
<td>117.73</td>
<td>0.00</td>
<td>177.98</td>
<td>462.94</td>
<td>-14.32</td>
<td>34.65</td>
</tr>
</tbody>
</table>

34
Figs. 6a and 6b show the CCs and the $T^E - \dot{E}^T$ diagram without considering changes in the stream pressures. The heat and exergy pinches are at 25°C and 0 K respectively, and the minimum temperature approaches both in regular and exergetic temperatures are zero. There is no heating requirement but 13.8 MW of cooling is necessary. In terms of exergy, the deficit is 8.1 MW (22.4 – 14.3), while the exergy destruction is 7.5 MW (14.3 – 6.8). The exergy requirement is then 15.6 (8.1 + 7.5). Notice that all stream conditions are at or below ambient temperature.

From Figs. 6a and 6b and according to the plus-minus principle for modifications for HRS design [14] one have two options for reducing the cooling or exergy requirement. These options are: a) to increase the heat sinks (exergy sources) and b) to reduce the heat sources (exergy sinks). If the first one is chosen, one would need to include a cold utility i.e. an external exergy source such as refrigeration, in addition to the compression work needed for taking the cold nitrogen stream from 6.3 to 120 bar. Thus, the second option for reducing the exergy requirement seems to be the solution. If one forces the hot nitrogen stream to reach both target conditions simultaneously, by means of an expansion, then the cooling demand of this steam is reduced and most of the total cooling demand of the system will come from the natural gas steam.

### 6.3 Introducing pressure manipulations

For this exercise, the expansion of the natural gas is left at the end of the liquefaction process. This means that the natural gas streams will be cooled, liquefied and subcooled at constant pressure. Later, by using a liquid expander, the LNG will be expanded until 1 bar. This is typically done by most of the industrialized liquefaction processes. Because the expansion of the LNG is done in liquid phase, the equations described in Section 3 are not valid; however, the temperature decrease in the the expansion is typically very small (>5 K). Assuming that after the liquid expander, the temperature of natural gas decreases only 3°C, the inlet temperature to the expander is $-165°C$. In this way, the minimum temperature difference in the cold end of the CCs is 3 K. The cooling and exergy requirements for the liquefaction of the natural gas are 13.66 MW and 7.82 MW, respectively. According to the discussion at the end of Section 6.2, the hot nitrogen stream will reach both target conditions (temperature and pressure) simultaneously after the expansion. By using either (18a) or (18b), one can calculate the inlet temperature in the nitrogen expander which is equal to $-52.64°C$. Thus for this stream, the cooling and exergy requirements have been reduced from 23.46 MW and 14.32 MW to 9.44 MW and 1.50 MW. The total cooling and exergy requirements are then 23.1 MW and 9.32 MW. Finally, for cold nitrogen stream is decided that the compression is done after heat has been exchanged with both hot streams. Then, the outlet temperature of the cold nitrogen stream is close to 22°C. The compression takes place in 6 stages of equal pressure ratio and cooling water is used in the intercoolers. The isentropic efficiencies for the compressor stages and expander are 80% and 85%, respectively. The modified stream data shown in Table 4 and 5 includes the effects of the changes in pressure.
Table 4. Modified stream data for heat exchanges (Δp=0)

<table>
<thead>
<tr>
<th></th>
<th>(T_s) (°C)</th>
<th>(T_t) (°C)</th>
<th>(\Delta H) (MW)</th>
<th>(T_s^{E_T}) (K)</th>
<th>(T_t^{E_T}) (K)</th>
<th>(\Delta \dot{E}_T) (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG</td>
<td>25.00</td>
<td>-165.00</td>
<td>-13.66</td>
<td>0.00</td>
<td>112.35</td>
<td>7.82</td>
</tr>
<tr>
<td>N2c</td>
<td>25.00</td>
<td>-52.64</td>
<td>-9.44</td>
<td>0.00</td>
<td>12.30</td>
<td>1.50</td>
</tr>
<tr>
<td>N2d</td>
<td>-168.00</td>
<td>22.00</td>
<td>23.11</td>
<td>117.73</td>
<td>0.02</td>
<td>-14.32</td>
</tr>
<tr>
<td>N2e</td>
<td>85.71</td>
<td>25.00</td>
<td>-46.96</td>
<td>6.08</td>
<td>0.00</td>
<td>-4.44**</td>
</tr>
</tbody>
</table>

* Total requirement of cold thermal energy for the five intercoolers and the aftercooler.

** Total exergy rejection for the five intercoolers and the aftercooler.

One should notice that the compression stages operate above ambient temperature while the rest of the unit operations operate below \(T_0\). The total cooling and power requirements are reported in both tables.

Table 5. Modified stream data for expanders and compression stages

<table>
<thead>
<tr>
<th></th>
<th>(T_s) (°C)</th>
<th>(T_t) (°C)</th>
<th>(P_s) (bar)</th>
<th>(P_t) (bar)</th>
<th>(\Delta \dot{E}_T) (MW)</th>
<th>(-W) (MW)</th>
<th>(\Delta \dot{E}_P) (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG</td>
<td>-165.00</td>
<td>-168.00</td>
<td>65.0</td>
<td>1.0</td>
<td>0.31</td>
<td>-0.17</td>
<td>-27.21</td>
</tr>
<tr>
<td>N2f</td>
<td>-52.64</td>
<td>-168.00</td>
<td>120.0</td>
<td>6.3</td>
<td>12.82</td>
<td>-14.03</td>
<td>-34.65</td>
</tr>
<tr>
<td>N2g</td>
<td>22.00</td>
<td>85.71</td>
<td>6.3*</td>
<td>120.0*</td>
<td>4.36</td>
<td>46.88**</td>
<td>34.65</td>
</tr>
</tbody>
</table>

* The compression is done in six stages with intercooling.

** Total power requirement for the six compression stages.

The CCs and the \(T^{E_T} - \dot{E}_T\) diagram with pressure changes included are shown in Figs 7a and 7b. One important feature of the \(T^{E_T} - \dot{E}_T\) diagram is shown in Fig. 7b. One can clearly see that the exergy source curve has a discontinuous slope change at the point (4.4; 0.0). Here, the representation of two exergy sources (one above \(T_0\) and the other below \(T_0\)) meet close to ambient temperature. These exergy sources are the streams exiting the compression stages (above \(T_0\)) and the nitrogen stream from 5 to 1 (below \(T_0\)). Hence, the HRS should be decomposed into two subsystems; one above \(T_0\) and the other below \(T_0\). Below ambient temperature, the cooling (refrigeration load) and heating requirements are zero (see left-hand-side of Fig. 7a). The exergy requirement and rejection are both zero, while the process-to-process exergy destruction due to driving forces is around 5.0 MW (quite large).

Fig. 7 Diagrams with compression and expansion operations included: (a) CCs and (b) \(T^{E_T} - \dot{E}_T\)
Below $T_0$, close to 35% of the exergy available in the exergy source (i.e. $18.8 - 4.4 = 14.4$ MW) is destroyed (5.0 kW). Above $T_0$, there is both heat and exergy surplus of 46.96 MW and 4.44 MW, respectively. Notice that there are two heat pinches: 25°C/22°C and -165°C/-168°C ($\Delta T_{\text{min}} = 3$ K), while there is only one exergy pinch at 117.73 K for the exergy source curve and 112.35 K for the exergy sink curve. The $\Delta T_{\text{min}}^{\text{EF}}$ is calculated by (19.b) to be 5.38 K. The power produced by the turbine and the liquid expander (14.2 MW) is not enough to overcome the power required by the compressor stages (46.88 MW). The exergy destructions in the compressor stages, turbine and liquid expander are calculated by (21) to be 7.87 MW, 7.80 MW and 26.73 MW, respectively. The flow diagram for the complete process is shown in Fig. 8. Actually, the flowsheet in Fig. 8 as well as the CCs in Fig. 7a and the exergy based curves in Fig. 7b correspond to the Reversed Brayton (RB) process for producing LNG.

Fig. 8 Flowsheet of the Reverse Brayton process

This is not a big surprise since this exercise was meant to illustrate the application of the new thermodynamic diagram by showing how one could develop the well-known RB process. In the RB process, the natural gas is liquefied with cold nitrogen (refrigerant) which is in gas phase in the entire cycle. The nitrogen cycle consists of: (i) one compression service consisting of four to eight compression stages with intercooling (COM-100-5), (ii) one aftercooler (AC-100) that will condition the nitrogen before the main heat exchanger, (iii) one turbine for expanding and cooling the nitrogen stream (TUR-100), and (iv) a main heat exchanger (HX-100) where nitrogen liquefies the natural gas stream. The main heat exchanger also acts as an economizer for the nitrogen stream coming from the aftercooler.

7. Conclusions

A new diagram for exergy targeting of Heat Recovery Systems (HRSs) where pressure is an important design variable has been proposed. The method is particularly suited for low temperature systems and could be used for designing LNG processes. The diagram uses a new energy quality parameter called exergetic temperature. These exergetic temperatures are used due to their linear relationship with exergy and for calculating exergy targets such as the minimum values for exergy requirement, exergy rejection and exergy destruction. An alternative exergy cascade that uses the transshipment model is proposed for finding the minimum exergy deficit and exergy surplus of the HRS. For the calculation of the minimum exergy destruction, the vertical heat transfer model is used. The Reverse Brayton process for the liquefaction of natural gas is used as a case study, where it was possible to illustrate the use of the alternative diagram for exergy targeting. It is worth mentioning that this representation can be intimately linked with the Extended Pinch Analysis and Design (ExPAnD) method under development in our research group.
Nomenclature

A \quad \text{energy level}

\dot{E} \quad \text{exergy flow, MW}

\dot{f}_{\text{is-eff}} \quad \text{isentropic efficiency factor}

\dot{H} \quad \text{enthalpy flow, MW}

p \quad \text{pressure, bar}

\dot{Q} \quad \text{heat flow, MW}

\dot{m}_{c_p} \quad \text{heat capacity flowrate, MW/°C}

R \quad \text{heat or exergy residual in the heat or exergy cascade}

\dot{S} \quad \text{entropy rate, MW/°C}

S \quad \text{process streams}

T \quad \text{temperature, °C [or K]}

U \quad \text{utility streams}

\dot{W} \quad \text{power, MW}

Greek symbols

\eta \quad \text{isentropic efficiency}

\kappa \quad \text{heat capacity ratio for ideal gas}

Subscripts and superscripts

0 \quad \text{ambient conditions}

D \quad \text{exergy destruction}

i \quad \text{heat or exergy source streams}

ise \quad \text{isentropic process}

j \quad \text{heat or exergy sink streams}

k \quad \text{temperature interval}

\lambda, m \quad \text{enthalpy intervals for above and below ambient temperature}

p \quad \text{pressure based exergy}

T \quad \text{temperature based exergy}

TM \quad \text{thermo-mechanical exergy}

Q \quad \text{exergy of heat}

References


Advances in the distribution of environmental cost of water bodies through the Exergy concept in the Ebro river

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Abstract:
The Physical Hydronomics (PH) methodology is a tool to properly calculate restoration cost of water masses in exergy terms, in the framework of the Second Law of Thermodynamics. This methodology makes possible to assess the quality degradation of water as well as the water consumption. An opportunity which that methodology brings up is the development of River exergy profiles which can be represented along the length of the river, for different periods and degradation statuses. Focussing on the Water Framework Directive milestones, fist novelty presented here consist on developing an hypothetical scenario corresponding to the state reached by applying the restoration Plan of Measures, therefore making possible to test their suitability by comparing that scenario with the Environmental Objectives, pursued by the Directive. Together with it, the second most relevant contribution which is presented here is the assessment of restoration cost among diverse water polluters, from physico-chemical parameters of the river according to the exergy degradation provoked individually by each of them.
The case study which is developed is the Ebro basin, an Spanish very representative river which flows into the Mediterranean sea. Important differences within the average rainfall values among the diverse areas of the Ebro and changing natural average total water resources are typical from this river. Results shown that quality restoration costs found in the agriculture user resulted to be the highest, in dry years, but quite similar to the ones fund in the urban user in wet years. On the other hand, degradation provoked by the hydroelectric user, never taken into account before in the PH spectrum, resulted to be the lowest, but increases in wet years. Considering changes in flow downstream dams due to their storing and delivering effect, it ranges during hydrologic periods, but it reaches maximum values during wet years.
The Plan of Measures proposed by 2015 is enough to fulfil with environmental objectives pursued by the Ebro river Environmental Authorities. Only punctual non-compliances were found during the simulated period. Reposition Cost varied among hydrological years: the more dry the year is, the higher reposition costs. In any case, the total investment cost to put into practice the measures projected in the draft version of the Ebro river management Plan seems to be enough to fulfil the already mentioned Environmental Objectives.

Keywords:
Exergy analysis, Ebro river, Restoration (environmental) costs.

1. Background
Methods, procedures and indicator parameters necessary for characterising the condition of water, as well as the strategies and instruments needed to protect this condition and to regenerate it (if necessary) were defined in the Water Framework Directive [1] which came into force in 2000. The effective milestones pursued by this European Directive are focussed mainly on evaluating the condition of all water bodies, as well as determining their ecological status by using quantitative
and qualitative parameters. The associated pressures, impacts and risks conditioning that status should be properly identified. Article 11 of the Directive bounds to the Member States to draw up river basin water plans including the programmes of measures to achieve the Environmental Objectives pursued for each water body of a given basin by 2015, and all the exceptions or difficulties to get the compliance [1].

Directive also emphasises on cost recovery. Its Article 9 states that EU countries “shall take account of the principle of recovery of the costs of water services”. Economic analyses should be carried out to ensure adequate contributions by different classes of users. The article does, however, note that Member States can take into account “social, environmental and economic effects” of cost recovery.

In this sense, focussing on the above mentioned milestones of the Directive, some improvements were introduced in the Physical Hydronomics methodology through the development of this work.

As it was stated in [2], any river state can be characterized by its exergy value (B, given in kWh), defined as the product of its flow (Q, given in m³/s) and its specific exergy (b, given in kJ/kg of water). On the one hand, the flow increases linearly from approximately cero, in the point were the river springs, until its maximum value, were the river dies. On the other hand, the specific exergy, that expresses the quality of the river (accounted by physical interactions taking place along the river course), decreases from its maximum value in the point were the river has its source, to the mouth, were its value is lower. Nevertheless, it still remains positive until the end of river course mainly due to the kinetic component of the exergy. The theoretical representation of the Q and b product should be a Gauss bell. However, in real case studies, the contribution of flow resulted to be much bigger (see Fig. 1). That is the reason why B and Q representations have similar shapes.

![Graphs showing exergy and flow along the river course](image)

**Fig. 1. Representation of Exergy along the river course, real sample (Own elaboration)**

Furthermore, Valero et al [3] showed that an Exergy gap between two states, 1 and 2, can be accounted and disaggregated in the corresponding quantity and quality terms as well, as indicated in (1)

\[
\Delta B_{2,1} = B_2 - B_1 = b_1 \Delta Q + Q_2 \Delta b = \Delta B_m + \Delta B_q
\]  

(1)
Where $\Delta Q$ and $\Delta b$ are the flow and specific exergy gaps between two exergy states (states 1 and 2), and $m$ and $q$ stands for quantity and quality exergy components, respectively.

The addition of all exergy components (potential, inorganic, organic, etc) expresses the total exergy of the given water resource. That reasoning was fruitfully applied in [4].

Then, PH brings up the opportunity to development different River exergy profiles which can be represented along the length of the river, for different periods and degradation statuses. First novelty presented here consist on developing an hypothetical scenario corresponding to the state reached by applying the already mentioned restoration Plan of Measures, therefore testing their suitability by comparing that scenario with the Environmental Objectives, pursued by the Directive. Additionally, individual scenarios for each user, could be also simulated and confronted to account the environmental cost of water, as well as fairly distribute this cost among different users. Both constitute key objectives of this work being a really important consequence of the river simulation.

In order to illustrate the applicability of the methodology proposed here, the Ebro River basin (described in section 3) was analysed. It was simulated with the help of a comprehensive hydrologic model, giving a complete vision of the basin. Discharge, composition and physical characteristics of water flows were compiled trough the Aquatool hydrographical simulation software [5] thus making possible not only to test the already mentioned Plan of Measures, but also to assess the degradation provoke for each user of the basin, individually.

**2. Methodology**

Quantity and quality data should be accurately provided for every stretch of the river in order to obtain the precise river profiles. As mentioned, these profiles are required to assess the cost necessary to bridge the gap between two given degradation states.

Then, the methodology followed in this work to develop the already mentioned milestones (to test the programme of measures and to allocate restoration costs among users) is developed in the first part of the section. For the sake of completeness, a table summarizing the accounting of the parameters to develop river scenarios is presented in Appendix A (Table A.1). Secondly, it was also mentioned that an hydrographical simulation tool is necessary to apply the methodology to real case study. The followed simulation process is deeply explained in the second part of this section.

**2.1. Definition of river scenarios.**

**2.1.1. Testing the Measures Plan**

With the aim of reaching the Ecological Status defined in the WFD some measures should be applied for each water body of a given basin when required. Therefore, a great opportunity given by the Aquatool model emerges since it allows simulating any defined state of the river. Traditionally, the environmental cost (EC) has been the main cost considered by PH. It is defined as the cost the reach the Environmental Objectives from the Present State of the river in future scenario (2015). Complementary, in this work, a new a hypothetic Measures State (MS) in which the potential measures conceived in Hydrologic Basin Plans are included is defined. It will make possible to asses the gaps between the Present State by 2015 (FS) of the river and the Measures State, and between Measure State and Objective State (OS), respectively. The effectiveness of such a Plan could be also easily tested, as well as the additional cost of non compliance of the PM initially though up in case of those measures were not enough to reach the Good Ecological State.

In this sense, the new defined river state (MS) makes possible to assess two additional costs:

- The Measures Costs (MC). It can be defined as the necessary cost to implement the PM presented by the competent authority, that is, the difference between the FS of the river and the MS.
- The non-compliance cost (NCC) which asses the gap between MS and OS. It informs about the accuracy of the implemented measures in the water body.
Following the guidelines of equation (1), the MC and NCC are determined by the difference between the FS and MS, and the OS and the MS, respectively, according to (2) and (3).

\[ MC = \Delta B_{MS-FS} = B_{MS} - B_{FS} = b_{FS} \Delta Q + Q_{MS} \Delta b \]  
\[ NCC = \Delta B_{OS-MS} = B_{OS} - B_{MS} = b_{MS} \Delta Q + Q_{OS} \Delta b \]  

These previously mentioned exergy states and costs are summarized graphically in Fig. 2.

**Fig. 2.** MC and NCC interpretation for different exergy components

It is interesting to be underlined in this point that by working with monthly simulated data, the temporal variability of results should be taking in mind, making possible to obtain positive NCC results in some months and negative in other months. Consequently, this accounting procedure, already presented and also tested in some study examples [6], gives valuable information and it could be used in forecast and planning management. By working with monthly simulated data, the temporal variability of results should be taking in mind. It makes possible to evaluate results to conclude the months where the PM was over or under sized, to propose some alternatives to the current PM, in case they where necessary.

Considering separately different exergy components, MC and NCC results should be accurately interpreted.

On the one hand, the quality of the river regarding to Inorganic Matter (IM) is lower when values of exergy are lower. The Inorganic Matter exergy component tends to decrease along the river due to human uses. That also implies an increase in salinity. Therefore, positive values of MC and NCC for the IM component implies the reduction of salinity by applying some measures, but also show the remaining necessity to bridge the gap between MS and OS by putting into practice additional measures. In this sense, a positive value of the NCC indicates that the PM within the watershed is not good enough because the OS has not been reached. On the other hand, a negative value, however, leads to the conclusion that the PM projected to that river has been oversized.
On the other hand, organic matter (OM) or Nitrogen (N) exergy components increase with concentration. Therefore, higher values imply lower quality. It can be assumed that, in that case, a negative value of organic matter component of the MS implies a reduction in the concentration, and a lower exergy value. Then, measures reduce the OM concentration of FS. That analysis is summarized in Table 1.

Table 1. MC and NCC analysis

<table>
<thead>
<tr>
<th>IM OM, N Interpretation</th>
<th>IM MC</th>
<th>IM NCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 0 &lt; 0</td>
<td>Measures improve the quality of river</td>
<td></td>
</tr>
<tr>
<td>&lt; 0 &gt; 0</td>
<td>Measures diminish the quality of river</td>
<td></td>
</tr>
<tr>
<td>a &gt; 0 &lt; 0</td>
<td>Measures are not good enough</td>
<td></td>
</tr>
<tr>
<td>b &lt; 0 &gt; 0</td>
<td>Measures have been oversized</td>
<td></td>
</tr>
</tbody>
</table>

2.1.2. Distribution of costs among users

The PH methodology makes possible not only to calculate restoration costs of water bodies, but also to allocate them among different users. To do that, different statuses of the river were developed, with the aim of studying separately the pollution charges of each use of the basin. Those statuses were used to account and allocate the Restoration Cost for each water user.

The first step consisted on defining different individual scenarios for each user. The developed statuses were:

- Without Users State (WUS) of the river is understood as the state of the river without any demand. It is similar to the natural state of the river.
- Urban Users State (UUS) is the state in which only urban demands are considered.
- Agriculture Users State (AUS) is defined as the resulting state by taking into account only the agriculture demands.
- Hydroelectric Users State (HUS) is the state in which only the hydroelectric facilities are taken into consideration. Its reposition cost comes from the energy necessary to restore the power generated by them.
- Dams State (DS). It is a state without uses but with the presence of dams. It was defined in order to separately calculate the affection (ΔB) due to the presence of these infrastructures, necessary to cover different demands. Dams change the available flow along time and space, since they manage the flow coming from the river to be stored or delivered. That lies in a changing gap of flow, and, therefore, in a quantitative degradation of water, that could be negative or positive considering the monthly balance of input and output flows.

Exergy gap between a scenario only with Dams (DS) and the scenarios reached by each of these users individually IUS were represented by ΔBi and calculated by applying (4).

\[ \Delta B_i = \Delta B_{DS-IUS} = B_{DS} - B_{IUS} = b_{IUS} \Delta Q + Q_{DS} \Delta b = \Delta B_m + \Delta B_q \]  \hspace{1cm} (4)

Additionally, the dams storing effect (ΔB_dams) was assessed as the exergy gap between a scenario DS, and the WUS scenario, by applying (5).

\[ \Delta B_{dams} = \Delta B_{WUS-DS} = B_{WUS} - B_{DS} = b_{DS} \Delta Q + Q_{WUS} \Delta b = \Delta B_m + \Delta B_q \]  \hspace{1cm} (5)

The exergy gap between the state without users and the real present state, the total restoration exergy gap (ΔB_{TOTAL}) it should be tested to be approximately equal to the addition of individual gaps (ΔB_{uses}) presented above (according to 6) as summarized next in an application example.

\[ \Delta B_{TOTAL} \approx \Delta B_{uses} = \sum \Delta B_i + \Delta B_{dams} \]  \hspace{1cm} (6)

Figure 3 summarizes that methodology.
Urban and irrigation users provoke a gap in the quality exergy component due to changes in water composition (inorganic, organic, or nitrogen and phosphorous content are affected by them). On the other hand, changes in quality exergy due to the hydroelectric uses are found in the potential component. Potential component depends on the height gap ($\Delta H$) in each river stretch. Since this exergy gap varies depending on the kind of hydroelectric technology, an accurate analysis of the main hydroelectric facilities located in the case study, was carried out with the help of monthly data from Endesa [7]. They were considered to assess the degradation provoked by this user.

2.1.2.1. Application example

In order to verify the methodology, it was necessary to test if the total restoration exergy gap ($\Delta B_{TOT}$) was equal to the addition of individual gaps defined for the previously mentioned individual scenarios ($\Sigma \Delta B_{USES}$). Data from the hydrologic period (2002-2006), from a simple real case study located in the Segre river, a main tributary of the Ebro river, were considered to carry out that test. Input data where calculated from the watershed organism “Confederación Hidrográfica del Ebro” [8]. The river characterization scheme includes a reservoir, and downstream, firstly, a gravity hydropower plant, and then, agriculture and urban plus industry demands. All the above mentioned states were considered in that simulation. Moreover, both quantity and quality flow data were obtained, in a monthly basis and for each simulated year and stretch. Quantity and quality components for each user could be studied individually. Table 2 includes final results for a representative hydrologic year (here, 2005-2006), for quantity and quality contributions to the total exergy gap, for OM, IM, and Nitrogen components, and for different users.

Table 2. Contribution to the quality and quantity exergy gaps, due to different uses

<table>
<thead>
<tr>
<th>% to the total exergy gap</th>
<th>Urban</th>
<th>Agric.</th>
<th>Hidro.</th>
<th>Dams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quality exergy gap $\Delta B_q$</td>
<td>68.98</td>
<td>19.02</td>
<td>11.93</td>
<td>0.00</td>
</tr>
<tr>
<td>Quantity exergy gap, $\Delta B_m$</td>
<td>2.46</td>
<td>34.39</td>
<td>0.00</td>
<td>63.15</td>
</tr>
</tbody>
</table>

It was tested that the ratios between the total exergy gap ($\Delta B_{TOT}$) and the addition of individual uses exergy gaps ($\Sigma \Delta B_{USES}$) are higher but similar than one (see Table 3). Consequently, when many users are included simultaneously in the scheme, degradation results to be a little higher than the...
addition of degradation scenarios assessed individually for each user. That is due to the non-linear behaviour of exergy in liquid solutions. Obtained ratios for quality and quantity components are summarized in Table 3.

Table 3. Ratios between PS exergy degradation and the addition of individual users states exergy gaps. Application example.

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>qOM</th>
<th>qNP</th>
<th>qIM</th>
<th>m</th>
<th>q,p</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔBPS/(ΔBUSES)</td>
<td>1.02</td>
<td>1.01</td>
<td>1.12</td>
<td>1.03</td>
<td>1.00</td>
</tr>
</tbody>
</table>

2.2. Modelling process

The relationships between waste loads and the resulting water qualities are always better described with mathematical models than only from the available data given by the River Basin Authorities. An adequate hydrological simulation tool could provide of enough compiled river data to characterize the river as exactly as the user wants, during a period of time and almost in every desired point, especially in those points where no data are available. Depending on how specific are its discrete simulation units, it can be really useful to complete the sometimes discontinuous or insufficient available data for a given case study. Moreover, hydrographical simulation tools can be a great operational support to analyze the river when simulations do not correspond to actual measurable situations.

With the help of the Aquatool software it was possible to generate different states, so obtaining enough physical and chemical data to correctly characterize each stretched of the river. Thus, it makes possible the representation of the river exergy profiles for different degradation states.

Input monthly flows data for the case study presented in next section (the Ebro river) for each simulated year within the 2002-2007 period were introduced in the Aquatool-GESCAL interface [5]. Point pollution discharges coming from the industry were also included to calibrate the simulation results (by comparing them with real data available from quality data stations). In particular, the modelled quality inputs parameters were sulphates, alkalinity, calcium, sodium, magnesium, chlorine, organic matter, nitrates, ammonium, and conductivity. Mass balances were previously carried out with the different water flows, by using the SIMGES program module, which deals with water flows (see Annex A for details).

Quality data given by quality control stations along the river course [8] were used to estimate the quality water inflows in river stretches. Water deterioration provoked by uses was calculated from the common return ratios applied for the Ebro, corresponding to different uses, 80 and 20 % for urban and agriculture, respectively, according to [9]. Typical elimination ratios of existing Wastewater Treatment Plants from [9] and pollution rates for different users found in [10] were considered. Additionally, monthly evolution of temperature, and dam related data, as evapotranspiration and level-capacity curves were obtained from [8].

Finally, quantity and quality flow data were then obtained, per month of each simulated year and stretch. Therefore, exergy profiles could be calculated for the simulated users-related states, as it was previously done for the current state of the river (FS). Then quantity and quality components for each user could be studied individually. Figures, divided by components and stretches can be shown in graphics, tables, or can be exported to operate in Excel dynamic tables (see Fig. 4).
3. The Ebro river basin: case study

This section includes a description of the Ebro River Basin, and also summarizes the main water uses in the basin, as well as the Plan of Measures projected by the Ebro river Basin water Authority (Confederación Hidrográfica del Ebro). It also covers the modelling process of this river basin with Aquatool.

3.1. Description

The Ebro river basin (see Fig. 5) is located in the north-east of Spain. It springs in Fontibre (Cantabria, 2000 meters high) and flows into the Mediterranean sea, in a Delta located in Amposta (Tarragona, Catalanian region). The Ebro river has a surface of 85500 km$^2$, with about 8000 km$^2$ of irrigated land. Most of this surface belongs to Spain. Only 506 km$^2$ are French and 444 km$^2$ belong to Andorra [11]. The Confederación Hidrográfica del Ebro is its management organism, framed within the Spanish Ministry of Environment, Farming and Agriculture. Its average rainfall is about 620 mm and its length is close to 930 km. There are important differences within the average rainfall values in the different Ebro areas. The highest values (more than 1500 mm) are found in the north area, but the central area of the basin has a rainfall around the 400 mm. The natural average total water resources there are 18200 hm$^3$/year (Average interannual), ranging between 29700 (máx.) and 8400 (mín) hm$^3$/year [12, 13].
3.2. Water uses in the Ebro river

The population of the area is approximately 3 million of people, with a gross domestic product (GDP) per capita around 25000 €/inhabitant and year. More that the 50 % of the income and the 50% of the total number of jobs correspond to the services sector [10].

The next most important sector is the industrial one. Around 3 million of people within the basin and nearly 1.5 million out of the basin (transfers) are supplied. That implies 550 hm\(^3\)/year of the urban water needs. The industrial water needs are 414 hm\(^3\)/year, and the supply guarantee, close to the 100%. Energy uses are characterized for being not water consumptive or return a high percentage of supplied water [11].

Regarding to agriculture uses, the irrigated surface under concession is close to the 800,000 ha [12]. Total water needs are around 6000 hm\(^3\)/year. The supply guarantee is limited, dependent on precipitations regime. Water sources are mainly coming from surface water bodies (91 %) and also from groundwater bodies (8%).

Main data related to high capacity infrastructures to supply water services (water reservoirs) are summarized in Table 4.

<table>
<thead>
<tr>
<th>Total Goverment (CHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of dams &gt; 1 hm(^3)</td>
</tr>
<tr>
<td>Flooded surface (has)</td>
</tr>
<tr>
<td>% on basin surface</td>
</tr>
<tr>
<td>Total water stock capacity (hm(^3))</td>
</tr>
<tr>
<td>stock capacity/natural resources</td>
</tr>
</tbody>
</table>

Since WFD is focussed on biological quality, it is important to remark the physico-chemical quality on surface water. It is summarized in Table 5. It also includes the characteristics of each quality category.

<table>
<thead>
<tr>
<th>AVERAGE QUALITY CHARACTERISTICS</th>
<th>% of control points</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1-A2 Simple or normal treatment + disinfection</td>
<td>78</td>
</tr>
<tr>
<td>A3 Intensive treatment +disinfection</td>
<td>17</td>
</tr>
<tr>
<td>&lt;A3 Not allowed as input for drinkable water</td>
<td>2</td>
</tr>
</tbody>
</table>

3.3. The Programme of Measures proposed by the Ebro River water management authorities

According to the Ebro river draft Management Plan, total projected budgets for the 2015 scenario ranges from 6000 to 10000 M€. Largest budgets to apply the actions considered in the program of measures for the period 2010-2015 in the Ebro river basin are the modernization of irrigation systems (30% of the total modernization budgets), water and sewage treatment accounts (10%) and water supply projects (7.4 %). The budgets in new irrigation (20%) and operational infrastructures associated with them (10%) are also important [14]. Its total demand is around 2022 hm\(^3\) per year, and the total surface of new modernized and low water consumption irrigated areas is 425000 hectares. In this sense, an intensive debate can be expected in society on the need to carry out the proposed irrigation. In Spanish basins with a more intensive water use, new irrigated are not included in the water plans. However, since the majority of the Ebro river basin population are in favour of the new irrigation, the moratorium called by some environmental groups has not had much effect on society, as long as the new irrigation complies with the objectives of environmental quality.
3.4. Modelling process

Figure 6 shows the Ebro river basin scheme as it was prepared to be used in the Aquatool software. The area where Mequinenza and Ribarroja dams are located is shown, in detail. In spite of the main course of the river considered here, the complete Ebro river basin simulated in Aquatool accounts for 27 dams, 72 river stretches, 45 water inputs, 111 catchments and 59 returns.

![Fig. 6. The Ebro river basin in Aquatool software, and zoom of the lower area of the river](image)

Present, measures, and individual scenarios for each user, where simulated. Quantity and quality contributions, for each chemical component where considered. Inorganic Matter (IM), which stands for inorganic salts and water; the Nitrogen (N) component, which accounts for nitrates, nitrites, ammonia contained in water, as well as organic matter (OM), thermal and potential components were calculated.

3.4.1. Calibration

Aquatool-DMA was chosen by the Ebro river Basin Authority as a support to test the fulfilment of the WFD and a help to write the Ebro river Management Plan. Since this work is somehow conceptually linked to the Confederación Hidrográfica del Ebro (CHE), it was considered other important advantage to choose Aquatool over the other softwares. It was decided that the simulated period should be the last four hydrologic years (October 2002- September 2006) from which enough complete and calibrate monthly data of flows could be facilitated by the Ebro river Basin Authority. The adequate calibrated flows given personally by the CHE staff which represented a great support to start with the development of the case study. Nevertheless, it is interesting to bring in this point the idea that the Management organism is used to the quantity model, but not to the quality model. That is the main reason why it was necessary to calibrate the model making possible to correctly work with quality data.
In this sense, it was necessary not only complete and improve the quantity model SIMGES by introducing more precise data such as the ones related with dams, to accurately obtain proper quantity results. It was also necessary to develop the GESCAL (quality model) with all requirements to be adequately compiled. Inputs, returns, point and non-point contamination, where monthly calibrated for the simulated period 2002-2006, for main stretches of the whole river and for each main component forming part of the water flow. Main components which were considered stand for organic matter, sulphates and nitrates.

An iterative process was required to attain optimal agreement between model output and field measurements. Calibration parameters had to be modified, running the program several times, by a manual trial-and-error process. SIMGES and GESCAL modules should be absolutely coherent. Then, if quantity simulation results change, it is necessary to run the quality module again to obtain proper results. Calibration parameters stand for different quantity and quality model data, in special punctual pollution inflows (simulating industrial pollution), returns, and non-point pollution. A quality control station was accurately selected in each stretch. Several punctual inputs were added in the model to simulate inflows from industry, along the basin. Average and maximum errors, and standard deviation were calculated in each point for different water components. Obtained average error between simulated and data taken from real stations resulted to be not higher than 10%.

4. Review and analysis of results

The most representative obtained figures are summarized next. As it was expected, the flow increases in the low Ebro. It can be also appreciated that it decreases along the simulated temporal period (see Figure 7). It was also checked that Natural State remains always higher than the other states, as expected.

Fig. 7. Present State flow along the Ebro river

Regarding to composition, the sulphates concentration is quite high (280 ppm) at the end of the upper river, but reaches its maximum value in the medium Ebro (380 ppm). It is also noticed also an increment in the salinity at the end of the river, close to the delta. According to the Organic matter,
in the upper Ebro values close to 4 ppm were found, and close to 6 ppm (maximum value) in the medium course (after industrial parks, and polluter tributaries). The nitrates concentration presents also maximum before the medium course of the river (12 ppm), and increases until 30 ppm in the medium Ebro, due to importance of irrigation in this area. The last significant increment is found at the end of the river, where the nitrates coming from the agriculture returns make the concentration rises until close to 14 ppm. These results are similar to the theoretical description of the basin (see Case Study section).

It can be concluded that proposed Measures are enough to fulfil the Ecological Objectives during the simulated period 2002-2006. Table 6 summarized the only 6 months of non-compliance in the Ebro. They are found mainly in September and November, in sulphates and Nitrates.

Table 6. Non-compliance in the Ebro river for the period 2002-2006

<table>
<thead>
<tr>
<th>Stretches</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003-2004</td>
<td>Sulphates</td>
<td>November</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>Nitrates</td>
<td>September</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>2005-2006</td>
<td>Sulphates</td>
<td>September</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>Nitrates</td>
<td>September</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

As an example, the difference between sulphates concentration in Measures and Objective States is represented in Figure 8, along the river for each simulated month. Non-compliances of table 5 are confirmed there. Some punctual positive results (which imply a concentration in MS higher than the maximum allowed concentration in OS) are found in stretches 6 to 9, during November and September.

Fig. 8. Sulphates non-compliance along the Ebro river
Exergy costs for each component and user were calculated, month by month, and aggregated by hydrologic year. For the sake of clearness, results for the representative dry year, 2005-2006 are summarized in Table 7. Restoration costs for quantitative ($\Delta B_m$) and qualitative ($\Delta B_q$) degradation were considered to share out degradation rates among users. The relative percentages from the total reposition cost, for different users, and for quantity ($m$) and quality ($q$) components were also assessed.


<table>
<thead>
<tr>
<th>Degrad (ΔB)</th>
<th>% Urban</th>
<th>% Agric</th>
<th>% Hidro</th>
<th>% Dams</th>
<th>TOTAL (ΔB, GWh/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta B_{OM,q}$</td>
<td>30.85</td>
<td>69.15</td>
<td>0.00</td>
<td>9894</td>
<td></td>
</tr>
<tr>
<td>$\Delta B_{IM,q}$</td>
<td>8.06</td>
<td>91.94</td>
<td>0.00</td>
<td>758</td>
<td></td>
</tr>
<tr>
<td>$\Delta B_{NP,q}$</td>
<td>75.55</td>
<td>24.45</td>
<td>0.00</td>
<td>693</td>
<td></td>
</tr>
<tr>
<td>$\Delta B_{p,q}$</td>
<td>0.00</td>
<td>0.00</td>
<td>100.00</td>
<td>911</td>
<td></td>
</tr>
<tr>
<td>$\Delta B_q$</td>
<td>29.68</td>
<td>62.89</td>
<td>7.43</td>
<td>12256</td>
<td></td>
</tr>
<tr>
<td>$\Delta B_m$</td>
<td>28.53</td>
<td>73.96</td>
<td>0.00</td>
<td>-2.49</td>
<td></td>
</tr>
</tbody>
</table>

The highest total values of quality components gap is found in the agriculture user. On the other hand, the contribution of hydroelectric is the lowest. Regarding to the dams storage, as it was explained previously, it was considered an exergy gap due to the variation of flow downstream reservoirs. That variation can be negative or positive by considering a monthly balance of flows. During the hydrologic period 2005-2006, total monthly balance of water storage results to be negative: the users demands increased the natural discharge from dams.

Previous results are compared next with the ones obtained for a wet hydrologic year (2002-2003). It is shown that the effect of dams increases, but, on the other hand, total reposition cost diminishes (see Table 8). Previous results consider both storing and delivering effects in the accounting (that is, not only the months when negative but also the months with positive net flow balances exist). In case of dry hydrologic years (2005-2006), the yearly balance results to be negative, that means, more water is delivered than received by the dam. In case of wet hydrologic analyzed years (2002-2003), the balance result to be positive.

Table 8. Exergy components for different users. Wet hydrologic year 2002-2003

<table>
<thead>
<tr>
<th>Degrad (ΔB)</th>
<th>% Urban</th>
<th>% Agric</th>
<th>% Hidro</th>
<th>% Dams</th>
<th>TOTAL (ΔB, GWh/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta B_{OM,q}$</td>
<td>66.93</td>
<td>33.07</td>
<td>0.00</td>
<td>2444</td>
<td></td>
</tr>
<tr>
<td>$\Delta B_{IM,q}$</td>
<td>31.65</td>
<td>68.35</td>
<td>0.00</td>
<td>330</td>
<td></td>
</tr>
<tr>
<td>$\Delta B_{NP,q}$</td>
<td>35.99</td>
<td>64.01</td>
<td>0.00</td>
<td>1203</td>
<td></td>
</tr>
<tr>
<td>$\Delta B_{p,q}$</td>
<td>0.00</td>
<td>0.00</td>
<td>100.00</td>
<td>1276</td>
<td></td>
</tr>
<tr>
<td>$\Delta B_q$</td>
<td>41.37</td>
<td>34.33</td>
<td>24.29</td>
<td>5253</td>
<td></td>
</tr>
<tr>
<td>$\Delta B_m$</td>
<td>13.58</td>
<td>73.46</td>
<td>0.00</td>
<td>13845</td>
<td></td>
</tr>
</tbody>
</table>

The ratios between the total exergy gap ($\Delta B_{TOT}$) and the addition of individual uses exergy gaps ($\Sigma \Delta B_{USES}$) are summarized in Table 9. It was stated previously that these ratios should be a little higher than one. Then, in spite of the computational effort, results seemed to be coherent, in mathematical terms.
Table 9. Ratios between PS exergy degradation and the addition of individual users states exergy gaps. Ebro river (hydrologic years 2002-2003 and 2005-2006)

<table>
<thead>
<tr>
<th>Year</th>
<th>ΔB_{PS}/(ΔB_{USES})</th>
<th>B_{R,OM}</th>
<th>B_{R,NP}</th>
<th>B_{R,IM}</th>
<th>B_{m}</th>
<th>B_{R,P}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002–2003</td>
<td>1.50</td>
<td>1.30</td>
<td>1.20</td>
<td>1.18</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>2005–2006</td>
<td>1.22</td>
<td>1.10</td>
<td>1.33</td>
<td>1.05</td>
<td>1.00</td>
<td></td>
</tr>
</tbody>
</table>

Total monetary restoration costs (TRC), and also the costs for each component, given in M€/year, are included in Table 10. In this sense, it was explained that PH assesses reposition costs considering an Objective State, according to the WFD milestones. Therefore, regarding to Dams effect, it is not possible to calculate the restoration economic costs, since the gap provoke by dams is compared with the Natural state of the river. Moreover, there is not a need to restore water flow variation due to dams: dams only provoke a displacement of flow availability during different hydrological periods, but not so much water losses (evaporation) occur. That is the reason why their effect is not included in Table 10 (restoration costs).

Table 10. Monetary restoration costs for different users (M€/year).

<table>
<thead>
<tr>
<th>YEAR</th>
<th>TRC (M€/year)</th>
<th>TOTAL</th>
<th>Urban</th>
<th>Agric</th>
<th>Hidro</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005-2006</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quantity</td>
<td>981</td>
<td>237</td>
<td>708</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Quality</td>
<td>3198</td>
<td>949</td>
<td>2011</td>
<td>238</td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>4179</td>
<td>1181</td>
<td>2925</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>2002-2003</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quantity</td>
<td>420</td>
<td>66</td>
<td>354</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Quality</td>
<td>964</td>
<td>399</td>
<td>331</td>
<td>234</td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>1384</td>
<td>324</td>
<td>958</td>
<td>102</td>
<td></td>
</tr>
</tbody>
</table>

Total environmental costs, defined by the WFD as the gap between present and Objective states were also calculated in order to furtherly distribute among diverse water users. To define the objective state, data of composition found in [15] were taken into account. They resulted to be around the 20% of total reposition costs already presented. The important gap between both costs stands for the Remaining Resource Cost (RRC), related to the difference between Objective and Natural states. Results regarding to the hydrologic year 2005-2006 are summarized next in Table 11.


<table>
<thead>
<tr>
<th>Urban</th>
<th>Agriculture</th>
<th>Hydroelectric</th>
<th>Environmental Costs(M€/year)</th>
<th>RRC (M€/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>63</td>
<td>7</td>
<td>981</td>
<td>420</td>
</tr>
</tbody>
</table>

Any comparison of the results obtained here with existing published official economic figures is somehow complicated, since PH gives operating costs, and only investment cost could be found in the draft version of the new Basin Plan [15].

Checking the Ebro River Water Treatment Plans (WWTP) installed in last 20 years [8], and considering the WWTP operation cost given in [16], the yearly water treatment operation cost during that period was calculated.

Then, the ratio between cost of operation and cost of investment given by the “Aragonian Water Institute” in [17], was used to calculate investment in WWTP during last twenty years. It was concluded that that investment was approximately 2700 M€.

According to the draft version of the Ebro management Plan [15], yearly Waste Water treatment cost are around 103 M€ per year. Then, the same ratio between investment and WWTP yearly exploitation cost already mentioned (which was found in [17]) was considered to calculate exploitation costs from the investment for 2015 given by CHE in [15]. These exploitation costs
resulted to be around 900 M€ per year, similar to the restoration cost due to changes in water composition (chemical component) according to results shown in this work.

5. Conclusions

This work was focussed on the assessment of restoration costs to fulfil with the Environmental Objetives pursued by the WFD. The PH methodology, based on a thermodynamic property named Exergy made possible to calculate these costs. Exergy depends on the physico-chemical characteristics of the studied resource. In this sense, PH made possible to analyze the seasonability of results, assessing not only the contamination rate of water bodies, but also its consumption. It makes also possible to assess water cost upon a physical objectives but after it also includes economic aspects.

The main contribution of this work lies not only in testing the Plan of Measures projected by the CHE in the Ebro river management plan, but also in the successful share of water uses degradation among the economic agents. Both constitute key milestones of this work. The improvements introduced in the PH methodology were mathematically tested with a sample real case, to be then applied to the whole Ebro river. That river basin was simulated with the Aquatool-DMA software, for different hypothetic states of the river. Therefore, the costs between them were accounted by comparison of its exergy profiles.

Results shown that total restoration costs found in the quality component of the agriculture user resulted to be the highest in analyzed dry years, but values for both users are quite similar in wet years. Focussing on quantitative figures, the highest restoration cost is found in the agriculture user. On the other hand, degradation provoked by the hydroelectric user resulted to be the lowest, but increases in wet years. The introduction of that user in the PH spectrum also constitutes an important novelty of this work.

The cost to restore the dams storage provokes a diminution of downstream river flows in some months and an increase in some others. The net yearly effect is shown for both dry and wet years, ranging from negative to positive balances, respectively.

According to the Aquatool-DMA results, the Plan of Measures (PM) proposed by 2015 is enough to fulfil with environmental objectives pursued by the Environmental Authorities, since only punctual non-compliances were found during the simulated period. More over, the total investment cost to put into practice the projected measures in the Ebro river by 2015 seems to be enough to fulfil the environmental objectives, according to obtained results.

Acknowledgments

The authors greatly acknowledge the financial support given to carry out this work, which is under the framework of the project ENE2010-18934 financed by the Spanish Ministry of Education and Science.
## Appendix A

**Table A.1. Assessment of flow and specific exergy in different river scenarios**

<table>
<thead>
<tr>
<th>River States</th>
<th>Starting Sources</th>
<th>Input parameters (results compilation)*</th>
<th>Compil. Tool</th>
<th>Considerations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q FLOW (Q)</td>
<td>PS</td>
<td>Flow data from real gauging stations</td>
<td>SIMGES</td>
<td>the river in the PS, with every inputs, demands and returns</td>
</tr>
<tr>
<td>FS</td>
<td>PS Aquatool simulation</td>
<td>Input flows, demands, returns, dams data</td>
<td>SIMGES</td>
<td>5% of water diminution (because of the Climate change), and higher demands</td>
</tr>
<tr>
<td>MS</td>
<td>FS Aquatool simulation, PHEBro proposed Measures</td>
<td>Input flows, demands, returns, dams data</td>
<td>SIMGES</td>
<td>MEASURES (PHEbro)**</td>
</tr>
<tr>
<td>OS</td>
<td>PHEBro proposed Env. flows, FS Aquatool simulation</td>
<td>-</td>
<td>-</td>
<td>PH Ebro, proposed env. Flows-Future State</td>
</tr>
<tr>
<td>NS</td>
<td>PS Aquatool simulation</td>
<td>Input flows</td>
<td>SIMGES</td>
<td>Modification of PS Aquatool scheme, only input flows</td>
</tr>
<tr>
<td>UUS</td>
<td>PS Aquatool simulation</td>
<td>Input flows, demands, returns, dams data</td>
<td>SIMGES</td>
<td>Modification of PS Aquatool scheme, only urban demands</td>
</tr>
<tr>
<td>AUS</td>
<td>PS Aquatool simulation</td>
<td>Input flows, demands, returns, dams data</td>
<td>SIMGES</td>
<td>Modification of PS Aquatool scheme, only irrigation demands</td>
</tr>
<tr>
<td>HUS</td>
<td>PS Aquatool simulation</td>
<td>Input flows, demands, returns, dams data</td>
<td>SIMGES</td>
<td>Modification of PS Aquatool scheme, only hydroelectric demands</td>
</tr>
<tr>
<td>DS</td>
<td>PS Aquatool simulation</td>
<td>Input flows, demands, returns, dams data</td>
<td>SIMGES</td>
<td>Returns: 100% of demands, with the same composition than catchments</td>
</tr>
</tbody>
</table>

| b compos.   | PS               | Quality data from real gauging stations | GESCAL       | the river in the PS, with every demands |
| FS           | PS Aquatool simulation | Input composition, returns composition, punctual and non-point pollution | GESCAL | 5% of water diminution (because of the Climate change), and higher demands |
| MS           | FS Aquatool simulation, PHEBro proposed Measures | Input composition, returns composition, punctual and non-point pollution | GESCAL | MEASURES (PHEbro)** |
| OS           | PHEBro proposed Obj, compositions | - | - | PH Ebro, proposed composition for different water components |
| NS           | PS Aquatool simulation | Input composition, non-point pollution | GESCAL | Modification of PS Aquatool scheme, only input flows |
| UUS          | PS Aquatool simulation | Input composition, returns composition, punctual OM and non-point pollution | GESCAL | Modification of PS Aquatool scheme, only urban demands |
| AUS          | PS Aquatool simulation | Input composition, returns composition, punctual SO4 and NO3, and non-point pollution | GESCAL | Modification of PS Aquatool scheme, only irrigation demands |
| HUS          | PS Aquatool simulation | Input composition, returns composition, non-point pollution, hydro-facilities data | GESCAL | Modification of PS Aquatool scheme, only hydroelectric demands |
| DS           | PS Aquatool simulation | Input composition, returns composition, non-point pollution | GESCAL | Returns: 100% of demands, with the same composition than catchments |

* Monthly values
** Lower and more concentrated returns (modernization), water treatment improvements
*** Final monthly values of each component of b, for different degradation states, were calculated from the Q, composition and physical parameters data in every stretch of the river, by using an specific equations solver software
Nomenclature

AUS: Agriculture Users State

\( b \): Specific exergy (kJ/kg water)

\( B \): Exergy (KWh)

CHE: Confederación Hidrográfica del Ebro (Ebro River Basin Authority)

DS: Dams State

EC: Environmental Costs

FS: Future State

GDP: Gross Domestic Product

HUS: Hydroelectric Users State

MC: Measures Costs

MS: Measures State

OS: Objective State

PH: Physical Hydronomics

PM: Plan of Measures

PS: Present State

RRC: Remaining Resource Costs

TRC: Total Restoration Costs

UUS: Urban Users State

WFD: Water Framework Directive

WUS: Without Users State

WWTP: Waste Water Treatment Plant

Subscripts and superscripts

IM: Inorganic matter

m: quantity component

N: Nitrogen-based components

OM: Organic Matter

p: potential

q: quality component

References


Application of the entropy generation minimization method to a solar heat exchanger: a pseudo-optimization design process based on the analysis of the local entropy generation maps

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Abstract:
This paper presents an application of the entropy generation minimization method to the pseudo-optimization of the configuration of the heat exchange surfaces in a Solar Roof Tile. An initial “standard” commercial configuration is successively improved by introducing design changes aimed at the reduction of the thermodynamic losses due to heat transfer and fluid friction. Different geometries (pins, fins and others) are analysed with a commercial CFD code that also computes the local entropy generation rate. The design improvement process is carried out on the basis of a careful analysis of the local entropy generation maps and the rationale behind each step of the process is discussed in this perspective. The results are compared with other entropy generation minimization techniques available in the recent technical literature. It is found that the geometry with pin-fins has the best performance among the tested ones, and that the optimal pin array shape parameters (pitch and span) can be determined by a critical analysis of the integrated and local entropy maps and of the temperature contours.

Keywords:
CFD, thermal convection, entropy, solar heat-exchanger, EGM.

1. Introduction

A fundamental thermodynamic theorem states that for whatever open process whose evolution can be approximated as a succession of quasi-equilibrium states and working in thermal contact with an ambient at $T_0$, the lost available power $|\dot{W}_{\text{rev}} - \dot{W}|$, i.e., the difference between the ideally produced power and the one really extracted, is proportional to the global rate of entropy generation $\dot{S}_{\text{gen}}$:

\[ \dot{W}_{\text{rev}} - \dot{W} = T_0 \cdot \dot{S}_{\text{gen}} [1]. \]

The lost power ($\dot{W}_{\text{rev}} - \dot{W}$) is always positive, regardless of whether the system is a power producer (e.g., an expander) or a power user (e.g., a compressor). Although not often exploited in real design applications, this theorem is of the utmost importance for the designer, in that it allows for a direct comparison of different configurations (“design options”) that either produce the same output with less irreversible losses or use the same amount of resource input to generate a larger output; both cases corresponding of course to a higher resource-to-end use efficiency. Naturally, the minimization of the entropy generation is not an easy task in practical cases, especially when complicated boundary conditions apply and/or when the operating point is varying in time. During the last three decades the Entropy Generation Minimization (EGM) method has become a well-established procedure in thermal science and engineering: it relies on the simultaneous application of the heat transfer and engineering thermodynamics principles, in pursuit of realistic models for heat transfer processes, devices and installations. The overwhelming majority of applications of the method for heat transfer problems employs lumped-sum parameter models:

\textsuperscript{\textcopyright} Corresponding Author
the global rate of entropy generation ($\dot{S}_{gen}$ [W/K]) is analytically expressed as a function of the topology and physical characteristics of the system (critical dimension, materials...) using correlations for average heat transfer rates and fluid friction available in literature. Then, by varying one or more of the design variables which $\dot{S}_{gen}$ depends upon, a minimum of the entropy generation rate is sought after; thence, an optimal geometry is determined. Many examples of this lumped-sum parameter model technique applied to fundamental heat transfer problems are presented in [1–5]. Pin-fins geometries are optimized with this method in [6,7], while plate-fins heat sinks are optimized in [8,9]. The key point of this deterministic approach is the analytical definition of $\dot{S}_{gen}$ as a function of critical design parameters, like geometry and working conditions. This function has to be inferred with the simultaneous application of principles of heat and mass transfer, fluid mechanics and engineering thermodynamics. Its ability to well describe the inherent irreversibility of the engineering system is closely linked to the “quality” of the correlations on which it relies. But, once we are able to actually write a semi-empirical analytic functional for $\dot{S}_{gen}$, finding its minimum is more a mathematical than a physical problem. One of the aims of the present work is to describe a different, heuristic, approach: the initial configuration is successively improved by introducing design changes based on a careful analysis of the local entropy generation maps obtained by means of CFD simulations. One of the advantages of this approach is that the rationale behind each step of the design process can be justified on a physical basis. This approach is particularly well suited for problems where a CFD simulation has to be carried out anyway (not explicitly for the purpose of a second-law analysis) and no reliable and explicit correlations for the mean heat transfer and fluid friction are available. Typical examples are turbomachinery and (convective) heat exchangers design problems. While this approach has been already adopted in some turbomachinery problems ([10,11]), examples for heat exchangers like the one covered in this work appear quite rarely in the archival literature. One example can be found in [12]. This approach consists in focusing the attention first on the local entropy generation rates $\dot{s}_T$, $\dot{s}_v$ and in considering the global one $\dot{S}_{gen}$ only after having carefully studied the implications of the local irreversibility on the overall design. It must be noted that, while $\dot{S}_{gen}$ cannot directly reflect the specific local features of the flow that are necessary for its phenomenological interpretation, it is nevertheless the global quantifier that allows us to identify which one of two different configurations is the better performer from a second-law perspective: if systems A and B have the same input and operate so that $\dot{S}_{gen,A} > \dot{S}_{gen,B}$, it can be inferred that system A operates more irreversibly than system B, therefore -ceteris paribus- B should be preferred. In order to calculate these local rates, both the velocity and temperature field have to be completely resolved, and therefore a CFD solver, i.e., a distributed-parameter model, is needed. Once the entropy rates are known, thanks to the visualization tool of the solver, we can display the maps of and $\dot{s}_T$, $\dot{s}_v$ so that the designer is able to literally see where the entropy is produced at higher rates and therefore where exergy is destroyed at a higher rate; it is possible to pinpoint the areas where we should focus our attention on.

2. Strategy for probing the solution space and description of the heuristic procedure

The entropy generation rate can be shown, for the case in study (i.e. in the absence of phase changes and chemical reactions), to consist of two parts [1]: one, called “viscous” ($\dot{s}_v$), that depends on the physical viscosity, on the local temperature of the fluid and on the second power of the local velocity gradient, and another, called “thermal” ($\dot{s}_T$), that depends on the physical conductivity, on the square of the local temperature of the fluid and on the second power of the local temperature gradient:
\[
\dot{S}_{\text{gen}} = \dot{S}_T + \dot{S}_V = \frac{k}{T^2} \left[ \left( \frac{\partial T}{\partial x} \right)^2 + \left( \frac{\partial T}{\partial y} \right)^2 + \left( \frac{\partial T}{\partial z} \right)^2 \right] + \frac{\phi}{T} \tag{1}
\]

\(\phi\) being the rate of \textit{viscous dissipation} per unit volume. Note that the entropy generation rate expressed in (1) is per unit volume (W/(K m³)). The global entropy generation rate \(\dot{S}_{\text{gen}}\) of the entire domain (W/K) is computed as the integral of the local rates over the entire volume \(V\):

\[
\dot{S}_{\text{gen}} = \int_V (\dot{S}_T + \dot{S}_V) dV = \int_V (\dot{S}_T + \dot{S}_V) dV = \dot{S}_T + \dot{S}_V \tag{2}
\]

As mentioned above, the approach adopted in this work consists in focusing the attention first on the local entropy generation rates \(\dot{S}_T, \dot{S}_V\) and in considering the global one \(\dot{S}_{\text{gen}}\) only after having carefully studied the implications of the local irreversible losses. In particular, the procedure for ‘optimising’ a design by means of an entropy generation analysis is the following:

1. Define a starting geometry or a family of starting geometries.
2. Acquire the geometries and create the computational grid to be imported into the CFD solver.
3. Compute the temperature and the velocity fields.
4. Compute and display the maps of \(\dot{S}_T, \dot{S}_V\).
5. Integrate the local values to obtain the global entropy generation rate \(\dot{S}_{\text{gen}}\).
6. Modify the design as suggested by a critical inspection of the local entropy maps.
7. Repeat the computation, and iterate until a feasible and acceptable “minimum” of \(\dot{S}_{\text{gen}}\) is obtained.

It is now clear that the process described above is not an optimization proper, but rather a heuristic design approach, essentially based on a thermodynamically sound trial-and-error procedure. Nevertheless, the amount of phenomenological information contained in the local entropy generation maps is so high that a convergence towards a better design is almost guaranteed ([10]).

3. The Solar Roof tile

3.1 The TAK plant

The object of this study is the solar roof tile, called TAK, which is part of a complex system (the TAK plant) to provide the heating and cooling of a house (Fig. 1). The TAK plant can be divided in four main sub-systems:

- **TAK sub-system**: consisting of south-facing roof-tiles through which a secondary fluid flows, XEN, whose physical properties are given in Tab. 1. A pump (P1 in Fig. 1) provides fluid circulation.

- **Heat Pump sub-system**: a first heat exchanger (EX1) allows connecting the TAK sub-system with a Heat Pump sub-system through the heat exchange between secondary and primary fluid. The primary fluid, flowing through the heat pump cycle, is refrigerant 407C. A second heat exchanger (EX2) is necessary for the heat transfer to the Domestic Water Heating sub-system. An expansion valve is inserted to complete the cycle of the heat pump.

- **House Heating/Cooling sub-system**: this is the sub-system that interacts with the internal space; it includes radiators, fan coils or radiant panels with all their respective customary auxiliary components (pumps, valves, exc.).

- **Domestic Water Heating sub-system**: a boiler (B1) contains the water necessary for domestic use. This water receives heat from water circulating through the coil, which is then channelled into the heat exchanger EX2 of the Heat Pump sub-system. Another boiler is connected to a valve that allows the mixing of hot water with cold water.
The aim of this study is to optimize the geometry of the roof tile in winter conditions. In this season, during the hours of sun irradiation, the secondary fluid, XEN, is pumped (P1) through the south-side tiles. The XEN is heated in the row of tiles and then flows into the evaporator (EX1) of the Heat-Pump where it is cooled again to repeat the cycle (1S-8S in Fig. 1). The primary fluid, the refrigerant R407C, is heated by the secondary fluid in the evaporator, compressed (C) and channelled into the condenser (EX2) where it condensates, heating the water flowing in the Heating sub-system (streams 1W to 9W). The hot water is first used to heat the domestic water (in the boiler B1) and then flows into the inertial tank (T1) that feeds the Heating System. If the inertial tank temperature is lower than the temperature of water leaving B1 (Stream 5W), the hot water by-passes the tank (5cW) and it is used directly by the Heating Systems.

3.2 The solar roof tile

The TAK roof tile consists of a lower part made of a suitable polymeric material with a sealed aluminium slab on top of it (Fig. 2). The aluminium slab has dimensions 378.5x157.3x0.5 mm while the height of the fluid channel is 3.5 mm, as shown in Fig. 3. It should be mentioned that, as we shall see later, many other geometries were proposed and analysed, but in the optimization process the dimensions just given and the peripheral edges and faces of the fluid channel were kept constant.

3.2.1 Working conditions

On the basis of the sizing and simulations of the complex system described above, the mass flow and inlet temperature of the first line of the roof tile have been determined to be:

\[ \dot{m} = 0.0044 \, \text{kg/s} \]  
\[ T_{\text{in}} = 30^\circ \text{C} \]  

As representative working conditions, the following values for the sun irradiation \( q_{\text{sun}} \) and external temperature \( T_{\text{ext}} \) are chosen:

\[ q_{\text{sun}} = 400 \, \text{W/m}^2, \]  
\[ T_{\text{ext}} = 10^\circ \text{C}, \]  

As mentioned above, this work presents an application of the entropy generation minimization method to the pseudo-optimization of the configuration of the heat exchange surfaces in this solar roof tile. A group of initial “standard” geometries is first presented and analyzed (see Section 3.2.2). Then two of them are successively modified by introducing design changes aiming at the reduction of the thermodynamic losses due to heat transfer and fluid friction. The different geometries (featuring pins, fins and others) are simulated with a commercial CFD code that also computes the local entropy generation rate. The design improvement process is carried out on the basis of a careful analysis of the local entropy generation maps and the rationale behind each step of the process is discussed in this perspective.

Table 1. XEN fluid data.

<table>
<thead>
<tr>
<th>Property</th>
<th>symbol</th>
<th>value</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>( \rho )</td>
<td>1106</td>
<td>kg/m(^3)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>( \mu )</td>
<td>0.003</td>
<td>Pa s</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>( c_p )</td>
<td>2698</td>
<td>J/(kg K)</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>( k )</td>
<td>0.29</td>
<td>W/(m K)</td>
</tr>
<tr>
<td>Prandtl number</td>
<td>( Pr )</td>
<td>27.9</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) Average winter values in a city like Rome (latitude \( \approx 42^\circ \text{N} \), at noon on a roof with a tilt angle of 30° [13].
Fig. 1. TAK plant flow chart.

Fig. 2. Exploded view of the TAK roof tile.
3.2.2 The Initial geometries

The starting geometries, proposed by the original patent holder, GreenMind Company, are reported in Fig. 4(a). Geometry A.0 presents 24 plastic pin-fins with a diameter of D = 2.24 cm. To this group of starting geometries we added Geometry E.0 (Fig. 4(b)), in which the heat transfer is enhanced by four aluminium plate-fins cold rolled on the slab. The fins are 1 mm thick, 3.5 mm high, their length is L=28 cm and their distance in the span-wise directions is δ=30 mm.

The main results of the simulations of the starting geometries are reported in Table 2 (for the simulation details, see Section 5), from which the following general considerations can be made:

- $\dot{S}_v$ is one or two orders of magnitude smaller than $\dot{S}_T$;
- $\dot{S}_v$ is proportional to the pressure losses ($\Delta p$); the higher $\dot{S}_v$, the higher $\Delta p$;
as $\dot{S}_r$ decreases, the average temperature of the aluminium slab, $T_{av, slab}$ decreases as well; lower $T_{av, slab}$ means lower heat losses and therefore a higher heat transfer rate $\dot{Q} = \dot{m} \cdot c_p \cdot \Delta T$ to the fluid.

Furthermore, it can be seen that geometry B presents the lowest $\dot{S}_r$ and the highest value of $\dot{S}_V$. In fact, the flow is confined to a relatively small area so the velocity is high and this ensures high heat transfer coefficients. At the same time, the high mean velocity, combined with the presence of many sharp curves, causes a quite high value of pressure losses and therefore of viscous dissipation. Geometry B is also the best performer from a thermodynamic point of view, nevertheless the relatively high pressure losses are a big drawback. Geometries C and D do not appear to have a big “potential” for an optimization process. For these reasons, the geometries chosen to apply to the optimization process described in Sections 1 and 2 are A and E.

### Tab. 2. Simulation results for the starting geometries. $T_{av, slab}$ the average temperature of the upper surface of aluminium slab; $\dot{Q} = \dot{m} \cdot c_p \cdot \Delta T$ represents the heat transfer rate to the fluid and $\Delta p$ is the pressure drop across the solar roof tile.

<table>
<thead>
<tr>
<th></th>
<th>$T_{av, slab}$ [K]</th>
<th>$\dot{Q}$ [W]</th>
<th>$\Delta T$</th>
<th>$\Delta p$ [Pa]</th>
<th>$\dot{S}_r$ [W/K]</th>
<th>$\dot{S}_V$ [W/K]</th>
<th>$\dot{S}_gen$ [W/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.0</td>
<td>304.91</td>
<td>10.665</td>
<td>0.91</td>
<td>25</td>
<td>1.39E-04</td>
<td>2.85E-07</td>
<td>1.39E-04</td>
</tr>
<tr>
<td>B</td>
<td>304.30</td>
<td>10.898</td>
<td>0.92</td>
<td>961</td>
<td>7.78E-05</td>
<td>1.10E-05</td>
<td>8.88E-05</td>
</tr>
<tr>
<td>C</td>
<td>304.43</td>
<td>10.841</td>
<td>0.91</td>
<td>278</td>
<td>9.80E-05</td>
<td>2.13E-06</td>
<td>1.01E-04</td>
</tr>
<tr>
<td>D</td>
<td>304.92</td>
<td>10.658</td>
<td>0.9</td>
<td>77</td>
<td>1.26E-04</td>
<td>1.39E-06</td>
<td>1.27E-04</td>
</tr>
<tr>
<td>E.0</td>
<td>304.32</td>
<td>10.777</td>
<td>0.91</td>
<td>19</td>
<td>1.11E-04</td>
<td>2.18E-07</td>
<td>1.11E-04</td>
</tr>
</tbody>
</table>

### 4. Alternative geometries

As stated before, the (“family” of ) geometries chosen for further development are geometry A and E. In the next paragraphs the variations on each of these two families are presented. In section 6, the results and the rationale behind each design change is discussed.

#### 4.1 Geometries of type E

Geometry E.1 presents 9 plate-fins 1 mm thick, 2 mm high, $L=28cm$ long and distanced $\delta=15mm$ in the spanwise direction (Fig. 5(a)). Instead, Geometry E.2 features 10 “split-entry-length”, 7.5 cm long, fins, along with the 9 plate-fins of geometry E.1 (see Fig. 5(b)).

![Fig. 5. Geometry E.1 (a) and half of geometry E.2 (b).](image-url)
For comparison, geometry E.3 (not shown) has been also designed and simulated. This geometry has 19 fins 28 cm long, 2 mm high and 1 mm thick. The only difference with geometry E.2 is that all the 19 (9+10) fins are 28 cm long.

4.2 Geometries of type A

The starting geometry of the A family presents 24 pin-fins with a diameter of $D = 2.24 cm$ made of plastic material. As a first design modification, the plastic fins are substituted with aluminium ones impressed with the slab, geometry A.1. This simple modification leads to a 15% improvement of the global entropy generation rate. For this geometry, the dimensionless pitches are $P_T^* = P_T/D = 2.34$ and $P_L^* = P_L/D = 1.41$, where $P_T$ and $P_L$ are the transverse (spanwise) and the longitudinal (streamwise) pitch, respectively.

In order to enhance heat transfer, it was decided to design a new geometry, A.2, with fins half the diameter of the current ones but keeping the same array geometry, i.e. same $P_T^*$ and $P_L^*$. Therefore, geometry A.2 presents 104 fins with a diameter of $D = 1.12 cm$, height of 3.5 mm, $P_T^* = 2.34$ and $P_L^* = 1.41$, as can be seen in Fig. 6. As will be seen later, at the bottom of the channel the fins are not effective; therefore, in geometry A.3, it is decided to limit the height of the fins to 2 mm.

Geometry A.4 features pins of different diameters placed in “strategic” positions determined by a careful analysis of the local entropy maps (see Section 6). As shown in Fig. 7, smaller fins are placed in between the columns and row of the original array.

Geometry A.5 (shown in Section 6), is obtained by simply inserting in A.3 another column of pin fins. Pins now become 161 (57 more than geometry A.3) and the characteristics parameters of the array are $P_T^* = 1.46$ and $P_L^* = 1.41$.

![Fig. 6. Geometry A.2 (half).](image)

![Fig. 7. Detail of geometry A.4.](image)
5. The numerical simulations

5.1 Meshing

Four starting geometries (A.0, B, C, D in Fig. 4(a)) were made available by the GreenMind Company which provided the relative IGES files. Once imported into GAMBIT, the mesh generator, all of the geometric features of the TAK deemed inessential for the goals of the present simulations were removed: only the fluid channel, the inlet and outlet ducts and the aluminium slab are retained. The obvious symmetry of the design, and with the exception of geometry B, only half of the TAK was modelled, discretized and simulated. As mentioned above, many other geometries were designed and tested (see Section 3) but are not reported here. The control volume of all geometries is always created starting from the “base” volume shown in Fig. 8.

![Fig. 8. Base geometry used in the optimization process.](image)

The following general procedure is applied to all geometries:

- The control volume is split in several smaller sub-volumes, as indicated in Fig. 9 for one representative geometry. This step produces a decomposition of the control volume necessary to successfully apply the Cooper meshing scheme.
- Each edge is meshed using an element size specific of the single volume given in Tab. 3 with the only exception of the fluid channel height, which is meshed with 16 elements.
- If the geometry features pins, a boundary layer with 10 rows is attached to the solid wall.
- The bottom surface of the fluid channel is meshed using a “paved” scheme, which allows meshing such a complex surface without further subdividing it. The drawback, of course, is the generation of an unstructured mesh, in which the regularity of the internal gridpoint is lost.
- The fluid channel volume is meshed with the Cooper scheme (GAMBIT automatically selects the source surfaces).
- The remaining volumes are meshed using again the Cooper scheme.
This procedure leads to a very high quality mesh; usually more than 98% of the cells have an Equisize skew < 0.55. The number of elements is highly dependent on the fin diameter D: it goes from 231761 to 1327432 for D = 2.24 cm and D = 0.56 cm, respectively. The meshes of finless geometries are usually composed by no more than 400000 elements. All meshes consist only of hexahedral or wedge elements. Thus the mesh can be directly read by the parallel solver and all the cells are eligible for grid adaption.

**Tab. 3. Mesh element size for the edges of the indicated sub-volumes.**

<table>
<thead>
<tr>
<th>Volumes</th>
<th>Element size [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid channel</td>
<td>11</td>
</tr>
<tr>
<td>Inlet</td>
<td>1</td>
</tr>
<tr>
<td>Outlet</td>
<td>1</td>
</tr>
<tr>
<td>Pins</td>
<td>D/24</td>
</tr>
<tr>
<td>Internal slab</td>
<td>1</td>
</tr>
<tr>
<td>External slab</td>
<td>5</td>
</tr>
</tbody>
</table>

**5.2 Boundary conditions and parameters setting**

All simulations have been processed by means of the CFD code FLUENT in Parallel mode, with 2 processors. After performing the grid check, the mesh has been scaled. Then the Pressure Based solver with the Green-Gauss Node Based gradient option at steady state has been chosen, and the energy equation enabled. The Laminar viscous model was selected, since the Reynolds number in all cases is well below the transition regime. In the Materials Panel a custom fluid, with the properties of the XEN fluid given above, is created. The boundary conditions are imposed as follows:

- **Inlet:** constant mass flow, equal to 1/2 of the valued given in (3), i.e. 0.0022 kg/s, and constant temperature $T_{\text{inlet}}=30^\circ\text{C}$.
- **Outlet:** constant atmospheric pressure.
- **Symmetry planes:** zero gradients of all variables.
- **External surface of the aluminium slab:** this Wall surface receives the solar irradiation. In order to take into account the presence of a glass and an air gap (5 mm thick) on top of the slab, a convective boundary condition is used. The Heat Transfer Coefficient and the Free Stream Temperature are 6.29 W/(m² K) and 60.29 °C, respectively. These values represent the overall...
heat transfer coefficient and the so called “solar air temperature”, respectively. They are based on the values given in (5) and (6).

- Fluid and Solid: these boundary conditions allow the definition of the fluid evolving through the roof tile as well as the material of the solid volumes. In this problem, the previously defined XEN is selected for the fluid volume, while the default material, aluminium, is retained for the solid parts.

For all remaining wall surfaces the default settings have not been modified so that adiabaticity, impermeability and no slip conditions are imposed.

All simulations are initially started with a first order discretization scheme, then, when convergence is obtained, the second order scheme is enabled and the iteration restarted until convergence is attained (all the scaled residuals below $10^{-7}$, except for the energy equation for with the threshold is set to $10^{-6}$).

5.3 Mesh refinement

The next step involves a critical process: the grid sensitivity analysis. Goal of the mesh refinement is to demonstrate the mesh ability to capture the smallest (modelled) scales of the fluid dynamics phenomena involved in the simulation. An improved grid should be able to better describe the fluid behaviour and in order to determine the grid “quality” enhancement a cornerstone function field is needed for a performance comparison: the cornerstone function adopted in this work is the thermal entropy generation rate, since in this case it is one or two order of magnitude larger than the viscous one. The adaption tool available in the solver permits to change the number of cells belonging to a grid, both by coarsening and refinement. Excluding a priori any possibility of coarsening that will lead to a worse grid, the refinement can be operated with a criterion based on the gradient magnitude of the objective function. This “gradient” is the difference of the values of the selected field function between two adjacent cells; therefore a large gradient indicates a potentially inaccurate numerical solution. The grid refinement should deliver a more efficient control volume, and to result in a better evaluation of the entropy generation rates. In fact, to increase the number of cells is tantamount to increase the numerical solver aptitude to capture the small-scale dissipative phenomena, which are reflected in the value of the entropy generation rates. In this perspective, a critical analysis on the magnitude distribution across the control volume of the gradient of the entropy generation rates was performed. In the refinement of the grid, the Refine Threshold has been set to approximately 5% of the values reported in the Max field (i.e. the maximum value of the adaption function). As suggested in [14], the adaption threshold value has not been changed during the successive mesh adaptions which were repeated until the variation in the entropy rates lower than a 4% was reached.

6. RESULTS AND DISCUSSION

6.1 Geometry E

The central idea is that we expect low values of the local entropy rates in areas where similar boundary layers merge. The word “similar” means that the two boundary layers must draw origin from the same boundary conditions: that is the same surface geometry and the same $\Delta T$. On the contrary, we expect high values of $\hat{s}_x$ and $\hat{s}_y$ inside the boundary layers, since these are zones where velocities and temperatures change rapidly; so, from a thermodynamic perspective, we would like to reduce them. Nevertheless, boundary layers are “necessary”: by definition, convective heat transfer is the energy transfer between a surface and a fluid moving over the surface. If we limit the surface area and thus the boundary layer, we also decrease the heat transfer to the fluid. A compromise is needed. A possible solution was found in the insertion of another plate in the middle of the channel, parallel to the mean flow direction and long enough to generate a thermal boundary layer which merges with the ones generated by the other plates at its end (Fig. 10). This “new”
boundary layer will cause a local increment of $\dot{s}_T$ and $\dot{s}_V$ at the entrance of the channel, but will reduce $\dot{s}_T = k (\Delta T)^2 / T^2$ downstream. In fact, the velocity profile becomes smoother and the presence of another heat transfer surface causes a local increment of the mean fluid temperature $T$. As we shall see later, the overall balance is favourable: the introduction of the middle plate causes a reduction of the total entropy $\dot{S}_{\text{gen}}$ generated in the system.

Fig. 10. Growth of the thermal boundary layer between two parallel plates with a “split-entry length” ($T_{\text{plate}} > T_{\text{fluid}}$).

In geometry E.0 of Fig. 4, the distance between the fins $\delta$ has been originally chosen by solving the thermal entry length problem so that the thermal boundary layers would merge right at the end of the fins, that is after a distance $L=L_{th}$ in the streamwise direction. The thermal entrance length $L_{th}$ is conventionally defined as the duct length required to achieve a value of the local Nusselt number $Nu_x$ equal to 1.05$Nu$ for fully developed flow (see [15]). A fully developed temperature profile starts where the thermal boundary layers merge. The dimensionless thermal entrance length is expressed as:

$$L'_{th} = \frac{L_{th}}{D_h \cdot Re \cdot Pr}$$

(7)

where $D_h$ is the duct hydraulic diameter, $Re$ is the duct Reynolds number and $Pr$ is the Prandtl fluid number. Fig.11 represents the plot of the temperature profile at a constant height $y = 1.75\text{mm}$ at four different sections ($z1, z2, z3, z4$) in the streamwise direction $z$; these four sections are defined as $z1 = 0$, $z2 = L/3$, $z3 = 2L/3$ and $z4 = L$, $L$ being the length of the fin. The thermal boundary layer starts growing at $z1$ and reaches its maximum thickness at $z4$.

Fig. 11. Temperature profile in the mid plane at different sections downstream (geometry E.0).
From Fig. 11 we find that the thermal boundary layer thickness $\delta_{th}$ at the end of the fin, $zA$, is $\delta_{th}=7.5 \text{mm}$. Therefore, since we want the thermal boundary layer to merge right at the end of the fins, the distance between them should be $\delta=2 \delta_{th}=15 \text{mm}$, which was therefore selected as the distance between the fins of geometry E.1. Once we know the dimensionless thermal entry length of the problem, it is possible to calculate the split-entry length fin of Fig. 10, which turns out to be $7.5 \text{cm}$ long. Accordingly, the ten intermediate fins of geometry E.2 (Fig. 5(b)) are $7.5 \text{cm}$ long.

Fig. 12 shows the contours of $\dot{s}_T$ at $y=2 \text{mm}$ for geometry E.1 and E.2. It can be seen how the presence of the middle fins causes a reduction of the local thermal entropy generation rate.

![Fig. 12. Contours of $\dot{s}_T$ at $y = 2 \text{mm}$ for geometry E.1 (a) and E.2 (b).](image)

The simulation results, for all the E-type geometries, are reported in Tab. 4. As shown in Tab. 4, even though the heat transfer area is significantly different, no appreciable variation of $Q$, and therefore of $\Delta T$, is obtained (at least in this first roof tile). Instead, the generated entropy appears to be more sensible to the variation of the heat transfer area. In fact, $\dot{S}_{gen}$ in E.2 is $11\%$ less than in E.1 while E.3 produces $14\%$ less entropy than E.1. The variation of the heat transfer area, though, is not proportional: only $5\%$ in the first case and $14\%$ in the second. Hence, it could be inferred that the shorter (interstitial) fins are more effective from a thermodynamic perspective.

**Table 4. Comparison between the main results obtained for geometries E.1, E.2 and E.3. $\Delta E2-1$ represents the percentile variation of the indicated quantities between E.1 and E.2; $\Delta E3-2$ represents the percentile variation of the indicated quantities between E.2 and E.3.**

<table>
<thead>
<tr>
<th></th>
<th>E.1</th>
<th>E.2</th>
<th>E.3</th>
<th>$\Delta E_{2,3}$</th>
<th>$\Delta E_{3,2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat transfer area $[\text{cm}^2]$</td>
<td>573.57</td>
<td>603.97</td>
<td>685.97</td>
<td>5%</td>
<td>14%</td>
</tr>
<tr>
<td>$T_{\text{av,slab}}$ $[\text{K}]$</td>
<td>304.60</td>
<td>304.52</td>
<td>304.43</td>
<td>-0.03%</td>
<td>-0.03%</td>
</tr>
<tr>
<td>$\dot{Q}$ $[\text{W}]$</td>
<td>10.777</td>
<td>10.811</td>
<td>10.842</td>
<td>0.32%</td>
<td>0.29%</td>
</tr>
<tr>
<td>$\Delta T$</td>
<td>0.909</td>
<td>0.911</td>
<td>0.913</td>
<td>0.24%</td>
<td>0.22%</td>
</tr>
<tr>
<td>$\Delta p$ $[\text{Pa}]$</td>
<td>19</td>
<td>20</td>
<td>22</td>
<td>3%</td>
<td>9%</td>
</tr>
<tr>
<td>$\dot{S}_T$ $[\text{W/K}]$</td>
<td>1.11E-04</td>
<td>9.83E-05</td>
<td>8.43E-05</td>
<td>-11%</td>
<td>-14%</td>
</tr>
<tr>
<td>$\dot{S}_v$ $[\text{W/K}]$</td>
<td>2.87E-07</td>
<td>2.26E-07</td>
<td>2.43E-07</td>
<td>4%</td>
<td>7%</td>
</tr>
<tr>
<td>$\dot{S}_{gen}$</td>
<td>1.11E-04</td>
<td>9.86E-05</td>
<td>8.45E-05</td>
<td>-11%</td>
<td>-14%</td>
</tr>
</tbody>
</table>
6.2 Geometry A
Fig.13-14, represent the contour of thermal entropy generation and temperature, respectively, at different height of the channel. $\dot{s}_T$ decreases towards the bottom of the channel (lower $y$), except in very small zones in the proximity of the fins where it remains high. In these zones of high temperature gradients, the local heat transfer coefficients are low and the fins are not effective. Therefore, it was decided to limit the height of the fins in geometry A.3 to 2 mm; this modification leads to an improvement in the fin effectiveness and in the global entropy generation which is reduced by 6% (Tab. 5). As shown in Fig. 13, $\dot{s}_T$ assumes the highest values in proximity of the lateral boundaries where the heat absorbed by the corners of the slab is exchanged with an almost stagnant fluid. Moreover, near the outlet, the entropy production is increased also by the mixing of the upper, hotter, fluid with the lower and colder part of the stream. High values of $\dot{s}_T$ are also found in between columns of fins, forming a sort of “entropy rivers” flowing along the roof tile.

Fig. 13. Contours of Thermal Entropy generation for Geometry A.2 at different height of the channel.

Fig. 14. Contours of Temperature for Geometry A.2 at different height of the channel.
Looking at the temperatures contours, Fig. 14, it can be seen that the thermal boundary layers generated by one row of fins do not merge with the thermal wake generated by the very next row. On the basis of these considerations, it was argued that an “optimal” (in a second law perspective) geometry, should feature a gradual increment of the transverse pitch \( P_T^* \) along the streamwise direction. In addition, the diameter of the fins should increase moving towards the bottom of the channel. In fact, the maximum thickness of the boundary layer increases in the streamwise direction as well as along \( y \). A fin of such geometry, however, would imply important technological issues and increased costs.

Two more configurations were devised: A.4 was designed to counteract the entropy generation due to the boundary effects, and A.5 to eliminate the entropic rivers.

![Fig. 15. Contours of the local Thermal Entropy Generation for Geometry A.4 at y=3mm.](image)

As can be seen comparing Fig. 13 and 15, the boundary effects have been limited but areas of high \( \dot{s}_T \) still persist. Geometry A.4 produces 9% less entropy than geometry A.3 (Tab. 5). As stated before, Geometry A.5, instead, is obtained by A.3 simply by inserting another column of pin fins. This design modification leads to a substantial improvement in the rate of entropy production which decays by 20% with respect to geometry A.3. In fact, looking at Fig. 16 and 17, the entropic rivers are no longer present and the individual thermal boundary layers originated on a single fin are actually no longer distinguishable since they all merge.
Comparing the results obtained for geometries A.3, A.4 and A.5, it seems that the entropic rivers, i.e. the entropy generated by a sub-optimal choice of the transverse pitch $P_T$, have more influence on $\dot{S}_{gen}$ than the local entropy production due to boundary effects, which, however, appear difficult to counteract.

Tab. 5. Simulation results for all the A-family geometries.

<table>
<thead>
<tr>
<th>$T_{av,slab}$ [K]</th>
<th>$Q$ [W]</th>
<th>$\Delta T$</th>
<th>$\Delta p$ [Pa]</th>
<th>$\dot{S}_T$ [W/K]</th>
<th>$\dot{S}_V$ [W/K]</th>
<th>$\dot{S}_{gen}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.0</td>
<td>304.91</td>
<td>10.665</td>
<td>0.91</td>
<td>25</td>
<td>1.39E-04</td>
<td>2.85E-07</td>
</tr>
<tr>
<td>A.1</td>
<td>304.76</td>
<td>10.720</td>
<td>0.91</td>
<td>25</td>
<td>1.18E-04</td>
<td>2.85E-07</td>
</tr>
<tr>
<td>A.2</td>
<td>304.56</td>
<td>10.795</td>
<td>0.91</td>
<td>26</td>
<td>9.92E-05</td>
<td>3.03E-07</td>
</tr>
<tr>
<td>A.3</td>
<td>304.47</td>
<td>10.827</td>
<td>0.91</td>
<td>25</td>
<td>9.35E-05</td>
<td>2.90E-07</td>
</tr>
<tr>
<td>A.4</td>
<td>304.40</td>
<td>10.854</td>
<td>0.91</td>
<td>26</td>
<td>8.55E-05</td>
<td>3.03E-07</td>
</tr>
<tr>
<td>A.5</td>
<td>304.29</td>
<td>10.894</td>
<td>0.92</td>
<td>32</td>
<td>7.46E-05</td>
<td>3.82E-07</td>
</tr>
</tbody>
</table>
6.3 Integrating the heuristic and the deterministic approach

Clearly, the optimization process described above can be applied, mostly, to a limited number of values of the fin diameter $D$: the heuristic approach, though powerful, has intrinsic limitations. However, a further study about the influence of the pin-fin array on the thermodynamic performance of the roof tile can be developed. Hence a deterministic approach was adopted. Following a procedure employed by many authors\footnote{See the already cited [1-2] and [6-9].}, a lumped-sum parameter model was developed to analytically express $\dot{S}_{gen}$ only in terms of the dimensionless transverse pitch $P^*_{T}$ and the fin diameter $D$. Details are given in [16].

The entropy generation model can be developed by considering the control volume CV shown in Fig. 18. The CV includes the pin fin array and a base plate. The side surfaces AEFG and BCJI and the top surface CJFE of this CV are regarded as impermeable and adiabatic. The incompressible fluid of density $\rho$ enters the volume at temperature $T_{in}$ and velocity $U_{in}$. $T_{base}$ and $T_{fin}$ are the average temperatures of the base plate and the fins, respectively. The total heat transfer rate over the boundary of the CV is

$$\dot{Q} = \dot{Q}_{fin} + \dot{Q}_{base}. \quad (8)$$

Assuming $T_{base} \approx T_{fin} \approx T_{wall}$, the global entropy generation in the CV can be written as ([1]):

$$\dot{S}_{gen} = \dot{S}_{T} + \dot{S}_{v} = \frac{\dot{Q} \cdot \Delta T}{T_{in}^2} + \frac{\dot{m} \cdot \Delta p}{\rho T_{in}}, \quad (9)$$

where $\Delta T = T_{wall} - T_{in}$ and $\Delta p = p_{in} - p_{out}$ is the pressure difference experienced by the fluid across the CV. As shown in Fig.19, the global entropy generation reaches its maximum for both high $P^*_{T}$ and
D; it tends to infinity for $P_T \to 1$ for any diameter due to a very steep increase of the viscous entropy. Moreover, the plot shows the existence of an optimal value of $P_T$ for each diameter, as found in [17] and [18]. However, the dependence of $\hat{S}_{gen}$ on the geometry parameter $P_T$ appears to be less pronounced for smaller values of $D$. In order to compare the results obtained with the above discussed simulations with those given by the model, two new geometries were designed and simulated. Geometry A.5.1 is simply geometry A.5 but the fin height is 3.5 mm instead of 2 mm.

Geometry A.6 features the same $P_T = 1.46$ and height as geometry A.5.1 but the fin diameter is $D = 0.56 \text{ cm}$ instead of 1.12 cm. With these values, the pins of geometry A.6 become 374, leading to a 20% increase of the heat transfer area. The simulations results are given in Tab. 6.

<table>
<thead>
<tr>
<th></th>
<th>$T_{av,slab}$ [K]</th>
<th>$Q$ [W]</th>
<th>$\Delta T$</th>
<th>$\Delta p$ [Pa]</th>
<th>$\dot{S}_T$ [W/K]</th>
<th>$\dot{S}_V$ [W/K]</th>
<th>$\dot{S}_{gen}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.5.1</td>
<td>304.36</td>
<td>10.868</td>
<td>0.92</td>
<td>40</td>
<td>8.15E-05</td>
<td>4.62E-07</td>
<td>8.19E-05</td>
</tr>
<tr>
<td>A.6</td>
<td>304.09</td>
<td>10.869</td>
<td>0.93</td>
<td>62</td>
<td>5.09E-05</td>
<td>5.92E-07</td>
<td>5.15E-05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>simulations</th>
<th>model</th>
<th>$\Delta \hat{S}_{gen}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.1</td>
<td>1.18E-04</td>
<td>4.78E-04</td>
<td>-304%</td>
</tr>
<tr>
<td>A.2</td>
<td>9.95E-05</td>
<td>2.60E-04</td>
<td>-161%</td>
</tr>
<tr>
<td>A.5.1</td>
<td>8.19E-05</td>
<td>1.71E-04</td>
<td>-109%</td>
</tr>
<tr>
<td>A.6</td>
<td>5.15E-05</td>
<td>5.22E-05</td>
<td>-1%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>simulations</th>
<th>model</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A.1/A.2</td>
<td>16%</td>
<td>46%</td>
<td></td>
</tr>
<tr>
<td>A.2/A.5.1</td>
<td>18%</td>
<td>34%</td>
<td></td>
</tr>
<tr>
<td>A.6/A.5.1</td>
<td>37%</td>
<td>70%</td>
<td></td>
</tr>
</tbody>
</table>
Tab. 7 and 8 show the comparison between the simulations results and those given by the model of Eq. (9). As shown in Tab. 7, the lumped-sum parameter model overpredicts $S_{gen}$ but the differences between the two groups of results become negligible if we consider geometries with lower entropy generation rates. For geometry A.6, almost the same values are obtained. Moreover, the trends are similar even though the model predicts entropy rate differences (between two “geometrically close” configurations) roughly double than those obtained with the simulations (see Tab. 8). A possible interpretation of this behavior is that the boundary effects introduce a sort of damping in the thermodynamic performance of the tile, limiting the differences of $S_{gen}$ from one geometry to the other. In conclusion, the model seems to represent well the global trend of $S_{gen}$. In fact, recalling Fig. 19, the model predicts almost the same optimal $P_rT$ for $D=1,12 cm$ that was found analyzing the local entropy maps. However, large numerical differences with the simulations results are found. In addition, these differences vary greatly as they depend on the values of the two independent variables $P_rT$ and $D$. Therefore, it is very difficult to assess if and to what extent they are caused by the influence of the boundary effects (not considered in the lumped model), or by the approximations intrinsic in the correlations the model relies on. As mentioned in Section 1, a deterministic approach also has its limitations. This doesn’t mean that the two approaches cannot be integrated. In fact, a possible procedure is to first select a pair $(P_rT, D)$ on the basis of the plot of $S_{gen}$ given by the model; then, to use the heuristic approach for the “fine tuning”. For example, as shown above, a careful analysis of the local entropy maps guides the designer in the choice of the optimal height of the fin, which is something the model cannot “see”. This said, further developments cannot ignore any longer the technological issues affecting the realization of the aluminum slab and fins. In order to have a complete picture of the problem, in fact, it would be necessary to estimate the costs associated with each configuration; in particular, the influence of the fin diameter, height and number. In this context, the exergy of the production process ought to be considered in the overall balance as well. Only after these factors have been considered and a selection criterion adopted, it would be possible to choose the final design of the Roof tile. Such analysis, however, is beyond the scope of this work.

7. CONCLUSIONS AND SUGGESTIONS

A careful and detailed description of the steps of the heuristic optimization of a particular type of heat exchanger has been presented. The thermodynamic fields, in all simulations, have been evaluated on a satisfactorily refined grid, using the thermal or the total entropy generation rate as an objective function. In this way, a sufficiently large and reliable database of “numerical experimental data” has been obtained. The pseudo-optimization process described in this work is an effective tool in the hands of an expert designer. In fact, it led here to a significant improvement of the thermodynamic performance. The adopted procedure for “optimizing” a design by means of an entropy generation analysis is not an optimization proper, but rather a heuristic design approach, essentially based on a thermodynamically sound trial-and-error procedure. It results from the direct
scanning of a finite (and in fact quite small) solution set and is similar to a (single or multiple parameter) sensitivity study. Nevertheless, the amount of phenomenological information contained in the local entropy generation maps is so high that a better design invariably emerges.

Among all the examined configurations, A.5 had the best performance from the point of view of both First and Second Law, quite superior to that of geometry B (the “best” among the starting ones). For the same $\Delta T = 0.92$, A.5 displayed pressure losses more than one order of magnitude lower than B (40 against 960 Pa). The calculated total entropy production was 10% lower.

The results of this study have quite general implications on the development of a general optimization criterion to be adopted in heat transfer problems. While it is well known that the optimal pin array shape parameters (pitch and span) can be determined by a critical analysis of the temperature contours, an optimization based on the integrated and local entropy maps shows that “optimal” arrays (i.e., those with optimal pitch and span) generate a flow path in which the individual thermal boundary layers originated on a single fin cannot be distinguished any longer because they all merge. Similar results emerged in the optimization process of geometry E. Another lesson can be learned from this latter case: even though the idea behind the development of this geometry originated from a simple 2-D physical reasoning, the introduction of the “split entry length” between two parallel fins proved to be an effective design modification aimed at the reduction of the entropy rate, and, at the same time, a possible way to optimize the heat transfer area.

### Nomenclature

\[
\text{Bejan number } \quad Be = \frac{\dot{s}_T}{\dot{s}_T + \dot{s}_v}
\]

**Greek symbols**

- $\delta$ distance between fins, mm
- $\eta$ efficiency
- $\mu$ dynamic viscosity, Pa s
- $\rho$ density, kg/m$^3$
- $\phi$ rate of viscous dissipation, W/(m$^3$)

**Subscripts and superscripts**

- * dimensionless
- $av$ average
- $ext$ external ambient air temperature
- $L$ longitudinal
- $in$ inlet
- slab aluminium slab
- $th$ thermal entry length
- $T$ thermal entropy generation
- $V$ viscous entropy generation

### References


COMPARATIVE ANALYSIS OF AMMONIA AND CARBON DIOXIDE TWO-STAGE CYCLES FOR SIMULTANEOUS COOLING AND HEATING

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Abstract:
The paper deals with the comparative analysis of the performance of cooling and heating systems operating with NH$_3$ (ammonia) or CO$_2$ (carbon dioxide), both natural refrigerants.
The study is based on the exergetic analysis that points out the location and the magnitude of a system malfunction. Both systems, with NH$_3$ or CO$_2$ operate in two stages. The exergetic analysis gives the direction of the structural optimization. The exergetic analysis has shown that the best structural schematic is not the same for the two agents. The exergetic analysis points out that the largest exergy destruction in the CO$_2$ cycle is due to the throttling process and offers solutions to diminish it.

Keywords:
Exergtic Analysis, Cooling and heating systems, Two stage refrigeration system, Structural optimization.

1. Introduction
Concerns for limiting the global warming phenomenon and the ozone depletion turned back the interest of the refrigeration industry towards the natural refrigerants NH$_3$ and CO$_2$ [1]. If ammonia, in spite of its very good thermodynamic properties does not match the requirements of safe refrigerant caused by toxicity and/or flammability, CO$_2$ keeps the standard of safety refrigerant.

Ammonia has by far the highest COP (Table 1) but for safety reasons Carbon dioxide is preferred in commercial and large transport refrigeration.

Table 1. Thermodynamic properties of the natural refrigerants NH$_3$ and CO$_2$

<table>
<thead>
<tr>
<th>Substance</th>
<th>Refrigerant</th>
<th>Normal Boiling Temperature [°C]</th>
<th>Critical Point [°C]</th>
<th>ODP</th>
<th>GWP</th>
<th>COP -15/30[°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>R-744</td>
<td>-55.6</td>
<td>31.0</td>
<td>0</td>
<td>1</td>
<td>2.56</td>
</tr>
<tr>
<td>Ammonia</td>
<td>R-717</td>
<td>-33.3</td>
<td>135.0</td>
<td>0</td>
<td>0</td>
<td>4.76</td>
</tr>
</tbody>
</table>

The problem of low critical temperature of Carbone dioxide is overcome by operating the system in the transcrical region. Many researches reveal the good efficiency of CO2 when used in heat pumps for hot water heating [2,3].
Carbon dioxide is characterized by environment friendliness, low price, easy availability, non-flammability, non-toxicity, compatibility with various common materials and compactness due to high operating pressures.
This paper attempts to give some answers about the conduct of CO\textsubscript{2} as refrigerant in systems for simultaneous cooling and heating in the aim of finding the best structure of the cycle.

To reveal the weaknesses of the CO\textsubscript{2} systems comparatively with the ones operating with NH\textsubscript{3}, an exergetic analysis was carried on. The exergetic analysis is the only one capable to point out a malfunction intrinsically connected to a specific process. Moreover the systems used for both refrigeration and heating offer two products represented by two quantities of heat – one received from the cold chamber and the other one transferred to the hot carrying agent. The two thermal energies have different temperature levels. Only the exergetic analysis that accounts for both the quantity of heat transferred and its temperature level in correlation with the ambient temperature can give the real measure of the system performance [4-6].

The comparative analysis of the exergy destruction and losses of the key pieces of the cooling and heating systems operating with NH\textsubscript{3} and CO\textsubscript{2} has revealed the weakness of each process due to the peculiar conduct of each one of the two refrigerants. Such a study done by Cavallini and Neksa [7] on a refrigeration system with CO\textsubscript{2} clearly shows that for this agent throttling is the most penalizing process.

In the present paper three schematics of two-stage refrigeration cycles have been analysed: a two-stage system with intermediary cooling performed by the environmental medium, a two – stage system with intercooling by the injection of a cold stream and a two-stage system with flash intercooling.

The comparative exergetic analysis performed on these different two-stage refrigeration cycles operating with CO\textsubscript{2} and NH\textsubscript{3} has shown that the best structural schematic is not the same for the two agents.

2. Schematic of a two-stage system with incomplete intermediary cooling

The constructive and operating characteristics of the system (Fig. 1) are: the cold carrying agent is water that is cooled in the evaporator from \( t_{v,\text{in}} = 15^\circ\text{C} \) to \( t_{v,\text{out}} = 8^\circ\text{C} \), the heat carrying agent is water whose temperature increases in the condenser from \( t_{c,\text{in}} = 45^\circ\text{C} \) to \( t_{c,\text{out}} = 55^\circ\text{C} \), the ambient temperature is \( t_0 = 25^\circ\text{C} \), the isentropic, mechanic and electric efficiencies of compressors and water pumps for NH3 are respectively \( \eta_s = 0.8 \), \( \eta_m = 0.83 \) and \( \eta_{el} = 0.9 \). For CO\textsubscript{2} the isentropic efficiency of the compression process has been calculated with the correlation \( \eta_{s,\text{cp}} = 0.9343-0.04478\cdot \pi_{sf} \) [8].

The NH\textsubscript{3} system is provided with a flash evaporator (Fig. 1a) while the CO\textsubscript{2} one operates with direct expansion evaporator and an internal subcooler-superheater (Fig. 1b).

2.1 Exergetic analysis

The two-stage refrigeration system offers to the customers two products – the exergy of the refrigerating power at the temperature level of the cold carrying agent \( \left| \frac{\dot{E}_{x,v}}{Q_v} \right| \) and the exergy of the thermal power at the temperature level of the heat carrying agent \( \left| \frac{\dot{E}_{x,c}}{Q_c} \right| \).

For the cooling process realized in the evaporator the Product and the Fuel of this operating zone are respectively (Fig. 1a):

\[
\dot{P}_v = \dot{E}_{x,\theta} - \dot{E}_{x,\theta} = \dot{m}_{v,w} \cdot c_{v,w} \left[ (T_9 - t_8) - T_0 \ln \frac{T_9}{T_8} \right]
\] (1)
The fuel consists of the total exergy ($\dot{E}_{X \text{TOT}}$) consumed on the refrigerant side (NH$_3$ or CO$_2$) to which the mechanical exergy consumed by the pump that runs the cold carrying agent is added [9].

For the evaporator, besides the fact that nothing from the power consumed by the pump to run the cold carrying agent is recovered, in addition, the heat generated by friction and taken away by the cold carrying agent represents a destruction that the compressors of the system have to supplementary compensate.

The exergy destruction due to pressure loss in the evaporator is:

$$\dot{I}_{v,f} = \frac{m_{v,w} \cdot v_{v,w} \cdot |\Delta p_v|}{\eta_s} + \frac{m_{v,w} \cdot v_{v,w} \cdot |\Delta p_v|}{\eta_s} \left( \frac{T_0}{T_{v,w}} - 1 \right).$$

(3)

The irreversibility of the heat transfer at a finite temperature difference in the evaporator leads to the exergy destruction:

$$\dot{I}_{v,\text{MT}} = \dot{Q}_{\text{mt}} \cdot T_0 \frac{T_{v,w} - T_v}{T_{v,w} \cdot T_v}.$$

(4)

For the heater (condenser for NH$_3$) the Product is represented by the increase in the thermal exergy of the heat carrying agent (Fig.1.a):
\[ P_{cd} = \dot{E}_{x11}^T - \dot{E}_{x10}^T = \dot{m}_{c,w} \cdot c_{c,w} \left[ (t_{11} - t_{10}) - T_0 \ln \frac{T_{11}}{T_{10}} \right]. \]  

\[ F_{cd} = \left( \dot{E}_{x4}^{TOT} - \dot{E}_{x5}^{TOT} \right) + \left( \dot{E}_{x10}^M - \dot{E}_{x11}^M \right) = \dot{m}_2 \left( h_4 - h_5 - T_0 (s_4 - s_5) \right) + \dot{m}_{c,w} v_{c,w} \frac{\nu}{\eta_s \cdot \eta_m \cdot \eta_{el}}. \]  

The exergy destruction in the heater is represented by:

\[ \dot{I}_{cd} = \dot{I}_{cd,f} + \dot{I}_{cd,\Delta T}, \]  

where

\[ \dot{I}_{cd,f} = T_0 \frac{\dot{m}_{c,w} \cdot v_{c,w} \cdot |\Delta P_h|}{\eta_s \cdot T_{c,w}}, \]  

and

\[ \dot{I}_{cd,\Delta T} = \dot{Q}_{cd} \cdot T_0 \left( \frac{T_c - T_{c,w}}{T_c \cdot T_{c,w}} \right). \]  

Denoting by \( W_{cp,t} \) and \( W_{p,t} \), the mechanical powers consumed by the system compressors and pumps – the exergetic balance equation on the customer side becomes (Fig. 1.a):

\[ \dot{W}_{cp1,t} + \dot{W}_{cp2,t} + \dot{W}_{p1,t} + \dot{W}_{p2,t} = (\dot{E}_{x9}^T - \dot{E}_{x8}^T) + (\dot{E}_{x11}^T - \dot{E}_{x10}^T) + \dot{I}_{cp1} + L_{cp1,m,el} + \dot{I}_{cp2} + L_{cp2,m,el} + \dot{I}_{cd,f} + \dot{I}_{cd,\Delta T} + L_{cd,P} + L_{p} + L_{v,\Delta T} + L_{v,f} + L_{v,P}. \]  

The exergetic efficiency is:

\[ \eta_e = \frac{\Delta \dot{E}_x^T + \Delta \dot{E}_x^T}{\sum \dot{W}_i}; \quad \eta_{ex, ev} = \frac{\dot{P}_v}{\dot{F}_v}; \quad \eta_{ex, cd(gh)} = \frac{\dot{P}_{cd}}{\dot{F}_{cd}}. \]

### 2.2 Influence of the variation of the operating parameters

The project states the refrigeration power and the temperature levels at which cold and heat are supplied to the customers.

The intermediary pressure of the two-stage system will be stated based on the maximum efficiency criterion.

For the refrigeration and heat pump systems presented in Fig. 1.a,b the temperatures in the key states of the cycles, the mass flow rates and the energy rates per 1 kW of cold are shown in Tables 2 and 3.

**Table 2. NH₃ system. Temperatures, mass flow rates and energy rates per 1 kW of cold (Fig. 1a)**

<table>
<thead>
<tr>
<th>( p_{at} ) [bar]</th>
<th>( m \cdot 10^3 ) [kg/s]/kW cold</th>
<th>( \dot{W}_{cp,t} ) [kW/kW cold]</th>
<th>( \dot{Q}<em>{cd} + \dot{Q}</em>{int} ) [kW/kW cold]</th>
<th>( t_2 ) [°C]</th>
<th>( t_4 ) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.0002</td>
<td>0.4063</td>
<td>1.4063</td>
<td>60.53</td>
<td>130.2</td>
</tr>
<tr>
<td>12</td>
<td>1.0002</td>
<td>0.4112</td>
<td>1.4112</td>
<td>76.87</td>
<td>131.7</td>
</tr>
<tr>
<td>14</td>
<td>1.0002</td>
<td>0.4144</td>
<td>1.4144</td>
<td>91.17</td>
<td>132.57</td>
</tr>
</tbody>
</table>
Table 3. CO\textsubscript{2} system. Temperatures, mass flow rates and energy rates per 1 kW of cold (Fig. 1b)

<table>
<thead>
<tr>
<th>p\textsubscript{in} [bar]</th>
<th>(\dot{m} \cdot 10^3) [kg/s/kW cold]</th>
<th>(\dot{W}_{cp,t}) [kW/kW cold]</th>
<th>(\dot{Q}<em>h + \dot{Q}</em>{int}c) [kW/kW cold]</th>
<th>(t_2) [°C]</th>
<th>(t_4) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>8.511</td>
<td>0.7573</td>
<td>1.7573</td>
<td>75.2</td>
<td>114.4</td>
</tr>
<tr>
<td>70</td>
<td>8.511</td>
<td>0.7652</td>
<td>1.7652</td>
<td>82.03</td>
<td>114.9</td>
</tr>
<tr>
<td>75</td>
<td>8.511</td>
<td>0.7738</td>
<td>1.7738</td>
<td>88.52</td>
<td>115.3</td>
</tr>
</tbody>
</table>

For both NH\textsubscript{3} and CO\textsubscript{2} cycles, temperature \(t_2\) at the discharge from the first stage compressor strongly recommend using the intercooler as well, for heating the thermal agent. The overall efficiency of the cycle increases in this way.

While for CO\textsubscript{2} temperatures at the discharge from compressors cause no problem, for NH\textsubscript{3} the second stage compressor operates at the highest avoidable temperature limit.

In Fig. 2 are presented the variation of the overall exergy efficiency and of the compression ratio in the first stage against the intermediary pressure for the two compared refrigeration systems.

Fig 2.a, NH\textsubscript{3} System. Variation of the exergetic efficiency and of the first stage compression ratio against the intermediary pressure for schematic Fig. 1.a

Fig 2.b, CO\textsubscript{2} System. Variation of the exergetic efficiency and of the first stage compression ratio against the intermediary pressure for schematic Fig. 1.b

Fig. 3.a, NH\textsubscript{3} System. Exergy destruction ratio related to the exergy of the total plant fuel against the intermediary pressure for schematic Fig. 1.a

Fig. 3.b, CO\textsubscript{2} System. Exergy destruction ratio related to the exergy of the total plant fuel against the intermediary pressure for schematic Fig. 1.b
In both cases, the lower is the intermediary pressure, with respect to the NH\textsubscript{3} system for the temperature limit in the discharge of the second stage compressor, the higher is the exergetic efficiency. In spite of the large operating pressures for the CO\textsubscript{2} system, the first stage compression ratio is approximately twice lower than for the NH\textsubscript{3} system leading for CO\textsubscript{2} to low mechanical work input.

The lower exergetic efficiency for CO\textsubscript{2} compared to the NH\textsubscript{3} system is due to higher exergy destructions.

The comparative analysis for the NH\textsubscript{3} and CO\textsubscript{2} systems (Figs 3.a,b) reveals a three times higher exergy destruction ratio with throttling for CO\textsubscript{2}. The large exergy destruction with throttling explains the lower exergetic efficiency for the CO\textsubscript{2} system compared with the NH\textsubscript{3} one.

Another larger exergy destruction ratio that leads to lower exergetic efficiency for CO\textsubscript{2} than NH\textsubscript{3} is in the gas heater. This characteristic recommends CO\textsubscript{2} for heating at higher temperatures i.e. hot water.

As expected, the lower compression ratio in the first stage for CO\textsubscript{2} is accompanied by the lower exergy destruction ratio in the compressor, compared to NH\textsubscript{3} (Figs 3.a,b).

In figures 4a,b the behaviour of the exergetic efficiency of the overall cycle, of the evaporate and of the condenser or gas heater is presented at the variation of the evaporator pressure drop.

For both systems the pressure drop in the evaporator has the same influence on the exergetic efficiency of the evaporator (Figs 4.a,b).

**3. Schematic of a two-stage system with intermediary cooling performed by the injection of a cold stream in the first stage discharged gas**

To diminish the temperature of the gas at the discharge from the high pressure compressor and to reduce in this way the accompanying exergy destruction due to heat transfer at a high temperature difference in the heater, the intermediary cooling is performed by the injection of a cold stream in the compressed gas between the two stages (Figs. 5. a,b).

For the flow charts presented in Figs. 5. a,b the temperatures in the key states of the cycles, the mass flow rates and the energy rates per 1 kW of cold are shown in Tables 4 and 5.
Table 4. NH₃ system. Temperatures, mass flow rates and energy rates per 1 kW of cold (Fig. 5a)

<table>
<thead>
<tr>
<th>Pₚ [bar]</th>
<th>mₙ₁ · 10³ [kg/s/kWcold]</th>
<th>mₙ₂ · 10³ [kg/s/kWcold]</th>
<th>Wₜ,c,p [kW/kW cold]</th>
<th>Qₜ,c [kW/kW cold]</th>
<th>t₂ [°C]</th>
<th>t₄ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.0002</td>
<td>1.083</td>
<td>0.413</td>
<td>1.413</td>
<td>60.53</td>
<td>115.90</td>
</tr>
<tr>
<td>12</td>
<td>1.0002</td>
<td>1.111</td>
<td>0.4112</td>
<td>1.412</td>
<td>76.87</td>
<td>105.02</td>
</tr>
<tr>
<td>14</td>
<td>1.0002</td>
<td>1.137</td>
<td>0.4144</td>
<td>1.412</td>
<td>91.17</td>
<td>96.23</td>
</tr>
</tbody>
</table>

Table 5. CO₂ system. Temperatures, mass flow rates and energy rates per 1 kW of cold (Fig. 5b)

<table>
<thead>
<tr>
<th>Pₚ [bar]</th>
<th>mₙ₁ · 10³ [kg/s/kWcold]</th>
<th>mₙ₂ · 10³ [kg/s/kWcold]</th>
<th>Wₜ,c,p [kW/kW cold]</th>
<th>Qₜ,c [kW/kW cold]</th>
<th>t₂ [°C]</th>
<th>t₄ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>11.77</td>
<td>17.69</td>
<td>1.068</td>
<td>2.068</td>
<td>43.31</td>
<td>85.52</td>
</tr>
<tr>
<td>65</td>
<td>11.77</td>
<td>19.72</td>
<td>1.090</td>
<td>2.090</td>
<td>50.01</td>
<td>81.31</td>
</tr>
<tr>
<td>70</td>
<td>11.77</td>
<td>22.23</td>
<td>1.115</td>
<td>2.115</td>
<td>56.34</td>
<td>77.49</td>
</tr>
</tbody>
</table>

The intermediary cooling performed by the injection of a cold stream leads for both agents to a decrease in the discharge temperature from the second stage compressor. For both agents the exergy destruction due to heat transfer at a finite temperature difference in the heater is expected to diminish. For CO₂ the quantity of heat transferred to the thermal agent increases (Tables 5 a,b).

For NH₃, the overall exergy efficiency remains practically unchanged, while for CO₂, it decreases (Fig. 6. a,b).

Fig. 5.a NH₃ System with intermediary cooling achieved by the injection of a cold stream

Fig. 5.b CO₂ System with intermediary cooling achieved by the injection of a cold stream
The exergy destructions related to the total input power are presented in figures 7a,b. The decrease in the exergetic efficiency of the CO$_2$ cycle is due to the rapid increase in the exergy destruction ratio of the throttling process (Fig. 7.b).

Compared to the schematic given in Fig. 1 characterized by a single throttling process, in the present case (Fig. 5.b) the cycle operates with two throttlings.

As expected, for CO$_2$, the exergy destruction ratio in the heater due to the intermediary cooling by the injection of a cold stream (Figs 5.b) is lower than the one corresponding to schematic presented in Figure 1 (Fig. 7.b).

4. Schematic of a two-stage system with flash intercooling

To continue to diminish the exergy destruction a schematic with flash intercooling is proposed (Figure 8.a,b).

For the flow charts presented in Figs. 8. a,b the temperatures in the key states of the cycles, the mass flow rates and the energy rates per 1 kW of cold are shown in Tables 6 and 7.
Table 6. \( \text{NH}_3 \) system. Temperatures, mass flow rates and energy rates per 1 kW of cold (Fig. 8a)

<table>
<thead>
<tr>
<th>( P_{\text{in}} ) [bar]</th>
<th>( \dot{m}_1 \cdot 10^3 ) [(kg/s)/kW cold]</th>
<th>( \dot{m}_2 \cdot 10^3 ) [(kg/s)/kW cold]</th>
<th>( \dot{W}_{\text{cp,t}} ) [kW/kW cold]</th>
<th>( \dot{Q}_{\text{cd}} ) [kW/kW cold]</th>
<th>( t_2 ) (^\circ\text{C})</th>
<th>( t_4 ) (^\circ\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.87</td>
<td>1.084</td>
<td>0.386</td>
<td>1.386</td>
<td>60.52</td>
<td>108.88</td>
</tr>
<tr>
<td>12</td>
<td>0.89</td>
<td>1.113</td>
<td>0.385</td>
<td>1.385</td>
<td>76.87</td>
<td>98.37</td>
</tr>
<tr>
<td>14</td>
<td>0.91</td>
<td>1.14</td>
<td>0.387</td>
<td>1.387</td>
<td>91.17</td>
<td>89.91</td>
</tr>
</tbody>
</table>

Table 7. \( \text{CO}_2 \) system. Temperatures, mass flow rates and energy rates per 1 kW of cold (Fig. 8b)

<table>
<thead>
<tr>
<th>( P_{\text{in}} ) [bar]</th>
<th>( \dot{m}_1 \cdot 10^3 ) [(kg/s)/kW cold]</th>
<th>( \dot{m}_2 \cdot 10^3 ) [(kg/s)/kW cold]</th>
<th>( \dot{W}_{\text{cp,t}} ) [kW/kW cold]</th>
<th>( \dot{Q}_{\text{h}} ) [kW/kW cold]</th>
<th>( t_2 ) (^\circ\text{C})</th>
<th>( t_4 ) (^\circ\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>5.71</td>
<td>22.04</td>
<td>1.068</td>
<td>1.97</td>
<td>43.31</td>
<td>75.92</td>
</tr>
<tr>
<td>65</td>
<td>6.19</td>
<td>28.65</td>
<td>1.090</td>
<td>2.061</td>
<td>50.01</td>
<td>70.56</td>
</tr>
<tr>
<td>70</td>
<td>6.9</td>
<td>48.62</td>
<td>1.115</td>
<td>2.397</td>
<td>56.34</td>
<td>64.66</td>
</tr>
</tbody>
</table>

Fig. 8.a \( \text{NH}_3 \) System with flash intercooling  
Fig. 8.b \( \text{CO}_2 \) System with flash intercooling
For NH\textsubscript{3} the exergetic efficiency has increased substantially (Fig. 9.a). This fact is due to the decrease in the total exergy destruction associated with throttling (Fig. 10.a).

For CO\textsubscript{2} the overall exergetic efficiency increases comparatively with the flash gas by-pass intercooling (Figs 6.b, 9.b) but remains inferior to the efficiency corresponding to the incomplete intermediary cooling (Figs 3.b, 9.b). The slight increase in the exergetic efficiency is mainly due to the decrease in the exergy destruction in the gas heater (Figs 7.b, 10.b).

5. Conclusion

The exergetic analysis is the only method capable to rate the performance of a system operating with thermal energies at different levels of temperature.

The exergetic analysis finds the location and the magnitude of a malfunction that occurs inside the borders of a system and is capable to give solutions for improvement.

The exergy destruction associated with throttling is responsible for the lower exergetic efficiency of the CO\textsubscript{2} system compared to the one that operates with NH\textsubscript{3}. For CO\textsubscript{2} the lower is the throttling process the higher is the overall efficiency. All the attempts to reduce the exergy destructions in the
gas heater or intermediary cooling processes have had no benefit as long as throttling has been increased.

The schematic from Fig. 1.b with the incomplete intermediary cooling has the lower throttling and consequently the higher overall exergetic efficiency.

For NH₃ the structural changes brought to the system in the aim to reduce the exergetic destruction associated with the intermediary cooling and heat transfer in the condenser have improved the performance of the cooling and heating system.

**Nomenclature**

Cd-Sc condenser-subcooler
Cp compressor
Ev evaporator

\( \dot{E}_x \) exergy current, kW
\( \dot{E}_{x^M} \) current of mechanical exergy, kW
\( \dot{E}_{x^T} \) current of thermal exergy, kW

\( \dot{E}_{x^T_Q} \) exergy of the heat current \( \dot{Q} \) at the average thermodynamic temperature \( T \), kW

\( \dot{F} \) fuel, kW exergy
\( h \) specific enthalpy, kJ/(kg K)

\( i \) exergy destruction due to internal irreversibility, kW
LS liquid separator

\( \dot{m} \) mass flow rate, kg/s
\( p \) pressure, kPa

\( \dot{P} \) product, kW exergy, EU/yr
\( \dot{Q} \) heat current, kW

\( \dot{Q}_o \) cooling charge, kW

\( s \) specific entropy, kJ/(kg K)
\( t \) temperature, °C

\( T \) temperature, K, average thermodynamic temperature, K
TV throttling valve

\( v \) specific volume, m³/kg

\( W \) mechanical power, kW

**Subscripts and superscripts**

c condenser
cp compressor
el electrical
f friction
h heater
i intermediary, inlet
m mechanical
o outlet
P pump
References

Comparison between Traditional Methodologies and Advanced Exergy Analyses for Evaluating Efficiency and Externalities of Energy Systems

Gabriele Cassetti*, Emanuela Colombo*

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Abstract:
The majority of the studies available in Oil and Gas Industry literature is often related to the downstream impact of the process chain, while less attention is given to the upstream side. In this frame, efficiency improvements in the sector would provide relevant contributions to the issue of the impact of the oil chain on environment and society. In the industrial sector, environmental impact and efficiency of energy systems are assessed through traditional methodologies (Environmental Impact Assessment, Life Cycle Assessment, Risk Analysis). Several innovative methodologies of analysis have been developed to evaluate the overall impacts of complex systems in terms of exergy consumption. These methodologies underline the tendency to extend the evaluation of the impact including the life time of the energy system by considering the exploitation of the involved resources (Cumulative Exergy Consumption, Exergetic Life Cycle Assessment), and including the interaction with the space around the system, by assessing the externalities from the environmental and the economic point of view (Thermoeconomics, Extended Exergy Accounting).

The purpose of this paper is to compare the different methodologies commonly used in the industrial sector to assess the environmental impact and the efficiency related to oil and gas sector with the methodologies based on advanced exergy analysis. To perform the comparison a decision model from multi-attribute method is developed and a hierarchical analysis based on the Analytic Hierarchy Process is performed. Methodologies are compared through a range of criteria based on input-output approach and declined in thirteen indicators concerning integrated assessment and environmental assessment.

This paper is part of a wider work aiming to develop a new approach to integrate the different peculiarities of the methodologies to reduce the environmental impact while increasing the technical and economic efficiency of the upstream chain of Oil and Gas sector, by analysing energy and exergy flows, material and waste flows and externalities of the global system.

Keywords:
Exergy, Upstream, Oil and Gas, Energy, Environmental Impact, Efficiency.

1. Introduction

Environmental impact of energy systems is one of the main issues for developing technologies, policies and programs in industrial sector.

A major challenge in the evaluation of the impact related to processes in energy systems is to include the overall externalities, as suggested by International Energy Agency (IEA) [1].

In industrial sector, externalities of energy systems are assessed through traditional methodologies (Environmental Impact Assessment [2], Life Cycle Assessment [3], Risk Analysis [4]). Several advanced methodologies of analysis have been developed to evaluate the overall impacts of complex systems in terms of exergy consumption. These methodologies underline the tendency to extend the evaluation of the impact of energy systems through time, by considering the exploitation of resources involved in the construction of the system ([5],[6]), and space, by assessing the externalities, environmental and economic concerns ([7],[8],[9]).

Purpose of this paper is to assess which methodology may be preferable to assess the environmental impact of Oil and Gas sector (O&G). Available methodologies are defined through an analysis of
the literature showing relevant dimensions of the issue, and a decision model based on a hierarchical analysis is developed.

2. Relevance and Environmental impact of Oil and Gas sector

In 2009, Oil and Gas represented the 52.7% of the World Total Primary Energy Supply (TPES) (79.5% considering globally fossil fuels with coal) for a total of 6403 Mtoe [1]. Despite the growing contribution of renewable technologies, IEA stats [10] that the contribution of oil and gas in 2035 will still cover the 52.2% of TPES in the Current Policy Scenario (CPS), and the 45.6% in the 450 Policy Scenario (450 PS). In CPS 2035, relative contribution of renewable technologies will slightly differ from today values (11%), because of the contemporary foreseen growing of the TPES from 12150 Mtoe in 2009 to 18048 Mtoe in 2035. The 450 PS 2035, on the other hand, foresees an increase of TPES up to 14920 Mtoe, with a consequently increase of renewables contribution to 18% [10].

These numbers lead to two important considerations: the first is that worldwide economic development requires more and more energy, and, the second, that the socio-economic and technical development path will strongly affect emissions in the environment since the share of fossil fuel (mainly Oil and Gas) in the energy supply is due to remain high [11].

CO$_2$ from energy represents indeed the 65% of global anthropogenic greenhouse-gas emissions (81% in Annex I countries, figure 1), and consequently fossil fuels contribution is relevant.

![Figure 1: Shares of anthropogenic greenhouse-gas emissions in Annex I countries, in 2009. Source: IEA, CO2 Emissions from Fuel Combustion – Highlights, 2011](image1)

Environmental impact of O&G sector has high relevance at global, regional and local. At the global scale, O&G impact is related to greenhouse-gas emissions (mainly CO$_2$ and CH$_4$) thus contributing to the anthropogenic share. In figure 2 the share by fuel in 2009 of TPES and CO$_2$ emissions is represented.

![Figure 2: Percent shares of World Total Primary Energy Supply and CO$_2$ emissions in 2009. (*Other includes nuclear, hydro, geothermal, solar, tide, wind, biofuels and waste). Source: IEA, CO2 Emissions from Fuel Combustion – Highlights, 2011](image2)
At local and regional scale, O&G impact concerns chemical pollution due to combustion processes and waste emissions: oxides of sulphur, nitrogen and carbon, organic compounds, such as hydrocarbons (fuel vapours and solvents), particulate matter, such as smoke and dust, metal oxides, especially those of lead, cadmium, copper and iron, hazardous air pollutants (HAP), persistent organic pollutants (POPs), odours. These pollutant has high effect on human health, materials and ecosystems as well as on acidification and eutrophication of waterbodies.

In this frame, efficiency improvements in the sector of O&G would provide relevant contributions to the issue of the impact on environment and society.

Moreover, the majority of the studies available in O&G industry literature is related to the downstream impact of the process chain, while less attention is given to the upstream side, but the contribution of the latter in the balance of global impact is much more relevant than the former [12]. In figure 3, O&G operations and relative emissions of CO₂ equivalent (CO₂e) are shown.

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**3. Methodologies**

The objective of the comparison between methodologies is to evaluate how the environmental impact of O&G sector may be assessed by different methodologies. The selected methodologies are: Environmental Impact Assessment (EIA), Life Cycle Assessment (LCA) and Risk Assessment (RA) in industrial sector; Cumulative Exergy Consumption (CExC), Exergoenvironmental Analysis and Extended Exergy Accounting (EEA) for those based on exergy analysis.

EIA, LCA and RA have been selected according to their wide diffusion in industrial sector and because the approach is standardized in policy framework. CExC, Exergoenvironmental Analysis and EEA have been selected on the base of a literature review on advanced exergy analyses of energy systems. Exergy based methodologies analysed belong to a wider ensemble of methodologies, among them it is worth to mention Exergetic Life Cycle Assessment by Cornelissen [6], Environomic method by Frangopoulos [15] and Exergoecological analysis by Valero [16].

The approach of the different methodologies will be described in detail in this paragraphs, where a specific attention is given to the exergy-based methodologies.

Indeed exergy is widely recognized to be appropriate to assess environmental impact of energy systems [5,6,7,8,9,13], for two main properties: (1) it allows to convert everything in a homogeneous unit, and (2) it allows to include the externalities of the process into the global evaluation [14,15].

Despite exergy allows to measure the quality of energy transformations occurring in a process as well as the quantity, exergy analysis has still low appeal in legislators and decision makers, probably due to the its very technical origin and the technical result that it supplies [9].
In terms of environmental impact there is still an open question in the literature related to the proper approach to follow for measuring the exergy destruction generated by the system into the environment. This means to define the transfer function between the exergy content and the pollutant concentration of a flow [5,9,15].

**Environmental Impact Assessment (EIA)**

EIA is the instrument based on the Directive 85/337/EEC of the European Commission, and ensures an ex ante environmental evaluation of projects [18], with the aim of preventing and mitigating impacts. EIA is performed for those projects considered having significant impact. The approach of EIA in evaluating impacts is essentially output-oriented and descriptive of the typology and quantity of waste generated by the system during its operating life. It includes also the description of the principal alternatives of impact scenario. EIA assesses the components of the environment potentially subject to impacts and describes the possible effects generated. The major criticisms of EIA are: 1) a limited consideration of alternatives, and 2) insufficient consideration of externalities derived from effects. EIA may represent an appropriate tool for assessing a single system, but it is not properly designed for evaluating the externalities. EIA Directive is usually implemented together with other two Directives aiming at managing the environmental strategies and reducing the impact of projects, the Strategic Environmental Assessment (SEA, Directive 2001/42/EC) and the IPPC Directive (Directive 2008/1/EEC) on the pollution of existing projects in the industrial sector. A limit highlighted in the Commission Report on the application and effectiveness of EIA [19] is the approach “compliance a commitment”, from which emerges that EIA is not well satisfactory in improving the environmental performances of a project.

**Life Cycle Assessment (LCA)**

LCA is a tool for the systematic evaluation of the environmental issue of a system through all stages of its life cycle. LCA derives from the approach of Life Cycle Thinking and it is an evolution of classical energy analyses. LCA tries to identify the overall impact through an input-output approach. The logic of this approach consists in the assessment of the energy and material inputs and outputs across the processes of a system. The main advantage of this approach is given by the holistic vision that carries out, so that it can be used to highlight the inter-linkages of environmental aspects. International Organization for Standardization (ISO) developed a standard set for guidelines (ISO14040[20]) for conducting LCA studies. LCA takes into consideration only the energy and environmental dimensions of the impact, and manages them separately [21]. LCA classifies the energy entering in the system in five main categories:

- **capital energy**, linked to the construction of machineries,
- **energy content of delivered fuel** $E_c$, necessary to the operations and processes,
- **production and delivery energy** $E_p$, to produce and transform energy and materials,
- **feedstock energy**, that is the energy content of input material that can be still used by the products,
- **energy consumed by labour**, divided in the daily energy supply needed by one person (10MJ/d) and the energy needed for their transportation.

Critical point of LCA is the allocation of loads. Allocation consists in relating the energetic and environmental loads of processes to specific co-products and sub-products as well as the fuel consumption of single components [21]. Other critics about LCA lie in impact assessment, in particular in the normalization of the impacts over the relative effects of processes. There are several normalizing methods, but none of them solves the intrinsic subjectivity of LCA:

- Proxy Approach (mandatory approach);
- Monetization of effects;
- Distance to target;
- Panel Approach (panel of scientists);
- Eco-indicator: weights the impact of process through the Triangle Method: Human Health, Ecosystem Quality, Resources.

**Risk Assessment (RA)**

RA is a very well recognized approach to identify risks and uncertainties related to industrial processes and activities [23]. RA typically involves measuring two quantities of risk: the magnitude of the potential event and the probability of occurrence. The concept of magnitude of a potential event is linked to the intensity of the caused effects and the vulnerability of the people and the environment exposed. RA covers an extremely wide number of activities and sectors, and its complexity is elevated. For the same reason, there is a wide number of standards related to RA. The most important European legislation relevant to RA is the Framework Directive 89/391/EEC [4].

Many different tools and techniques can be adapted to the specific situation, e.g. calculation of complex event probability, risk mapping, probabilistic cost estimating. The principal target of RA is Human Health and the objective is the minimization of probability of occurrence of uncontrolled events. For this reason, RA is often related to the complementary practice of Health, Safety and Environment (HSE), that actively monitors any potential risk issue regarding safety, security and environment. The first step of a RA consists in the identification of all the sources of risk related to an activity or a process, since the lack of knowledge of all the possible risks can lead to an insufficient level of safety. The identification of risk requires the utilization of adequate methodologies, e.g. historic analysis, control lists, what-if analysis, HAZOP, etc, that must guarantee all possible sources of risk and danger to be identified. The principal result of a RA is a hierarchy of all the possible undesired events related to their associated risk and a systemic knowledge of the cause-effect relations involving the processes. RA can be approached with a Plan – Do – Check – Act method. Finally, RA represents an instrument to put in place pro-active policies of intervention in the system.

**Cumulative Exergy Consumption (CExC)**

The objective of CExC is the assessment of the exergy of natural resources, renewable and non-renewable, absorbed by all the subsystems of the productive chain of a given product. The relevant aspect of cumulative exergy analysis rather than cumulative energy is the capability to determine the influence of non-ideality of processes in the final result, so to localize and quantify inefficiencies along the chain of processes and set the improvements. On the other hand, the calculation of cumulative energy consumption requires much less information, as far as CExC requires the knowledge of the exergy content of primary resources extracted from environment [26]. The cumulative consumption of exergy of non-renewable resources is defined thermo-ecological cost, and expresses the consumption of non-renewable exergy involved in the production of a final product. The statement at the bases of thermo-ecological cost is that the final cost of a product results from the sum of thermo-ecological cost of delivered materials, semi-finished products and energy carriers. Performing the analysis of a system relatively to a given region, the specific thermo-ecological cost of a general waste $k$ generated by the system has the following expression [26]:

$$ (\kappa_k = (\beta \sigma_k)/(DCP + \sum_{1}^{k} p_k \sum \{P_k \sigma_{1k} \} ) $$

(1)

where B is the annual domestic consumption of non-renewable exergy, DCP the domestic consumption product in monetary units, $\sigma_k$ is the monetary index of harmfulness of $k$-th waste and $P_k$ is the annual production of the $k$-th aggressive component of waste products rejected to the environment in the considered region. CExC may be finally performed to minimize the non-renewable exergy depletion in a chain of processes. The expression of the objective function
representing the non-renewable exergy depletion on annual basis, assuming a singular output of the

given process, has the form:

\[ P_t A = \tau n \left( \sum_{j} G_{ij} \rho_{ij} \right) + \sum_{k} \left( 1/\tau \left( G_{im} \rho_{im} (1 - u_{im}) \right) + \sum_{r} \left( G_{ir} \rho_{ir} \right) \right) \]

(2)

where \( G_{ij} \), \( \rho_{ij} \) are the nominal flow rate and specific thermo-ecological cost of the \( j \)th rawmaterial,

semi-finished product or energy carrier supplied to the production process, \( G_{ik} \), \( \rho_{ik} \) are the nominal

flow rate and index of the specific thermo-ecological cost of the \( k \)th deleterious waste product

generated in the considered process and rejected to the environment, \( \tau_n \) is the annual operation time

with nominal capacity, \( \tau \) the nominal life time of the installation expressed in years, \( u_{im} \) is the

expected recovery factor of the \( m \)th material, \( G_{ir}, \rho_{ir} \) are the consumption and specific thermo-

ecological cost of the \( r \)th materials or energy carrier used for the construction of the installation,

\( G_{ir}, \rho_{ir} \) are the predicted consumption and specific thermo-ecological cost of thermaterials or

energy carrier used in repairs.

**Exergoenvironmental Analysis**

The approach of Exergoenvironmental Analysis derives from Exergoeconomics [27] and has the

objective to combine an exergy analysis with an environmental assessment method as the LCA

[21]. Aim of the analysis is mainly to overcome the limitations affecting LCA: allocation of

environmental loads and energy consumption for each component. Exergoenvironmental Analysis

consists of three main steps: the first is an exergy analysis of the energy conversion system, the

second is a LCA of the relevant components and the relevant input streams of system and finally an

environmental impact is assigned to each exergy stream and each component of the system. The

environmental impact is expressed by a quantitative indicator: the Eco Indicator 99 [21] or the

Recipe indicator [30]. These indicators are internationally recognized as instruments for

environmental assessment [29,30] and decline the environmental impact in three damage categories:

Human Health, Ecosystem Quality and Resources. The final indicator represents the synthesis of

the three categories and the impact is expressed in terms of points (Pts). The environmental impact is

assigned to the exergy streams involved in the process through the SPECO approach [27] in order to

obtain the environmental impact rate \( \bar{b}_{ij} \) for each stream (expressed in Pts/s). \( \bar{b}_{ij} \) is calculated as the

product of the specific environmental impact \( b_j \), the average environmental impact associated with

the production of \( j \)th stream per exergy unit of the same stream (Pts/GJ exergy), times the exergy

rate \( \dot{E}_{ij} \):

\[ \bar{b}_{ij} = b_j \dot{E}_{ij} \]

(3)

In addition to the impact associated to each exergy stream, the component-related impact \( \dot{Y}_{ik} \)

associated to the \( k \)th over its lifecycle is considered:

\[ \dot{Y}_{ik} = \dot{Y}_{ik}^{CO} + \dot{Y}_{ik}^{OM} + \dot{Y}_{ik}^{DI} \]

(4), where \( \dot{Y}_{ik}^{CO} \), \( \dot{Y}_{ik}^{OM} \)

and \( \dot{Y}_{ik}^{DI} \) are the impact related to the construction (including manufacturing, transport and

installation), operating and maintenance (including pollution formation) and disposal of the \( k \)th

component, respectively. The assessment of the environmental impact at component level aims at

developing improved design options. The final step of the analysis is the identification of the

environmental relevant components and the sources of impacts in the system.

**Extended Exergy Accounting (EEA)**

EEA is a methodology that has the objective to assess the overall amount of resources, expressed in

terms of exergy, globally absorbed by a system over its life cycle span. The originality of EEA is

represented by the improved concept of primary resource, since it is extended to all the externalities

generated by system, not only material and energy streams: also capitals, labor (in terms of

workhours) and environmental costs are converted in equivalent exergy. This peculiarity simplifies
the operation of comparison among systems of different nature, since all non-homogenous measures are converted in a homogeneous unit. EEA includes the principal characteristics of CExC, as the cumulative exergy absorbed in the productive chain of a product, and Exergoeconomics, since also economic issue is included. Unlike Exergoeconomics, capitals in EEA are converted in equivalent exergy through the econometric factor $\beta$, defined as $\beta = \frac{M2}{S}$, where $M2$ is a monetary indicator that expresses the amount of circulating money in a given society at a given period, and $S$ is the cumulative salary of labor in the same period. As consequence, the extended exergy of a system may differ in function of the place where the system is built and the result being strictly related to local context and this may represent a limitation mainly when more than one country are involved within the supply chain of a product or a process.

EEA is indeed based on the assumption that the global input of exergy resources in the system has the objective to maintain the labor, assumed as product of the society. The equivalent exergy of capitals $E_K$ involved in the system is then expressed as:

$$E_K = \beta \cdot E_L$$  \hspace{1cm} (5)

where $E_L$ is the equivalent exergy of labor and it is defined as:

$$E_L = f \cdot e_{surv} \cdot N$$  \hspace{1cm} (6)

where $f, e_{surv}$ and $N$ are the amplification factors of exergy consumption from the society, the minimum exergy necessary to human survival, equal to $\frac{1.05 \times 10^7}{(person \cdot day)}$ [31] and population respectively. Avoided impact, or zero impact [9], approach is used by EEA for assessing environmental impact of systems. Environmental impact of an output stream from the system is defined as an exergy flow non in equilibrium with the environment reference state and the exergetic cost $E_{ENV}$ of all the abatement systems required to the zero impact is calculated. Also abatement systems are expressed in terms of extended exergy. The global extended exergy consumed by the $k$th system is finally:

$$EE_k = EE^{CO}_k + EE^{OM}_k + EE^{DI}_k$$  \hspace{1cm} (7)

where $EE^{CO,OM,DI}_k$ is the extended exergy of construction, operation and maintenance, and dismantling of system, respectively. Each component of (7) is defined as:

$$EE^{j}_k = \sum_j CExC + E^{j}_L + E^{j}_K + E^{j}_{ENV}$$  \hspace{1cm} (8)

where $j$ is equal to CO,OM,DI alternatively.

Finally, it is worth mentioning that extended exergy do not include a number of impacts which may affect the overall consumption of resources by the system. In particular biodiversity loss of an ecosystem is not considered and also the social impact on the quality of life, or the human capital are at the moment not included within the extended exergy concept. This limitations must be kept into account when using information coming from an extended exergy evaluation.

### 4. Methodology of the comparison

The approach used to develop the comparison between the methodologies derives from multi-attribute decision methods. Taking into account the goal of the analysis (environmental impact of O&G upstream chain), the Analytic Hierarchy Process (AHP), developed by Saaty [32] and based on hierarchical analysis, is selected as investigating method.

The choice of the AHP model is based on its key characteristics that make it suitable for the application to the case under study:
• a hierarchical analysis, defined around a specific goal, carries out a general cost-benefit analysis not requiring an initial knowledge of specific indicators;
• the construction of a hierarchy makes possible to break down in simpler sub-problem any complex problem and the definition of a set of indicators (qualitative and/or quantitative) becomes more feasible. The pairwise comparison makes the procedure more user-friendly;
• the result of AHP model is a vector that represents the level of preference to attribute to each alternative.

To apply the AHP to a defined problem a step by step procedure is followed. First, the specific goal is divided in three sub-problems, corresponding to three different criteria, so that the combination of the three criteria produces the solution for the goal. After the definition of the criteria, a series of indicators, related to each criterion is defined. Indicators are used to evaluate each alternative (in this case, each methodology) in pairwise comparisons. In order to rank the alternatives in function of their performance related to the goal, the Saaty scale [35], defined for the specific problem, is used.

Definition of the hierarchy of a specific goal
The specific goal of the study, as previously underlined, is the evaluation of the best methodology to analyse the environmental impact of the Oil & Gas chain. Accordingly to the literature [36,37,38], the most appropriate methodology to achieve the given goal should be able to
- to evaluate impact at the global and local level,
- to evaluate the process from the perspective of the overall system,
- to extend the analysis to the life cycle,
- to consider cumulative processes,
- to evaluate the impact over the different dimensions of environment: air, soil and water,
- to require a consistent, but not too wide data set as input,
- to allow homogeneous comparison between technical, environmental and economic elements,
- to assure data to be available,
- to be more general as possible compared to the context,
- to estimate alternative scenarios,
- to optimise the process efficiency,
- to allow a comprehensive evaluation of resource consumptions,
- to evaluate externalities.

The above statements have been aggregated in three criteria representing the main dimensions of relevance for achieving the specific goal, and thirteen indicators have been carried out. This structure has been proposed by the Authors and its subjectivity, although supported by literature review, may affects the final solution. Therefore, a sensitivity analysis of the relative weights of criteria and indicators have been performed:

- **Criterion Strategy**, expressing the insights and peculiarities of the methodology. The indicators for this criterion are:
  - Scale, aiming at investigating if the environmental impact is evaluated at local or global or both scales;
  - Level, aiming at investigating if the environmental impact is considered at the level of the single component (or partial portion of the system) or at the level of the overall system;
- Time Frame, same question as above related to the temporal frame (operating life or lifecycle);
- Spatial Frame: same question as above related to the capability of predicting cumulative processes of productive chains or simply to evaluate current processes;
- Environmental dimensions, aiming at considering the impact over the whole set of environmental dimensions: air, water and soil.

**Criterion Input, defining the typology of input that the methodology requires for being applied. It has four indicators:**
- Data set extension, aiming at investigating the amount of the data required for the methodology to be applied,
- Data set availability, aiming at investigating the availability of the data,
- Data set homogeneity, aiming at providing a uniform unit of measure for the technical, environmental and economic elements,
- Context: aiming at evaluating the context-dependency of the methodology or its general applicability.

**Criterion Output, defining the typology of output that the methodology is able to provide, has four indicators:**
- Alternative Scenarios: aiming at investigating if alternative scenarios are generated by the methodology,
- Efficiency: aiming at investigating if the methodology allows efficiency optimization or at least efficiency assessment or does not consider this element,
- Resource consumption: aiming at investigating if the methodology assesses the overall resource consumption of the system,
- Externalities, aiming at evaluating if the model is able to account for the externalities generated by the system.

According with this assumption the hierarchy developed for this goal, is proposed in figure 4.

![Fig. 4 Hierarchy for O&G impact assessment. First row: the goal; second raw: the criteria; third raw: the indicators](image_url)

The hierarchy gathers indicators selected from integrated assessment and environmental evaluation literature. The criterion Strategy reflects the issues mostly involved in Risk Assessment [39] and regulatory frameworks, as EPA [40]. Indeed, environmental laws and regulation stress the evaluation of impacts over all the compounds of environment: atmosphere, lithosphere and hydrosphere.

Input and Output criteria are developed on the basis of integrated assessment literature [22,41,42]. In particular, Input indicators have the objective to assess the computational effort needed to gather the necessary information required by the single methodology. This indicator may appear less relevant than the other two, but it reflects an essential phase in any kind of analysis, the data
collection. The complexity and the completeness of this phase is crucial for all the other phases of the analysis as well as the quality of the output.

Output indicators follow the approach of the International Atomic Energy Agency (IAEA) in assessing the different dimensions of sustainable development [43].

It is worth mentioning the absence of indicators referring directly to exergy: indeed, exergy may be seen as an instrument able to improve the performances of a methodology, but the peculiarity of using exergy is not relevant for the goal of the analysis.

The thirteen indicators are qualitative indicators, therefore it is possible to compare each alternative through qualitative pairwise comparisons using the AHP.

Weight assignment to all the elements of each level of the hierarchy
To build up the hierarchy, the weights of the indicators referred to the relative criterion are equal, as well as the weight of each criterion referred to the goal. On the consequence, defining the weight of a general criterion as \( w_c \), and the weight of a general indicator \( w_i \), the model assigns a weight to each criterion of \( w_c = 1/3 = 0.333 \), and to each indicator, \( w_{isp} = 1/5 = 0.20 \), \( w_{imp} = 1/4 = 0.25 \). It is clear that the choice to maintain the same \( w_c \) for each criterion leads to different \( w_i \), only due to the different number of indicators defined for each criterion. In the sensitivity analysis performed, indeed, the weight \( w_i \) will be set equal for each indicator.

Pairwise comparisons and priority vector
To perform the pairwise comparison between alternatives, the Saaty ranking scale is used (table 2).

<table>
<thead>
<tr>
<th>Table 2 Saaty Scale of absolute numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensity of importance</strong></td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>2,4,6,8</td>
</tr>
</tbody>
</table>

According to the literary review of each methodology [5,6,7,8,9,13,14,15,16,18,19,20,21,23,24,25,26,27,28], values of Saaty scale have then been associated tool and gas characteristics as previously stated [36,37,38].

In table 3, the corresponding Saaty scale for oil and gas sector is shown. According to the explanation of Saaty scale values, the value of 1, corresponding to “Equal Importance” is assigned if the two alternatives \( a \) and \( b \) compared present the same performance on the indicator, and a value of 9, corresponding to “Absolutely more important”, if the performance between the two alternatives is relevant. For those indicators having a middle scale value, a value of 5, corresponding to “Much more important” is set.

Taking as example the indicator “Scale”, we will assign the value 1 if both methodologies \( a \) and \( b \) analyse the system at the local scale (or both at the global, or global and local). The value 5 will be assigned to \( a \) if \( a \) analyses the system at the global scale while \( b \) only at the local scale (or if \( a \) analyses the global and local scale, while \( b \) only the global). Finally, we will assign the value 9 to \( a \) if \( a \) analyses the global and local scale, while \( b \) only the local scale.

Once the assignment has been set, the Super Decisions Software, developed by Creative Decision Foundation [44] was used.
Table 3. Saaty scale values for O&G Impact Evaluation

<table>
<thead>
<tr>
<th>STRATEGY</th>
<th>Scale</th>
<th>1 Local</th>
<th>5 Global</th>
<th>9 Local and Global</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level</td>
<td>1 Component</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 System</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9 Component and System</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time Frame</td>
<td>1 Operating Life or Partial Cycle</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9 Lifecycle</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spatial Frame</td>
<td>1 Single Process</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9 Cumulative Processes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Environmental Dimensions</td>
<td>1 Single Environmental Dimension</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 Full Environmental Dimensions</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>INPUT</th>
<th>Dataset Extension</th>
<th>1 Wide Input Dataset required</th>
<th>9 Reduced Input Dataset required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dataset Homogeneity</td>
<td>1 Non homogeneous Input Dataset</td>
<td></td>
<td>Homogeneous Input Dataset</td>
</tr>
<tr>
<td>Dataset Availability</td>
<td>1 Scarce Availability of Input Dataset</td>
<td></td>
<td>High Availability of Input Dataset</td>
</tr>
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<td>Non relevant affection</td>
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<td>Assessment</td>
</tr>
<tr>
<td></td>
<td>5 Assessment</td>
<td></td>
<td>Optimization</td>
</tr>
<tr>
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<td>1 Environmental Focus</td>
<td></td>
<td>Environm., and Economic or Social Focus</td>
</tr>
<tr>
<td></td>
<td>5 Environm., Economic and Social Focus</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9 Environm., Economic and Social Focus</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resource consumption</td>
<td>1 Non assessment</td>
<td></td>
<td>Assessment</td>
</tr>
<tr>
<td></td>
<td>9 Assessment</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5. Results and discussion

The result of the calculation is the priority vector representing the ranking of the alternatives from the one which has the closest performance to satisfy the goal, to the least. Alternatives are ranked on descending order.

The priority vector, normalised to the best alternative, is reported in histogram form in figure 5. The preferable methodology to better reach the goal according to the decision model presented, seems to be the Exergoenvironmental Analysis. EEA and LCA are second and third priority, respectively. The results may be better understood by breaking down the evaluation into the three criteria. To do this, the priority vector of a single criterion is considered. The software allows to evaluate the contribution of each indicator $i$ on the criteria $c$ referred to each alternative $a$ (figures 6, 7, 8).

Exergoenvironmental Analysis is globally preferred, mainly due to criterion Input (figure 6) with respect to EEA. On the other side, while EEA seems more appropriate for the criterion Output
(figure 7) and Strategy (figure 8), the effect does not compensate the associated penalty to criterion Input. Under the criterion Strategy, EEA seems to be preferred since it allows an approach to the problem which is based on an holistic view of the system, oriented to a global scale, at the level of the overall system, considering lifecycle and cumulative processes. Exergoenvironmental analysis has a weak performance in this indicator since it is more focused on the single component (rather than on a system) evaluated over the operating life (rather than the lifecycle).

In criterion Output, the preferred methodology results to be again EEA mainly because of its capability to account for overall externalities. Exergoenvironmental analysis follows with a high score where the reduced value in predicting externalities is balanced by the increased value attributed to efficiency optimisation.
Under the criterion Input, the ideal methodology is Exergoenvironmental analysis, followed by LCA. This result is due to the high level of standardization nowadays reached by LCA database in industrial sector, which is also used by Exergoenvironmental analysis. The latter is able to provide the data in more homogeneous framework by using exergy-based indicators. Under this criterion EEA is affected by a penalty mainly due to the very extended dataset required and the current scarce availability of necessary data.

Anyway it is relevant to observe that Exergoenvironmental analysis and EEA are very close in the priority vector, thus demonstrating that they may be valid alternatives which can be used accordingly to the different relevance that the decision maker gives to each single indicator and/or criterion.

Even LCA performs very well being slightly penalised by the criterion output where it is affected by low score in efficiency optimisation and externalities, both considered of high relevance for the goal.

The result of analysis confirms, as anticipated by the literature review in paragraph 3, the high potential of exergy-based methodologies in criterion Output, since from the output of the analysis depend the actions that the decision maker may subsequently operate to reduce the impact of the Oil&Gas sector. This consideration, due to the capability of these methodologies to convert all the externalities generated in exergy flows, represent effective tools able to supply a more profitable and complete information to manage the environmental issue.

As initially mentioned, a sensitivity analysis on the relative weights of criteria $w_c$ can be performed. By assigning a $w_c$ proportional to the number of indicator for each criterion, the singular $w_i$ assumes the value $w_i = 1/13 = 0.08$, while $w_{c_{str}} = 5/13 = 0.385$, $w_{c_{int}} = 4/13 = 0.308$ and $w_{c_{out}} = 4/13 = 0.308$, respectively.
As we may see, the result of the sensitivity analysis presents a rank reversal in the priority vector, in favour of EEA. Exergoenvironmental Analysis maintains however a good performance, as well as LCA and CExC. The result so confirms the utility represented by exergy based analysis. Indeed, they are still considered globally preferable to analyse the specific problem analysed with respect to traditional methodologies, for the characteristics previously mentioned.

6. Conclusion

The objective of the present work is to define the most appropriate methodology to evaluate the environmental impact of Oil and Gas sector. A comparison between methodologies from industrial sector (Life Cycle Assessment, Environmental Impact Analysis, Risk Assessment) and exergy based methodologies (Cumulative Exergy Consumption, Extended Exergy Accounting and Exergoenvironmental Analysis) is developed by using a decision model based on Analytic Hierarchy Process. The problem is broken in three main criteria: Strategy, Input and Output, equally weighted, and thirteen indicators are used. For attributing values to these qualitative indicators a sensitivity analysis has also been performed to reduce subjectivity.

The application of AHP in the selection of the methodologies in the case analysed leads to results consistent with the literature on the subject and represents an effective tool in the end of the analysis for avoiding a priory choices.

In particular, results show that Exergoenvironmental analysis and EEA represent very useful tools for assessing externalities, consumptions and efficiencies and provide an objective and compact final indicator, while LCA is well appreciated being the best trade-off among computational load and effectiveness of results provided.

The analysis confirms the relevance of exergy-based methodologies to provide proper indication to decision makers, since they synthetize distributed information and help to reduce the range of subjectivity in operating actions. Also by modifying the weight of criteria $w_e$ in the model, results show that exergy based methodologies are still highly competitive with traditional analysis.

It is necessary to mention that exergy is a useful tool to \textit{integrate} an analysis, but it cannot be the exclusive tool on which the analysis should be based. Indeed exergy and the logic of extensions to externalities are at the moment not able yet to include some aspects that the decision maker must take into consideration as, for example, the safety of the workers and the population around the system or the biodiversity loss that it can generate in the environment.

Finally, it is worth mentioning that some subjectivities, intrinsic of the model, are still affecting the evaluation but it is shifted from the choice of the methodologies to the definition of the hierarchy of the problem, thus making it more explicit and therefore more manageable, arguable, defendable or not.

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Comparison of entropy generation figures using entropy maps and entropy transport equation for an air cooled gas turbine blade

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Abstract:
In the design and analysis of turbomachinery components, there are studies for the application of Second Law based methods. Since entropy generation can be considered as one of the most important parameters affecting the performance of turbomachinery, accurate calculation of entropy may be utilized as a design parameter. Therefore, an improvement in such a design parameter may as well increase the efficiency of the whole system which is the desired aim of the overall design procedure.

There are several methods available for the calculation of entropy generation. One method could be possible if complete quantitative descriptions of velocity and temperature fields are available. Field distributions of viscous and thermal entropy rates can be computed by post processing the available velocity and temperature data using positive definite entropy equation. There are several studies about this method in the literature one of them being about an air cooled gas turbine stator blade by Natalini and Sciubba [1].

In this study, results obtained in [1] are compared with the results obtained through direct solution of entropy transport equation. Entropy transport equation has been implemented to a commercial CFD software as a User Defined Scalar (UDS) and solved as an additional equation to continuity and Navier-Stokes equations. Results are then compared for both solutions. It is concluded that such an approach could offer significant improvements in loss and entropy production in turbomachinery flows.

It is seen that the direct calculation of entropy production as a part of the solution process produces a much smoother variation emphasizing the entropy generation within the blade boundary layers and wakes and the diffusion of the generated entropy within the blade passage that is mainly generated due to the temperature differences between the blade surface and the gas

Keywords:
Entropy; Turbomachinery; Second Law; CFD; Gas Turbine; Efficiency

1. Introduction

Loss predictions in turbomachinery could be based on the direct solution of the entropy generation equation. The entropy production actually can be used as a performance parameter if it can be calculated accurately as a part of the flow solution. One of the first ideas of utilizing the so called Entropy Generation Minimization (EGM) technique was developed by Bejan [1]. Bejan indicates that EGM, in addition to the importance of the first law of thermodynamics, shall have an important role in the analysis of systems involving heat transfer and viscous dissipation phenomena, which are dominant in turbomachinery flows demonstrating the necessity of entropy generation calculation.

In the design and analysis of turbomachinery components, the performance deterioration due to various real flow effects such as secondary flows, profile losses or tip-leakage losses is generally represented through semi-empirical loss coefficients. Instead of relying on these coefficients one can use entropy generation rates as a consistent and quantitative measure of lost work due to irreversibilities, which can be calculated globally using the inlet and exit values of calculated pressures and temperatures of a system. However, if complete quantitative descriptions of velocity and temperature fields are available, one can compute field distributions of local viscous and
thermal entropy generation rates by post-processing the available data. One such example for an air-cooled gas turbine stator blade can be found in Natalini and Sciubba [2]. The effective loss of work or destruction of exergy (Sciubba [3]) is related to the entropy generation through the Gouy-Stodola theorem as explained in Bejan [1] and Natalini and Sciubba [2].

Drost and White [4] realized the lack of entropy generation applications to complex problems and pointed out that up to that time there was no integration of the entropy generation equations with the CFD codes. They emphasized that since no analytical formulations of local entropy generation in turbulent flows exist in open literature, that part of the calculation could not be benchmarked for turbulent flows. Kock and Herwig [5], calculated the entropy generation for a heated pipe. In the study, the entropy production mechanisms were divided into four different groups such as the ones due to mean and fluctuating velocity fields and heat flux. The study concluded that the entropy production can be a parameter to define the efficiency of the system analyzed. McEligot et al. [6], on the other hand, performed a calculation of entropy production using the already available DNS data by Abe et al [7] instead of using a CFD code. Their study was mainly concentrated on the near wall region where they compared two different approaches about pointwise calculation of entropy generation.

All of the above mentioned studies reveal the importance of calculating the entropy generation as a performance parameter. However, all of them are based on a calculation that requires the solution of the velocity and temperature fields. Adeyinka and Naterer [8] proposed a more direct approach which involves including the Reynolds Averaged Entropy Transport equations, known as the Reynolds Averaged Clausius-Duhem equality, as a part of the solution process in turbulent flows. This technique of course involves a closure problem, similar to the closure of Reynolds stresses in the momentum equation, related to the calculation of mean entropy generation in terms of other mean flow quantities. A closure model was proposed by Adeyinka and Naterer [8] and tested in a turbulent channel flow between two parallel plates using Direct Numerical Simulation (DNS) data obtained by Moser et al. [9].

This paper presents an implementation of this approach to the 2D gas turbine blade section problem given in Natalini and Sciubba [2]. The Reynolds Averaged Entropy Transport and the necessary modeling equations are implemented to Ansys Fluent v14.0 [10] as User Defined Scalar (UDS). The model is applied to the air-cooled gas turbine blade configuration. The results are compared with those obtained by post-processing the temperature and velocity fields obtained by solving full Navier-Stokes equations using a Reynolds stress closure.

2. Entropy Production Modelling

For the formulation of entropy generation there are several methods available in the literature. One is the so called positive definite entropy generation equation as given below and in [8]:

$$\dot{S}_{\text{gen}} = \frac{k}{T^2} \left( \frac{\partial T}{\partial x_i} \right)^2 + \frac{\tau_{ij} \partial u_i}{T} \frac{\partial u_j}{\partial x_i}$$  \hspace{1cm} (1)

where $\dot{S}_{\text{gen}}$ is the rate of entropy production and stress tensor $\tau_{ij}$ can be stated as:

$$\frac{\tau_{ij}}{T} = \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$  \hspace{1cm} (2)

The first term on the right hand side of Eq. (1) represents the entropy generation due to thermal effects whereas the second term is for the viscous entropy generation.

Using Eq. (1) together with Eq. (2), it is possible to obtain the total entropy generation rate. However, as can be seen from the components of Eq. (1) and (2), it requires the computation of the
flow fields for temperature and velocity. This is of course possible through the computation of Reynolds Averaged Navier-Stokes equations.

The other possible method is the use of entropy transport equation given as:

$$\frac{\partial S}{\partial t} + \frac{\partial F_1}{\partial x_j} \equiv \dot{p}_s$$

(3)

where $S$ and $F_1$ are the entropy per unit volume and flux of entropy respectively.

After Reynolds averaging Eq. (3) and several manipulations using Eq. (1) it is possible to obtain the transport equation for the rate of entropy generation [2]:

$$\frac{\partial \rho S}{\partial t} + \rho \frac{\partial \overline{u_i u_i T}}{\partial x_i} - \kappa \frac{\partial T}{\partial x_i} \left( \frac{\partial T}{\partial x_i} \right)^2 + \frac{\partial \overline{u_i u_i T^2}}{\partial x_i} + \frac{\partial \overline{u_i u_i T}}{\partial x_i} + \frac{\partial \overline{u_i u_i T^2}}{\partial x_i} + \left\{ \frac{k}{T} \frac{\partial T}{\partial x_i} \right\}^2$$

(4)

The left hand side of Eq. (4) is the entropy production rate, $\dot{p}_s$. The first four terms on the right hand side are entropy generation rates due to molecular diffusion of the temperature field, diffusive entropy transport due to fluctuating velocity, viscous dissipation of the mean velocity field and dissipation of turbulent kinetic energy, respectively. The terms in braces are responsible for entropy production due to irreversible fluctuating velocity and fluctuating temperature fields [8].

Inclusion of Eq. (4) in the solution process is a more direct way of calculating the entropy generation rates in turbulent flows, though obviously it requires modelling effort related to the closure problem.

### 3. Methodology

Equation (4) can be written as:

$$\frac{\partial \rho S}{\partial t} + \rho \frac{\partial \overline{u_i u_i T^2}}{\partial x_i} - k \frac{\partial T}{\partial x_i} \left( \frac{\partial T}{\partial x_i} \right)^2 = \text{Source terms}$$

(5)

Since the flows considered in this study are steady, first component on the left hand side is equal to zero.

The gradient of entropy can be defined as:

$$\frac{\partial \rho S}{\partial x_i} = \rho \frac{\partial \overline{u_i u_i T^2}}{\partial x_i} - k \frac{\partial T}{\partial x_i} \left( \frac{\partial T}{\partial x_i} \right)^2$$

(6)

Substituting Equations (6) and (7) into Eq. (5) gives:

$$\frac{\partial \rho S}{\partial x_i} = \text{Source terms}$$

(7)

where,

$$\text{Source terms} = \frac{k}{T} \left( \frac{\partial T}{\partial x_i} \right)^2 + \rho \frac{\partial \overline{u_i u_i T^2}}{\partial x_i} + \frac{\partial \overline{u_i u_i T}}{\partial x_i} + \frac{\partial \overline{u_i u_i T^2}}{\partial x_i} + \left\{ \frac{k}{T} \frac{\partial T}{\partial x_i} \left( \frac{\partial T}{\partial x_i} \right) \right\}^2$$

(8)

The right hand side of Eq. (8) requires heavy modelling effort and these models are mostly non-existent in the open literature. The terms other than the first four, involve temperature fluctuations, could either be modeled using the STTAss (Small Thermal Turbulence Assumption) as given in...
Kramer-Bevan [11] or additional transport equations could be solved as explained [12]. STTAss model assumes the fluctuating part of temperature is small compared to the mean temperature and Taylor series expansions can be used to model the fluctuating temperature by including only the linear terms.

The terms that need modelling are \( \overline{u_tT'} \), \( \overline{T'^2} \) and \( \overline{u_tT'}^{1/2} \). Some model equations are proposed by Hanjalic and Jakirlic [12] for the first two terms but no model equation has been encountered for the last term. In our future studies we will investigate the effects of modeling these terms in detail using either one of these approaches.

The model equation for \( \overline{u_tT'} \) is given as [12]:

\[
\frac{D}{Dt}(\overline{T'u'_j}) = -u'_ik \frac{\partial \overline{T'}}{\partial x_k} - (1 - C_{2T}) \overline{(T'u'_k)} \frac{\partial \overline{y}}{\partial x_k} - (1 - C_{3T}) \beta gT'^2 + C_{1T} \frac{\partial}{\partial x_k} \left( u'_k u'_l \frac{\partial T'}{\epsilon} \right) - C_{1T} \frac{\partial}{\partial x_k} \left( C_{1T} \frac{\partial (T'u'_l)}{\epsilon} \right)
\]

and the model equation for \( \overline{T'^2} \) is:

\[
\frac{D}{Dt}(\overline{T'^2}) = -2 \overline{(T'u'_l)} \left( \frac{\partial \overline{T'}}{\partial x_i} \right) + \frac{1}{2R} \frac{\partial}{\partial x_i} \left( \frac{\partial}{\partial x_i} \left( \frac{\partial \overline{T'^2}}{\partial x_i} \right) \right)
\]

For which the recommended coefficients are given in Table 1

<table>
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<th>( C_{T2} )</th>
<th>( C_T )</th>
<th>( C_{1T} )</th>
<th>( C_{2T} )</th>
<th>( C_{3T} )</th>
<th>( R )</th>
</tr>
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<tbody>
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<td>3.5</td>
<td>0.55</td>
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</tr>
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Eq. (8), (9) and (10) are implemented in Fluent, using the UDS feature, which enables the solution of an additional scalar transport equation. There are two main parameters for the implementation of Eq. (8); diffusivity and source terms. After these terms are defined and a converged solution is obtained, it is possible to postprocess the results to obtain the distributions of the solved scalar, in this case the entropy.

4. Results

The methodology is applied to the two-dimensional cascade problem given in Natalini and Sciubba [2]. This is an air-cooled turbine stator cascade. For the purpose of this study, the air cooling holes inside blade have not been modeled, but the blade surface is kept at constant temperature. The boundary conditions are applied as given in [2] such as the blade surface and the air temperatures are 1118 K and 1300 K, respectively. The inlet velocity is \( V_g = 103 \text{ m/s} \). The inlet conditions for turbulence are \( k_g = 0.01 V_g^2 \) and \( C_g = 0.006 V_g^2 \) for the turbulent kinetic energy and dissipation rate of turbulent kinetic energy, respectively.
Velocity inlet boundary condition has been applied as inlet boundary condition and pressure outlet as the outlet boundary condition. Upper and lower surfaces have been selected as periodic. They are half pitch distance away from the chord representing surfaces exposed to the flow conditions.

In order to obtain a wall $y^+$ value around 1, a boundary of 40 layers is attached for the accurate calculation of especially the viscous phenomena. A total of 25000 elements are used. The number of grid points is decided after a grid convergence study up to about 50000 elements, which showed that the calculated total entropy generation rate values do not change much after about 25000 elements. The details of the geometry and the mesh can be seen in Figure 1.

The calculated entropy generation rates within the cascade are presented in Figure 2. The distribution obtained through solving Reynolds-Averaged Entropy Transport equation (Equations (7) and (8)) as a part of the CFD solution is given in Figure 2. Figures 5b and 5c present the viscous and thermal entropy generation rate values, respectively, obtained through post-processing the obtained velocity and temperature field data. Equations (11) and (12) given below are used for this purpose:

\[
S_V = \frac{2}{T^\mu} \left\{ \left( \frac{\partial u}{\partial x} \right)^2 + \left( \frac{\partial v}{\partial y} \right)^2 + \frac{1}{2} \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right)^2 \right\}
\]

(11)

\[
S_T = \frac{k_{\text{gen}}}{T^2} \left\{ \left( \frac{\partial T}{\partial x} \right)^2 + \left( \frac{\partial T}{\partial y} \right)^2 \right\}
\]

(12)

It is seen that the direct calculation of entropy production as a part of the solution process produces a much smoother variation emphasizing the entropy generation within the blade boundary layers and wakes and the diffusion of the generated entropy within the blade passage that is mainly generated due to the temperature differences between the blade surface and the gas. The results obtained through equations (11) and (12) show that viscous entropy production is much larger than the thermal one, the high entropy regions are confined to the very near wall and the leading and trailing edge zones (consistent with the distributions given in Natalini and Sciubba [2]). In addition, the diffusion characteristics of entropy are not captured as well as the one presented in Figure 5a. Figure 5d shows the spatial distribution of the absolute value of the difference between the results.
presented in 5a and the sum of the distributions given in 5b and 5c. As is evident, main differences occur near the leading and trailing edge zones as well as within the wake regions of the blades. Since the diffusion characteristics of entropy generation are not captured by using equations (11) and (12), these show up as elevated levels of the difference value within the passage, mostly after the mid-chord position. Of course one needs more detailed comparisons with experimental data, and the effects of ignoring the temperature fluctuation related terms in equation (9) have to be investigated.

![Figure 2](image.png)

**Figure 2.** (a) Calculated total entropy generation rate through solving equations (8) and (9); (b) and (c) viscous and thermal entropy generation rates, respectively, as calculated using equations (11) and (12) by post-processing the calculated velocity and temperature fields; (d) the absolute value of the difference between the distribution presented in (a) and the sum of the distributions presented in (b) and (c).

In addition to Figure 2, further analysis has been conducted using the modelling approaches for the equations (9) and (10). However, the implementation of these terms into Fluent requires the solution of four additional transport equations. Several solutions have been obtained but the validity of these results is not presented in this study at the moment.
5. Conclusions
The effect of calculating the entropy generation rate directly using the Reynolds-Averaged Entropy Transport equation is demonstrated by comparing the obtained results with the ones that are calculated by post-processing the velocity and temperature fields for a two-dimensional turbine cascade configuration. Results show that there could be significant differences especially in the spatial distributions of entropy fields. This type of approach could offer significant improvements in entropy and loss prediction in turbomachinery flows. In the meantime, this may require more time budgets. This will be understood when more detailed test cases are studied. However, this approach needs more studies especially for accurate modeling of temperature fluctuations and temperature-velocity correlations in the entropy transport equation. Accurate modelling techniques are available in the literature but it was observed that the application of such techniques is very tedious but will be conducted in the future studies.

6. Acknowledgements
It is greatly acknowledged the support of Prof. Sciubba and Giorgio Giangaspero from University of Rome ‘La Sapienza’ and Dr. Derek Baker from Middle East Technical University. They put great value on the publication of this paper.

7. Nomenclature
$\dot{S}$ entropy generation rate, W/m$^3$ K
$k$ thermal conductivity, W/m K
$T$ temperature K
$x$ cartesian coordinate
$u$ velocity m/s
$S$ entropy per unit volume
$F_i$ flux of entropy
$k_t$ turbulent thermal conductivity W/m K
$C_v$ specific heat J/kg K

Greek symbols
$\tau_{ij}$ stress tensor
$\mu$ dynamic viscosity kg/m s
$\varepsilon$ dissipation of turbulent m$^2$/s$^3$

kinetic energy
$\gamma$ ratio of specific heats
$\rho$ density kg/m$^3$

8. References


Conventional and advanced exergetic evaluation of a supercritical coal-fired power plant

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Abstract:

A conventional exergy analysis can highlight the main components having high thermodynamic inefficiencies, but cannot consider the interactions among components or the true potential for the improvement of each component. By splitting the exergy destruction into endogenous/exogenous and avoidable/unavoidable parts, the advanced exergy analysis is capable of providing additional information to conventional exergy analysis for improving the design and operation of energy conversion systems. This paper presents the application of both a conventional and an advanced exergy analysis to a supercritical coal-fired power plant to quantify the interactions among components of the overall system and to reveal the potential for the performance enhancement of a system component.

The results show that the ratio of exogenous exergy destruction differs quite a lot from component to component. In general, almost 90% of the total exergy destruction within turbines comes from their endogenous parts, while that of feedwater preheaters contributes more or less 70% to their total exergy destruction. Moreover, the boiler subsystem is proven to have a large amount of exergy destruction caused by the irreversibilities within the remaining components of the overall system. It is also found that the boiler subsystem still has the largest avoidable exergy destruction; however, the enhancement efforts should focus not only on its inherent irreversibilities but also on the inefficiencies within the remaining components. A large part of the avoidable exergy destruction within feedwater preheaters is exogenous; while that of the remaining components is mostly endogenous indicating that the improvements mainly depend on advances in design and operation of the component itself.

Keywords:

Supercritical Power Plant, Advanced Exergy Analysis, Improvement Strategy

1. Introduction

Nearly 45% of global electricity generation is derived from coal while natural gas and nuclear energy make up about 20% and 15%, respectively [1,2]. Despite the rapid growth of cleaner sustainable energies, the heavily dependence of world energy on coal is expected to continue for decades. It has been well known that the supercritical coal-fired power plants are energy systems with high fuel consumption, low efficiency, and relatively large amounts of pollutants and greenhouse gas emissions. Consequently, efficiency improvements of both existing units and plants under construction are of particular importance.

Exergy analysis can identify the location, the magnitude, and the sources of thermodynamic inefficiencies in a thermal system [3], and thus provide information for improving the overall efficiency and the cost effectiveness of a system or for comparing the performance of various systems [4]. Throughout the last decades, this conventional exergy analysis has been discussed and applied to a wide variety of coal-fired power plants, for example, see Refs. [5-9]. However, conventional exergy analysis is always used to evaluate the performance of an individual component at certain operation conditions, without considering the interactions among components or the actual achievable best behavior of the component under investigation.

The advanced exergy analysis was proposed and developed in [10-18] to evaluate energy conversion systems by splitting the exergy destruction into endogenous/exogenous and...
avoidable/unavoidable parts, which are crucial for improving complex systems. Therefore, more comprehensive, practical and not just rigorous information on how and to what extent the components can be improved is provided by an advanced exergy analysis to explicitly develop strategies for system performance enhancement. In the last years, advanced exergy analyses have been successfully applied to many energy conversion systems including simple and complex systems. At first, systems such as a simple gas-turbine-based cogeneration system [11], a simple vapor-compression refrigeration machine [15], and a novel cogeneration system for vaporizing liquefied natural gas [17] were used for demonstrating the theory development and applications. Later applications include more complex systems such as a cogeneration power plant based on gas turbine [12], and a three-pressure level combined cycle [18]. The results of these applications show that considering the interactions among components and the energy-saving potentials makes the approach a promising and powerful tool for effectively improving complex energy systems, such as coal-fired power plants.

However, until now no supercritical coal-fired power plant has been analyzed and evaluated using this method. Hence in this paper both conventional and advanced exergy analyses were performed to an existing modern supercritical pulverized-coal power-generation unit, in order to formulate some recommendations for system improvement.

2. Methodology

2.1. Conventional exergy analysis

It is assumed that the system boundaries are at the temperature $T_0$ of the reference environment, and therefore, there are no exergy losses associated with the kth component [19]. As a consequence, the exergy loss term actually only appears at the level of the overall system. Hence, the exergy balance of the kth component is expressed as

$$\dot{E}_{F,k} = \dot{E}_{P,k} + \dot{E}_{D,k}.$$  

(1)

For the overall system, it becomes

$$\dot{E}_{F,\text{tot}} = \dot{E}_{P,\text{tot}} + \sum_k \dot{E}_{D,k} + \dot{E}_{L,\text{tot}}.$$  

(2)

The exergetic efficiency of the kth component is written as

$$\epsilon_k = \frac{\dot{E}_{P,k}}{\dot{E}_{F,k}} = 1 - \frac{\dot{E}_{D,k}}{\dot{E}_{F,k}}.$$  

(3)

To identify the part of total fuel exergy input destroyed within the kth component, the exergy destruction ratio is defined as

$$y_{D,k} = \frac{\dot{E}_{D,k}}{\dot{E}_{F,\text{tot}}}.$$  

(4)

2.2. Advanced exergy analysis

In an advanced exergy analysis, the exergy destruction within each component is split to better reveal its sources (endogenous/exogenous) and its potential for reduction (avoidable/unavoidable) [18]. The endogenous part is the exergy destruction obtained when all other components operate ideally and the component being considered operates with its real efficiency. The exogenous part of the exergy destruction within the considered component, is caused by irreversibilities in the remaining components and by the structure of the overall system, and is the difference between total exergy destruction of the component at real conditions and the endogenous part. The unavoidable part is the part that cannot be eliminated, even if the best available technology in the near future
would be applied. Finally the avoidable part is the difference between the total exergy destruction within the component in the real plant and the unavoidable part of exergy destruction. [15].

2.2.1. Endogenous/exogenous exergy destruction

To consider the interactions among components, the exergy destruction within the kth component is expressed, as equation (5) shows, as the sum of endogenous and exogenous exergy destruction:

\[ \dot{E}_{D,k}^{EN} = \dot{E}_{D,k}^{EX} + \dot{E}_{D,k}^{EN} \] (5)

Since it is also important, how and to what extent one component affects another component[17], the exogenous exergy destruction can be further split as

\[ \dot{E}_{D,k}^{EX} = \sum_{r=1}^{n} \dot{E}_{D,r}^{EX,r} + \dot{E}_{D,k}^{EX} \] (6)

where \( \dot{E}_{D,r}^{EX,r} \) is the effect of exergy destruction within the rth component caused by the exergy destruction of the kth component. It can be seen that the total exogenous exergy destruction is comprised of two terms, a sum term and a term called mexogenous exergy destruction \( E_{D,k}^{EX} \) due to the simultaneous interactions of all \((n-1)\) components.

2.2.2. Avoidable/unavoidable exergy destruction

Due to technical and economic limitations and manufacturing methods, each component has an unapproachable best thermodynamic behavior in the near future that determines the unavoidable part of exergy destruction. When each component operates with its best possible conditions, the unavoidable process is established, to obtain the ratio \((\dot{E}_{D} / \dot{E}_{P})_{k}^{UN}\) for the component. This ratio is the key parameter for calculating the unavoidable part of exergy destruction of individual components in a real process. Therefore, the exergy destruction of the kth component can also be written as

\[ \dot{E}_{D,k} = \dot{E}_{D,k}^{UN} + \dot{E}_{D,k}^{AV} \] (7)

where the unavoidable part can be calculated by

\[ \dot{E}_{D,k}^{UN} = \dot{E}_{p,k}^{EN} \cdot (\dot{E}_{D} / \dot{E}_{P})_{k}^{UN} \] (8)

2.2.3. Combination of the splitting

By further combining the two splitting concepts, the avoidable-endogenous/avoidable-exogenous and unavoidable-endogenous/unavoidable-exogenous terms can be obtained by

\[ \dot{E}_{D,k}^{UN,EN} = \dot{E}_{p,k}^{EN} \cdot (\dot{E}_{D} / \dot{E}_{P})_{k}^{UN} \] (9a)

\[ \dot{E}_{D,k}^{UN,EX} = \dot{E}_{D,k}^{UN} - \dot{E}_{D,k}^{UN,EN} \] (9b)

\[ \dot{E}_{D,k}^{AV,EN} = \dot{E}_{D,k}^{EN} - \dot{E}_{D,k}^{UN,EN} \] (9c)

\[ \dot{E}_{D,k}^{AV,EX} = \dot{E}_{D,k}^{EX} - \dot{E}_{D,k}^{UN,EX} \] (9d)

In order to calculate each part of the exergy destruction within all components, five sorts of processes including real, theoretical, hybrid I, hybrid II and unavoidable processes should be considered and simulated. In a theoretical process, all components operate under their theoretical conditions, while in a hybrid I process only the component being considered is set at its real condition to compute its endogenous exergy destruction. Simulations of totally \((C_n^2 - n)\) hybrid II
processes enable us to quantify the interaction between any two components operating under their real conditions with \( n \) being the total number of components. The unavoidable process where each component operates under its unavoidable conditions is simulated for obtaining the unavoidable ratios of all components.

### 3. Plant descriptions

The supercritical power plant, as shown in Fig.1, has a total installed power capacity of 671MW, consisting of a boiler subsystem and a turbine subsystem and an electrical generator. The properties of bituminous coal are listed in Table 1.

![Fig. 1. Schematic diagram of the overall supercritical power generation unit](image)

#### Table 1. Approximate analysis of coal (wt. %; as received)

<table>
<thead>
<tr>
<th>Item</th>
<th>value</th>
<th>Item</th>
<th>value</th>
<th>Item</th>
<th>value</th>
<th>Item</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>2.10%</td>
<td>Carbon</td>
<td>57.52%</td>
<td>Oxygen</td>
<td>2.78%</td>
<td>Sulphur</td>
<td>2.00%</td>
</tr>
<tr>
<td>Ash</td>
<td>23.70%</td>
<td>Hydrogen</td>
<td>3.11%</td>
<td>Nitrogen</td>
<td>0.99%</td>
<td>LHV</td>
<td>21981kJ/kg</td>
</tr>
</tbody>
</table>

The boiler subsystem with dry ash extraction and single reheat is simulated by two components: boiler and air preheater. The coal combustion process and the heat transfer between flue gas and working fluid occur in the boiler. In this way, the theoretical condition of boiler subsystem can be readily specified.

The main steam is expanded in the high-pressure turbine and then the steam is reheated and expanded through the stages of intermediate-pressure and low-pressure turbines. The intermediate-pressure turbine (IPT) is considered in two parts: from the inlet to steam extraction (IPT1) and from steam extraction to outlet (IPT2). Similarly, the low-pressure turbine (LPT) is considered in five parts (LPT 1 through LPT5). A surface condenser is used to remove to the environment heat from exhausted steam. To increase the thermodynamic average temperature of the working fluid in the boiler, a feedwater regenerative system with three high-pressure heaters, four low-pressure heaters and a deaerator is configured. The condensate and feedwater pumps are driven by electric motors and a secondary steam turbine with the same steam supply as for the deaerator.
Table 2. Thermodynamic properties of all material flows

<table>
<thead>
<tr>
<th>No</th>
<th>( m, \text{ kg/s} )</th>
<th>( T, \ ^\circ\text{C} )</th>
<th>( p, \ \text{bar} )</th>
<th>( E_{\text{tot}}, \text{MW} )</th>
<th>( No )</th>
<th>( m, \text{ kg/s} )</th>
<th>( T, \ ^\circ\text{C} )</th>
<th>( p, \ \text{bar} )</th>
<th>( E_{\text{tot}}, \text{MW} )</th>
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<td>1.000</td>
<td>0.85</td>
<td>22</td>
<td>29813.6</td>
<td>30.79</td>
<td>1.000</td>
<td>81.39</td>
</tr>
<tr>
<td>2</td>
<td>619.385</td>
<td>330.41</td>
<td>1.000</td>
<td>61.40</td>
<td>23</td>
<td>395.497</td>
<td>35.79</td>
<td>0.059</td>
<td>1.27</td>
</tr>
<tr>
<td>3</td>
<td>68.802</td>
<td>25.00</td>
<td>1.000</td>
<td>1603.07</td>
<td>24</td>
<td>395.497</td>
<td>35.94</td>
<td>17.24</td>
<td>1.96</td>
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<td>4</td>
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<td>1.000</td>
<td>15.97</td>
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<td>395.497</td>
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<td>15.84</td>
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<td>26</td>
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<td>48.85</td>
<td>27</td>
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<td>47.50</td>
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<td>211.95</td>
<td>303.7</td>
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<td>569.00</td>
<td>41.10</td>
<td>632.49</td>
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<td>522.217</td>
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<td>149.16</td>
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<td>20.58</td>
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<td>38.592</td>
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<td>1.333</td>
<td>1.13</td>
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<td>0.68</td>
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<tr>
<td>18</td>
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<td>0.208</td>
<td>3.41</td>
<td>39</td>
<td>69.452</td>
<td>41.49</td>
<td>0.208</td>
<td>0.30</td>
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<td>0.073</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

The simulation of the supercritical coal-fired power plant was conducted with the help of the software EBSILONProfessional and the main thermodynamic parameters of each flow are listed in Table 2.

4. Simulations for the advanced exergy analysis

Defining the theoretical and unavoidable conditions of each component is the most important task for the calculation of different parts of exergy destruction. In this section, the theoretical and unavoidable conditions of different components of the energy system are discussed.

4.1. Theoretical conditions

The theoretical operation conditions for each component should follow the assumptions: \( E_D=0 \), (if possible), or otherwise \( E_D=\text{min} \).

With regards to the features of the power plant, many parameters in the theoretical process are the same as in the real process: for example, temperature and pressure of superheated steam, temperature of reheated steam, pressure levels of steam extractions, back pressure of turbine, and the inlet temperature of cooling water flowing into condenser remain unchanged when a component is under theoretical conditions. However, the temperature and pressure of feedwater into boiler, the pressure of reheated steam, the temperature of steam extraction as well as the outlet temperature of cooling water flowing out of the condenser always vary with the conditions assumed for the corresponding component.

For turbines, fans and pumps, both the isentropic efficiency and the mechanical efficiencies should equal to \( I \) to guarantee no exergy destruction during the corresponding process.
For heat exchangers, it is apparent that the working condition with no entropy generation is normally unachievable due to the existence of a pinch point. Only the state where the exergy destruction is minimal can be achieved by assuming no pressure drop and zero temperature difference at the pinch point.

The combustion process in this case is not considered separately but is integrated into the component boiler with the heat transfer process. However, there are still some assumptions referring to the combustion process for defining the theoretical conditions of the boiler. The chemical composition of flue gas should be kept the same as in the real conditions to make sure that the excess air/fuel ratio is equal to that of the real process. In addition, no pressure drop occurs to satisfy the theoretical conditions of combustion process. Detailed explanations are given in [13].

4.2. Unavoidable conditions

The unavoidable conditions refer to the best unapproachable working conditions associated with the technical and economic limits related to the considered component. In general, it would be better if the best performance characteristics can be derived in conjunction with some kind of investment-efficiency curves or the best practice of the same type components under operation. If no such resources are available, the best behavior is determined more than less arbitrarily, depending highly on the understanding and practical experience of the analyzer. In this paper the unavoidable conditions of each component are chosen as listed in Table 3.

### Table 3. Assumptions of theoretical and unavoidable conditions

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Real Process</th>
<th>Unavoidable Process</th>
<th>Comp.</th>
<th>Real Process</th>
<th>Unavoidable Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPT1</td>
<td>$\eta_i=0.89$, $\eta_m=0.998$</td>
<td>$\eta_i=0.92$, $\eta_m=1$</td>
<td>H7</td>
<td>$\Delta T_p=2.9$, $\Delta T_p=5.5$</td>
<td>$\Delta T_p=1.5$, $\Delta T_p=3.0$</td>
</tr>
<tr>
<td>HPT2</td>
<td>$\eta_i=0.88$, $\eta_m=0.998$</td>
<td>$\eta_i=0.92$, $\eta_m=1$</td>
<td>H6</td>
<td>$\Delta T_p=3.1$, $\Delta T_p=5.5$</td>
<td>$\Delta T_p=1.5$, $\Delta T_p=3.0$</td>
</tr>
<tr>
<td>IPT1</td>
<td>$\eta_i=0.92$, $\eta_m=0.998$</td>
<td>$\eta_i=0.96$, $\eta_m=1$</td>
<td>H5</td>
<td>$\Delta T_p=6.3$, $\Delta T_p=5.5$</td>
<td>$\Delta T_p=3.0$, $\Delta T_p=3.0$</td>
</tr>
<tr>
<td>IPT2</td>
<td>$\eta_i=0.93$, $\eta_m=0.998$</td>
<td>$\eta_i=0.96$, $\eta_m=1$</td>
<td>DA</td>
<td>$\Delta p=0.4$</td>
<td>$\Delta p=0.1$</td>
</tr>
<tr>
<td>LPT1</td>
<td>$\eta_i=0.94$, $\eta_m=0.998$</td>
<td>$\eta_i=0.96$, $\eta_m=1$</td>
<td>FP</td>
<td>$\eta_i=0.84$, $\eta_m=0.998$</td>
<td>$\eta_i=0.87$, $\eta_m=1$</td>
</tr>
<tr>
<td>LPT2</td>
<td>$\eta_i=0.96$, $\eta_m=0.998$</td>
<td>$\eta_i=0.97$, $\eta_m=1$</td>
<td>H3</td>
<td>$\Delta T_p=4.9$, $\Delta T_p=5.5$</td>
<td>$\Delta T_p=3.0$, $\Delta T_p=3.0$</td>
</tr>
<tr>
<td>LPT3</td>
<td>$\eta_i=0.92$, $\eta_m=0.998$</td>
<td>$\eta_i=0.94$, $\eta_m=1$</td>
<td>H2</td>
<td>$\Delta T_p=3.0$, $\Delta T_p=5.5$</td>
<td>$\Delta T_p=1.5$, $\Delta T_p=3.0$</td>
</tr>
<tr>
<td>LPT4</td>
<td>$\eta_i=0.74$, $\eta_m=0.998$</td>
<td>$\eta_i=0.85$, $\eta_m=1$</td>
<td>H1</td>
<td>$\Delta T_p=2.8$, $\Delta T_p=5.5$</td>
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<td>LPT5</td>
<td>$\eta_i=0.82$, $\eta_m=0.998$</td>
<td>$\eta_i=0.85$, $\eta_m=1$</td>
<td>ST</td>
<td>$\eta_i=0.80$, $\eta_m=0.998$</td>
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</tr>
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<td>$\Delta T_p=3$</td>
<td>GT</td>
<td>$\eta_m=0.986$</td>
<td>$\eta_m=0.998$</td>
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<tr>
<td>CP</td>
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<td>BO</td>
<td>$\eta_i=0.980$, $\Delta p_{th}=40.5\eta_i=0.995$, $\Delta p_{th}=20$</td>
<td>$\Delta p_{th}=1.90$, $\alpha=1.2$, $\Delta p_{th}=0.50$, $\alpha=1.03$</td>
</tr>
<tr>
<td>H8</td>
<td>$\Delta T_p=2.9$, $\Delta T_p=5.5$</td>
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<td>AH</td>
<td>$T_{es}=127$</td>
<td>$T_{es}=90$</td>
</tr>
</tbody>
</table>

### Table 4. Results from the conventional exergy analysis at the component level

<table>
<thead>
<tr>
<th>Comp.</th>
<th>$E_{ex, MW}$</th>
<th>$E_{p, MW}$</th>
<th>$y_p, %$</th>
<th>$\epsilon, %$</th>
<th>Comp.</th>
<th>$E_{ex, MW}$</th>
<th>$E_{p, MW}$</th>
<th>$y_p, %$</th>
<th>$\epsilon, %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPT1</td>
<td>186.55</td>
<td>175.69</td>
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<td>94.2</td>
<td>H7</td>
<td>7.72</td>
<td>6.05</td>
<td>0.11</td>
<td>78.4</td>
</tr>
<tr>
<td>HPT2</td>
<td>51.10</td>
<td>47.63</td>
<td>0.23</td>
<td>93.2</td>
<td>H6</td>
<td>7.07</td>
<td>6.17</td>
<td>0.06</td>
<td>87.2</td>
</tr>
<tr>
<td>IPT1</td>
<td>101.99</td>
<td>98.2</td>
<td>0.25</td>
<td>96.3</td>
<td>H5</td>
<td>18.93</td>
<td>15.93</td>
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<td>84.41</td>
<td>81.36</td>
<td>0.20</td>
<td>96.4</td>
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<td>19.81</td>
<td>0.20</td>
<td>86.7</td>
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<td>78.22</td>
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<td>96.2</td>
<td>FP</td>
<td>20.80</td>
<td>18.6</td>
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<td>81.56</td>
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<td>97.2</td>
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<td>24.41</td>
<td>21.81</td>
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<td>93.3</td>
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<td>94.0</td>
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<td>35.76</td>
<td>34.13</td>
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<td>25.72</td>
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<td>71.6</td>
</tr>
</tbody>
</table>
5. Results and discussions

The results from the conventional and the advanced exergy analysis at the component level are summarized in Tables 4 and 5.

### Table 5. Results of advanced exergetic analysis at the component level (Unit: MW)

<table>
<thead>
<tr>
<th>Comp Name</th>
<th>$\dot{E}_{EN}^D$, MW</th>
<th>$\dot{E}_{EX}^D$, MW</th>
<th>$\dot{E}_{EN}^U$, MW</th>
<th>$\dot{E}_{EX}^U$, MW</th>
<th>$\dot{E}_{EN}^A$, MW</th>
<th>$\dot{E}_{EX}^A$, MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPT1</td>
<td>9.90</td>
<td>0.96</td>
<td>7.25</td>
<td>3.61</td>
<td>6.67</td>
<td>3.23</td>
</tr>
<tr>
<td>HPT2</td>
<td>3.05</td>
<td>0.42</td>
<td>2.16</td>
<td>1.31</td>
<td>1.87</td>
<td>1.18</td>
</tr>
<tr>
<td>IPT1</td>
<td>3.64</td>
<td>0.16</td>
<td>2.59</td>
<td>1.21</td>
<td>2.47</td>
<td>1.17</td>
</tr>
<tr>
<td>IPT2</td>
<td>2.69</td>
<td>0.37</td>
<td>2.04</td>
<td>1.01</td>
<td>1.77</td>
<td>0.92</td>
</tr>
<tr>
<td>LPT1</td>
<td>2.78</td>
<td>0.28</td>
<td>2.38</td>
<td>0.68</td>
<td>2.10</td>
<td>0.68</td>
</tr>
<tr>
<td>LPT2</td>
<td>2.13</td>
<td>0.24</td>
<td>1.92</td>
<td>0.46</td>
<td>1.65</td>
<td>0.48</td>
</tr>
<tr>
<td>LPT3</td>
<td>2.31</td>
<td>0.31</td>
<td>1.92</td>
<td>0.70</td>
<td>1.72</td>
<td>0.59</td>
</tr>
<tr>
<td>LPT4</td>
<td>11.46</td>
<td>1.29</td>
<td>6.28</td>
<td>6.46</td>
<td>5.72</td>
<td>5.74</td>
</tr>
<tr>
<td>LPT5</td>
<td>7.84</td>
<td>1.15</td>
<td>7.15</td>
<td>1.84</td>
<td>6.23</td>
<td>1.61</td>
</tr>
<tr>
<td>COND</td>
<td>15.30</td>
<td>3.81</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CP</td>
<td>0.15</td>
<td>0.02</td>
<td>0.12</td>
<td>0.05</td>
<td>0.10</td>
<td>0.04</td>
</tr>
<tr>
<td>H8</td>
<td>1.18</td>
<td>0.16</td>
<td>1.12</td>
<td>0.21</td>
<td>0.99</td>
<td>0.19</td>
</tr>
<tr>
<td>H7</td>
<td>1.21</td>
<td>0.46</td>
<td>1.41</td>
<td>0.26</td>
<td>1.15</td>
<td>0.06</td>
</tr>
<tr>
<td>H6</td>
<td>0.61</td>
<td>0.29</td>
<td>0.71</td>
<td>0.19</td>
<td>0.54</td>
<td>0.07</td>
</tr>
<tr>
<td>H5</td>
<td>2.17</td>
<td>0.83</td>
<td>2.47</td>
<td>0.53</td>
<td>2.02</td>
<td>0.15</td>
</tr>
<tr>
<td>DA</td>
<td>2.03</td>
<td>1.02</td>
<td>2.89</td>
<td>0.16</td>
<td>2.12</td>
<td>-0.09</td>
</tr>
<tr>
<td>FP</td>
<td>1.70</td>
<td>0.50</td>
<td>1.72</td>
<td>0.49</td>
<td>1.34</td>
<td>0.37</td>
</tr>
<tr>
<td>H3</td>
<td>2.28</td>
<td>0.32</td>
<td>2.16</td>
<td>0.44</td>
<td>1.96</td>
<td>0.33</td>
</tr>
<tr>
<td>H2</td>
<td>1.58</td>
<td>0.96</td>
<td>1.99</td>
<td>0.55</td>
<td>1.45</td>
<td>0.13</td>
</tr>
<tr>
<td>H1</td>
<td>1.15</td>
<td>0.49</td>
<td>1.25</td>
<td>0.38</td>
<td>1.00</td>
<td>0.15</td>
</tr>
<tr>
<td>ST</td>
<td>3.20</td>
<td>1.72</td>
<td>3.50</td>
<td>1.42</td>
<td>2.31</td>
<td>0.89</td>
</tr>
<tr>
<td>GT</td>
<td>9.79</td>
<td>0.00</td>
<td>1.35</td>
<td>8.45</td>
<td>1.35</td>
<td>8.45</td>
</tr>
<tr>
<td>BO</td>
<td>615.20</td>
<td>86.68</td>
<td>676.29</td>
<td>25.60</td>
<td>608.98</td>
<td>6.23</td>
</tr>
<tr>
<td>AH</td>
<td>16.91</td>
<td>7.09</td>
<td>11.46</td>
<td>12.53</td>
<td>11.56</td>
<td>5.34</td>
</tr>
</tbody>
</table>

5.1. Conventional analysis

It is very clear from Table 4 that 45% of the total input fuel exergy is destroyed in the boiler due to coal combustion and heat transfer under high temperature differences. The air preheater, turbines and condenser follow with much lower values of exergy destruction. The regenerative subsystem has little exergy destruction, whereas the secondary turbine and the generator have relatively large exergy destruction value.

From the perspective of the conventional analysis, the greater the irreversibility in a component, the higher the priority for improvement must be for increasing the efficiency of the overall system. Hence, the boiler should be given the first priority for the reduction of total inefficiencies. Then, the air preheater, the first and the last two stages of turbine have relatively high priorities, because these components have large operational exergy destruction.
5.2. Advanced analysis

5.2.1. Interactions among components

To investigate how and to what extend one component exerts impact on another, each $E_{D_{r,k}}^{EX}$ is calculated and listed in Table 6, which also contains the endogenous exergy destruction of each component. It is apparent that the interactions between different components can be positive or negative. The former indicates that the exergy destruction in the $k$th component increases with the introduction of additional irreversibilities in the $r$th component. On the contrary, the latter means that adding inefficiencies in the $r$th component contributes to a reduction of the exergy destroyed in the $k$th component. These two distinct impacts can be the results of mass flow changes or thermodynamic property variation of material flows flowing through the $k$th component due to the introduction of additional irreversibility in the $r$th component. For example, when evaluating the interaction between components IPT1 and H3, introducing irreversibility in H3 reduces the outlet temperature of feedwater. This requires more steam extraction in the following feedwater preheater H2. Since the total mass flow rate is kept almost unchanged, the mass flow of steam through IPT1 is reduced. However, the impact of thermodynamic inefficiency in boiler on IPT1 results from large flow property changes. For example, we can assume that the irreversibilities in the boiler increase because of an increase in the pressure drop in the reheater. If the pressure at the outlet of the first part of the intermediate-pressure turbine (IPT1) remains constant, then the steam temperature at that point will increase, leading to a reduction in the exergy destruction within IPT1. Thus, increasing the exergy destruction in the boiler (component $r$) leads to a reduction in the exergy destruction within the IPT1 (component $k$). This explains the negative sign related to the interaction between these two components (see Table 6, third row and second to last column).

The exergy destruction within each turbine stage is mainly affected by the other stages, especially the stages with large irreversibility, the directly-connected feedwater preheater as well as the electrical generator. The irreversibilities in other turbine stages all have contributions to the exergy destruction in the considered turbine stage, whereas the inefficiencies of its corresponding feedwater preheater have a negative influence (negative sign in Table 6) on it due to the change of mass flow rate. In addition, the generator greatly affects the exergy destruction of each turbine stage, when the total generated power, as assumed here, remains constant.

With its constant pressure, the condenser has no effect on other components but its own exergy destruction greatly depends on other components, especially the turbine, secondary turbine, generator and the boiler. Good performance of these components can reduce the mass flow of main steam.

The pumps, condensate and feedwater pumps, are almost independent of all other components with the exception of the interaction between feedwater pump and boiler, since the pressure drop in boiler directly determines the pressure head provided by feedwater pump.

Although the regenerative subsystem is affected by the irreversibilities in turbine, the effects tend to be rather small. The performance of each feedwater preheater mostly relies on its preceding component. Hence, performance the enhancement of the feedwater heating system requires the best possible better operation conditions of all preheaters.

The components secondary turbine, feedwater pump, turbine, feedwater preheater and air preheater have a large effect on the boiler. The interaction between boiler and air preheater is intensive, thus, these components should be optimized as one unit.

5.2.2. Endogenous/exogenous exergy destruction

Table 5 shows that a large part of the exergy destruction in all components is endogenous. However, for different types of components, the proportions of exogenous part differ significantly. All the exergy destruction in generator is endogenous. Nearly 10% of exergy destructions of turbine stages are considered as exogenous, while the average ratio of exogenous part in the regenerative system almost reaches 30%, which indicates that the effect of system topology contributes largely
to their exergy destruction. The boiler, air preheater and condenser are the three components with
the largest absolute exogenous destruction values, especially that of boiler reaching 86MW. In
addition, all the exogenous exergy destructions are positive which means that the performance of
any component improves with the performance enhancement of the remaining system components.

5.2.3. Unavoidable/avoidable exergy destruction

The real potential for improving a component is not fully revealed by its total exergy destruction but
by its avoidable part. With the exception of boiler, 20%-40% of exergy destruction of the most
components can be generally avoided with that part of the exergy destruction of generator and air
preheater reaching 86% and 50%, respectively. The energy-savings potential from the generator
also should call for attention, since the work saved is pure exergy and even a slight change of its
efficiency contributes largely to total fuel consumption. Moreover, if the combustion process is
stable and fulfils a much higher burnout rate under even lower oxygen ratio, and the temperature of
flue gas exhaust would further decline to around 90°C, which is now allowed due to the
development of acid-resistant materials, up to 38MW of exergy could be saved just in the boiler.
Finally, the potential in other components such as the secondary turbine should also be emphasized.

5.2.4. Combined analysis

The boiler subsystem has the largest avoidable exergy destruction; however, most of it is exogenous.
For boiler the avoidable/endogenous part is slightly less than 25% of total avoidable part, while that
of air preheater achieves nearly 45%. This indicates that the strategy for reducing the exergy
destruction within the boiler should focus more on the components with a large effect on the boiler,
such as turbine, secondary turbine and the last feedwater preheater. The irreversibilities occurring in
air preheater itself and boiler have a similar contribution to the total avoidable exergy destruction
within air preheater. To improve the air preheater, the entire boiler subsystem should be considered.
The generator also has a large amount of avoidable/endogenous exergy destruction, reaching almost
9MW. The performance enhancement of this component in isolation can have great benefits to the
reduction of overall fuel consumption. More or less 90% of avoidable exergy destruction of turbines
is endogenous, which indicates the improvement measurements for turbines should be concentrated
on the components themselves.

5.3. Improvement strategy

Considering both the interactions among components and the potential for improving components,
more effective and efficient improvement priorities can be proposed. The generator should be the
first component to be enhanced in a separate way. Then, the turbines with high endogenous
avoidable exergy destruction should also be improved separately. Subsequently, the measurements
for enhancing feedwater regeneration subsystem with high proportion of exogenous avoidable
exergy destruction should be concentrated on its subsystem level, since each individual preheater is
mainly affected by its preceding one. The separate enhancement of only one feedwater preheater
actually contributes little to the reduction of overall subsystem energy consumption. Finally, the
boiler and air preheater can be improved by reducing both their inherent irreversibilities and the
inefficiencies in the components with large contribution to their total exergy destruction, mainly the
generator, turbines, last high-pressure feedwater preheater as well as feedwater pump. Given the
combustion mode and boiler configuration, the effective approach for reducing fuel consumption is
the combustion optimization with low air ratio and a further decrease of the exhaust gas temperature
but not the rearrangement of heating surface configuration.

6. Conclusions

Exergy destruction in each component calculated in conventional exergy analysis is split, according
to the sources and controllability. Considering detailed interactions among components and real
potentials for improving components, the following conclusions can be obtained:
Table 6. Endogenous exergy of component k and the exogenous part caused by component r
k
r HPT1 HPT2 IPT1 IPT2 LPT1 LPT2 LPT3 LPT4 LPT5 COND CP H8 H7 H6 H5 DA FP H3 H2 H1 ST GE
HPT1 9.90 0.08 0.06 0.04 0.04 0.03 0.04 0.18 0.12 0.00 0.00 0.01 0.00 0.01 0.01 0.00 0.03 0.04 0.03 -0.09 0.06 0.15
HPT2 0.14 3.05 0.02 0.01 0.01 0.01 0.01 0.05 0.04 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.01 0.02 -0.03 0.00 0.02 0.04
IPT1 0.10 0.03 3.64 0.02 0.02 0.01 0.01 0.07 0.05 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.01 -0.05 -0.01 0.01 0.02 0.05
IPT2 0.08 0.02 0.02 2.69 0.01 0.01 0.01 0.05 0.03 0.00 0.00 0.00 0.00 0.00 0.00 -0.01 0.01 0.00 0.00 0.01 0.01 0.04
LPT1 0.08 0.02 0.03 0.02 2.78 0.01 0.01 0.05 0.03 0.00 0.00 0.00 0.00 0.00 -0.03 0.00 -0.01 0.00 0.00 0.01 -0.02 0.04
LPT2 0.06 0.02 0.03 0.02 0.02 2.13 0.01 0.04 0.03 0.00 0.00 0.00 0.00 -0.01 0.00 0.00 -0.01 0.00 0.00 0.01 -0.02 0.03
LPT3 0.07 0.02 0.03 0.02 0.02 0.02 2.31 0.04 0.03 0.00 0.00 0.00 -0.01 0.00 0.01 0.00 -0.01 0.00 0.00 0.01 -0.02 0.03
LPT4 0.33 0.10 0.15 0.11 0.11 0.08 0.09 11.46 0.14 0.00 0.00 -0.06 -0.01 0.01 0.03 0.01 -0.06 0.02 0.01 0.04 -0.10 0.17
LPT5 0.23 0.07 0.10 0.08 0.07 0.06 0.06 0.31 7.84 0.00 0.00 -0.01 0.01 0.01 0.02 0.00 -0.04 0.01 0.00 0.03 -0.07 0.11
COND 0.43 0.13 0.18 0.13 0.14 0.10 0.11 0.57 0.39 15.30 0.00 0.03 0.01 0.02 0.03 0.01 0.16 0.03 0.01 0.03 0.30 0.22
CP
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.15 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
H8
0.03 0.01 0.01 0.01 0.01 0.01 0.01 0.02 0.02 0.00 -0.01 1.18 0.00 0.00 0.00 0.00 0.01 0.00 0.00 0.00 0.01 0.02
H7
0.04 0.01 0.01 0.01 0.01 0.00 0.01 0.02 0.02 0.00 0.00 0.25 1.21 0.00 0.00 0.00 0.01 0.00 0.00 0.00 0.01 0.02
H6
0.02 0.01 0.01 0.00 0.00 0.00 0.00 0.01 0.01 0.00 0.00 0.00 0.17 0.61 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.01
H5
0.06 0.02 0.05 0.04 0.04 0.00 0.01 0.04 0.03 0.00 0.00 0.00 0.00 0.30 2.17 0.00 0.01 0.00 0.00 0.01 0.01 0.03
DA
0.06 0.02 0.04 0.03 -0.01 0.01 0.01 0.04 0.02 0.00 0.00 -0.04 -0.03 -0.06 0.62 2.03 0.00 -0.02 0.00 0.00 0.01 0.03
FP
0.05 0.01 0.01 0.01 0.01 0.01 0.01 0.03 0.02 0.00 0.00 0.00 0.00 0.00 0.00 0.01 1.70 0.01 0.00 -0.01 0.01 0.02
H3
0.06 0.02 0.08 0.01 0.01 0.01 0.01 0.04 0.03 0.00 0.00 0.00 0.00 0.00 0.00 0.18 -0.12 2.28 -0.05 -0.01 0.01 0.03
H2
0.09 0.03 -0.01 0.01 0.01 0.01 0.01 0.03 0.02 0.00 0.00 0.00 0.00 0.00 0.00 -0.03 0.02 0.61 1.58 -0.03 0.01 0.02
H1
0.07 0.00 0.01 0.01 0.01 0.00 0.00 0.02 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 -0.02 0.22 1.15 0.01 0.02
ST
0.09 0.03 0.02 0.01 0.01 0.01 0.01 0.06 0.04 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.63 0.01 0.01 -0.03 3.20 0.05
GE
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 9.79
BO
7.00 2.11 3.39 2.63 2.66 2.03 2.21 10.93 7.48 0.00 -0.01 0.33 0.23 0.30 0.64 0.12 1.84 0.32 -0.04 1.37 3.67 8.98
AH
0.26 0.07 0.10 0.07 0.07 0.06 0.06 0.30 0.21 0.00 0.00 0.01 0.01 0.01 0.02 0.00 0.04 0.01 0.03 -0.20 0.09 0.25

124

BO AH
0.05 0.00
0.02 0.00
-0.21 0.00
0.02 0.00
0.01 0.00
0.01 0.00
0.01 0.00
0.06 0.00
0.04 0.00
0.24 0.00
0.00 0.00
0.01 0.00
0.01 0.00
0.01 0.00
0.04 0.00
0.04 0.00
0.27 0.00
0.00 0.00
-0.01 0.00
0.00 0.00
0.50 0.00
0.00 0.00
615.20 19.25
4.74 16.91


1. The ratio of exogenous exergy destruction differs quite a lot from component to component. In general, inherent irreversibilities in turbines contribute more or less 90% to their total exergy destruction, while this proportion drops down to 70% when it comes to feedwater preheaters. The boiler subsystem also has a large amount of exergy destruction caused by the inefficiencies in other components.

2. The boiler subsystem still has the largest avoidable exergy destruction; however, the enhancement efforts should be made not only to its inherent irreversibilities but also to inefficiencies of the remaining components. Moreover, around 60% of the avoidable exergy destruction of feedwater preheaters is exogenous. For the remaining components efforts should mainly focus on improving the components themselves.

3. Due to the interactions among components, the improvement priorities refer not only to the components that should be modified, but also to the sequence for optimization. We believe that the improvement of the boiler subsystem will be more meaningful if the remaining important components are improved first and can provide persuading good performances.

Acknowledgement
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Nomenclature
\( \dot{E} \) exergy rate, MW
\( \dot{m} \) mass flow rate, kg/s
\( h \) enthalpy, kJ/kg
\( p \) pressure, bar
\( T(t) \) temperature, K (ºC)
\( \gamma \) exergy destruction ratio, %
\( n \) number of components

Greek symbols
\( \Delta \) difference
\( \eta \) energy efficiency
\( \varepsilon \) exergy efficiency
\( \gamma \) ratio
\( \alpha \) air/fuel ratio

Superscripts
\( p \) pinch point
\( rh \) reheated steam
\( s \) isentropic
\( T \) theoretical
\( tot \) overall system

Subscripts
0 thermodynamic environment
c combustion
D destruction
d drainage
ex exhaust
F fuel
k kth component
L loss
sh superheated steam
m mechanical
P product

Abbreviations
AH air preheater
BO boiler
COND condenser
CP condensate pump
DA deaerator
FP feedwater pump
GE generator
H heater
HPT high-pressure stage group
IPT intermediate-pressure group
LHV lower heating value
LPT low-pressure group
ST secondary turbine
References

Energy and exergy analyses of charging process in Encapsulated Ice Thermal Energy Storage systems

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Abstract:
Encapsulated ice Thermal Energy Storage (TES) is an effective means to conserve energy and costs for warmer climates. In this strategy, water is encased in a capsule and placed in a large storage tank. During off-peak hours, a vapor compression refrigeration cycle is used to chill the brine solution for freezing the encapsulated water. During peak hours, this ice is used as a heat sink for space cooling purposes, and can save considerable amounts of money, as well as help lower peak electricity demand. In this paper, we numerically investigate the solidification process of a capsule in the storage tank. Using FLUENT software, we simulate the freezing process and evaluate system performance based on inlet Heat Transfer Fluid (HTF) temperature and flow rate, as well as capsule geometry. In all, 105 test cases are compared; seven capsule shapes, five inlet HTF temperatures and three inlet HTF flow rates. The results were assessed thermodynamically in terms of energy efficiency, exergy efficiency and entropy generation. It is found that the energy efficiencies are not indicative of overall system performance, since in all cases they are found to be above 99.96%, as viscous dissipation is the only mode of loss. However, exergy efficiencies range from 78% to 92% and provide much better insight into system performance. It is found that the most effective way to increase efficiency of the solidification process is to increase inlet HTF temperature to closer to that of the freezing point of water. This is due to the fact that surprisingly, viscous dissipation has very little effect on entropy generation, and hence, exergy efficiency, when compared to other modes of losses. As a result, the actual capsule geometry is relatively inconsequential to system performance. These findings indicate that encapsulated ice TES designers could increase flow rates considerably during charging processes and as a result realize energy and cost savings.

Keywords:

1. Introduction
With urban population density increasing in many temperate, tropical and subtropical cities, the demand for space heating and cooling increases along with it. There are many strategies which deal with increasing building efficiency, for example Combined Heat and Power (CHP) and Combined Cooling, Heat and Power (CCHP) scenarios, each with its own set of challenges. However, for the vast majority of cases, producing power on-site is not an option, so many opt for Thermal Energy Storage (TES) system in order to alleviate costs associated with space cooling on a daily basis.

One of the main advantages of TES for cooling purposes is its ability to help better match power supply with demand. This is done through loading the chiller to produce a cold storage during low demand (night) ties, which can be used during high demand (day) times. This helps not only to reduce operational costs, but it reduces peak electricity usage on the local grid, ultimately helping to lower Green House Gas (GHG) emissions.

There are many types of cold TES forms, and all fall into either latent or sensible storage. Although sensible cold TES storage is receiving interest as of late, for example in chilled water systems, latent systems are becoming more popular due to the high specific latent energy stored in water. Though many types of ice storage systems are popular, most fall under either the ice-on-coil [1-3] or encapsulated ice [4-7] types.
Encapsulated ice systems utilize a latent medium (de-ionized water) which is contained within a capsule, usually made of plastic. Such capsules are placed in a storage tank, and a Heat Transfer Fluid (HTF) is used to transfer heat to and from the thermal storage tank. Advantages of this type of system are that it is usually less costly, due to the mass production of capsules (for example, [8]), and is easier to operate and maintain.

Concerning encapsulated ice TES systems, very few studies have been performed to investigate the efficiency of such systems according to capsule geometry and/or Heat Transfer Fluid (HTF) characteristics. The authors have completed a number of investigations (for example [9-12]) investigating thermodynamic performance of encapsulated ice TES systems. In particular, the authors investigated in [12] a cold TES discharging process in which other geometries besides spheres [8] are considered. This study is a continuation of the aforementioned work, and is concerned with the charging process. There are very few works which investigate such a process – none which numerically investigate the charging (freezing) process while taking into consideration geometrical and HTF properties. In this paper, we vary the inlet HTF temperature and flow rate, capsule geometry (rectangular, spherical and cylindrical) in order to determine what effects they have on overall energy and exergy efficiency.

2. Mathematical Modeling

This study is concerned with numerical simulation of the charging (freezing) process of a capsule filled with de-ionized water, by using thermodynamic relations. In order to facilitate this, we use Fluent 6.3 software to obtain the required data for thermodynamic post-processing. However, before continuing with the mathematical modelling inherent in Fluent software, we make known the assumptions used as follows:

- Capsules will have a wall thickness of 5mm and inner volume 268ml.
- HTF and Phase Change Material (PCM) will have piecewise constant thermo physical properties.
- Heat penetration from storage tank wall is negligible.
- Density change during solidification is negligible.

Since this is a continuation from the study in [12], material properties will then be identical, and are shown in Table 1. The PCM is assumed to be water, the HTF to be ethylene glycol (30% by mass) [13], and the capsule is assumed to be polyvinyl chloride (PVC).

<table>
<thead>
<tr>
<th>Material</th>
<th>( \rho ) [kg/m(^3)]</th>
<th>( C ) [kJ/kg·K]</th>
<th>( \mu ) [kPa·s]</th>
<th>( k ) [W/m·K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capsule</td>
<td>1380</td>
<td>9.00</td>
<td>N/A</td>
<td>0.160</td>
</tr>
<tr>
<td>PCM (solid)</td>
<td>917.4</td>
<td>2.11</td>
<td>N/A</td>
<td>2.108</td>
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<tr>
<td>HTF</td>
<td>1053</td>
<td>3.57</td>
<td>5.03</td>
<td>0.422</td>
</tr>
<tr>
<td>PCM (liquid)</td>
<td>1000</td>
<td>4.20</td>
<td>1.52</td>
<td>0.558</td>
</tr>
</tbody>
</table>

2.1. Heat Transfer and Fluid Flow

In order to facilitate the presentation of equations, Figure 1 shows a simplification of the domain in question. The left side shows the basic concept for simulation: here the capsule is immersed in a sub-cooled, flowing HTF, which initiates freezing of the capsule. The right side shows a further simplification by describing the simulation as three domains of interest \( \Omega_i \) and subsequent boundaries \( \Gamma_i \), where \( i = \{1,2,3\} \), in order to facilitate the presentation of governing equations in a Cartesian coordinate system. All simulations are performed in three dimensions using a Cartesian coordinate system. Figure 2 should be consulted for a more detailed view of the geometries simulated.
Figure 1: Simplification of domain description used in this study.

The momentum, continuity and energy equations govern the HTF, occupying $\Omega_1$:

$$\rho \left( \frac{\partial u_i}{\partial t} + u_j \frac{\partial u_i}{\partial x_j} \right) = - \frac{\partial p}{\partial x_i} + \mu \frac{\partial^2 u_i}{\partial x_j^2} \quad \text{in } \Omega_1$$ \hfill (1)

$$\frac{\partial u_i}{\partial x_i} = 0 \quad \text{in } \Omega_1$$ \hfill (2)

$$\rho \frac{Dh}{Dt} = \frac{Dp}{Dt} + k \frac{\partial^2 T}{\partial x_i^2} + \Phi \quad \text{in } \Omega_1$$ \hfill (3)

which uses the material derivative and viscous dissipation function, respectively:

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + u_j \frac{\partial}{\partial x_j}$$ \hfill (4)

$$\Phi = \mu \left[ 2 \left( \frac{\partial u_i}{\partial x_i} \right)^2 + \left( \frac{\partial u_i}{\partial x_2} + \frac{\partial u_2}{\partial x_1} \right)^2 + \left( \frac{\partial u_2}{\partial x_3} + \frac{\partial u_3}{\partial x_2} \right)^2 + \left( \frac{\partial u_3}{\partial x_1} + \frac{\partial u_1}{\partial x_3} \right)^2 \right]$$ \hfill (5)

In the PVC capsule, domain $\Omega_2$, we must solve only the sensible energy equation:

$$\rho \frac{Dh}{Dt} = k \frac{\partial^2 T}{\partial x_i^2} \quad \text{in } \Omega_2$$ \hfill (6)

The PCM domain $\Omega_3$ again uses only the energy equation, but with a slight complication due to latent heat presence:

$$\rho \frac{DH}{Dt} = k \frac{\partial^2 T}{\partial x_i^2} \quad \text{in } \Omega_3$$ \hfill (7)

where $H$ and $h$ are functions of temperature:

$$H(T) = h_o + C(T - T_o) + H_i$$ \hfill (8)

$$h(T) = h_o + C(T - T_o)$$ \hfill (9)
The latent heat term $H_l$ is evaluated according to the process in [14-16], and depends on the liquid fraction $\beta$ of each cell:

$$H_l = \beta L$$  \hspace{1cm} (10)

$\beta$ takes on a value between 0 and 1 (completely solid and completely liquid, respectively).

In order to simulate the computational domain, the boundary value problem needs the necessary boundary and initial conditions. To begin with, all domains are initialized at a temperature $T_{ini}$, where $T_{ini} > T_{sf}$:

$$T(t = 0) = T_{ini} \quad \text{in } \Omega_1, \Omega_2, \Omega_3$$  \hspace{1cm} (11)

Additionally, at the beginning of each simulation, all cells are initialized with zero velocity:

$$u_i(t = 0) = 0 \quad \text{in } \Omega_1, \Omega_2, \Omega_3$$  \hspace{1cm} (12)

As far as boundary conditions are concerned, we have the no-slip boundary between capsule and PCM:

$$u_i = 0 \quad \text{on } \Gamma_2$$  \hspace{1cm} (13)

We also require the temperature and velocity at the inlet, $\Gamma_3$,

$$T = T_{in}, \quad u_i = -Q/An_i \quad \text{on } \Gamma_3$$  \hspace{1cm} (14)

where $n$ is the outward pointing unit normal. At the outlet, $\Gamma_4$, we impose fully developed conditions in both temperature and velocity:

$$\frac{\partial T}{\partial n_i} = \frac{\partial u_1}{\partial n_i} = \frac{\partial u_2}{\partial n_i} = \frac{\partial u_3}{\partial n_i} = 0 \quad \text{on } \Gamma_4$$  \hspace{1cm} (15)

$\Gamma_5$ is included for symmetry purposes, and serves to lessen the computational cost. This boundary is considered a slip boundary condition and is fully developed in the direction of symmetry:

$$\frac{\partial T}{\partial n_i} = 0, \quad u_i \cdot n_i = 0 \quad \text{on } \Gamma_5$$  \hspace{1cm} (16)

2.2. System Thermodynamics

In order to evaluate the performance of the charging processes, we are interested in the energy and exergy efficiencies, as well as entropy generation. Since this study is a continuation of [12] and uses the same thermodynamic evaluation process as in [11], we will omit much of the derivation of the governing thermodynamic equations. It should also be noted that this study omits the thermodynamic treatment of the refrigeration system used to charge the capsules, instead treating only the output of such systems, i.e. the cold HTF, as the only input to the control volume in this analysis.

For the energy efficiencies, we first present the energy balance on our control volume:

$$\Delta E_{sys} = E_{in} - E_{out}$$  \hspace{1cm} (17)

Here, the total change in energy of the system can be accounted for by considering the energy change in material 1, 2 and 3 (corresponding to domains $\Omega_1$, $\Omega_2$ and $\Omega_3$, respectively) and the difference in total energy in and out is accounted for through analysis of the total enthalpy $H$, total volume flow $X$ and average inlet and outlet pressure, $P_{in}$ and $P_{out}$, respectively. Then, as in [11], the energy efficiency is calculated as follows:
\[ \eta = \frac{\Delta E_1 + \Delta E_2 + \Delta E_3}{\Delta E_1 + \Delta E_2 + \Delta E_3 - X(P_{in} - P_{out})} \]  

(18)

where the energy changes in each domain are calculated as follows:

\[ \Delta E_1 = m_1 C_1 (\overline{T}_{f,1} - T_{ini}) \]  

(19)

\[ \Delta E_2 = m_2 C_2 (\overline{T}_{f,2} - T_{ini}) \]  

(20)

\[ \Delta E_3 = m_3 [C_f (T_{sf} - T_{ini}) + C_s (\overline{T}_{f,3} - T_{sf}) - L] \]  

(21)

Here, the subscripts \( fl \) and \( s \) refer to the PCM in liquid and solid states, respectively, and \( sf \) refers to the solidification temperature. Volume weighted average temperatures are recorded and used to evaluate the temperature terms in the above equations, while area weighted average pressures are used to record incoming and outgoing total pressures.

For the exergy efficiencies, we proceed in the same way, by first writing the exergy balance equation:

\[ \Delta \Xi_{sys} = \Xi_{in} - \Xi_{out} - \Xi_d \]  

(22)

\[ \psi = \frac{\Delta \Xi_1 + \Delta \Xi_2 + \Delta \Xi_3}{\Delta \Xi_1 + \Delta \Xi_2 + \Delta \Xi_3 + \Delta \Xi_d} \]  

(23)

where the exergy differences in each domain over the course of the simulation can be calculated as:

\[ \Delta \Xi_1 = m_1 C_1 \left( \overline{T}_{f,1} - T_{ini} - T_o \ln \frac{\overline{T}_{f,1}}{T_{ini}} \right) \]  

(24)

\[ \Delta \Xi_2 = m_2 C_2 \left( \overline{T}_{f,2} - T_{ini} - T_o \ln \frac{\overline{T}_{f,2}}{T_{ini}} \right) \]  

(25)

\[ \Delta \Xi_3 = m_3 \left[ C_f \left( T_{sf} - T_{ini} - T_o \ln \frac{T_{sf}}{T_{ini}} \right) + C_s \left( \overline{T}_{f,3} - T_{sf} - T_o \frac{\overline{T}_{f,3}}{T_{sf}} \right) + L \left( \frac{T_o}{T_{sf}} - 1 \right) \right] \]  

(26)

The destroyed exergy must also be calculated, and is a result of generated entropy as

\[ \Xi_d = T_o S_{gen} \]  

(27)

In order to calculate \( S_{gen} \), we must write the entropy balance equation as

\[ \Delta S_{sys} = \Delta S_1 + \Delta S_2 + \Delta S_3 = S_{in} - S_{out} + S_{gen} \]  

(28)

where the individual components are evaluated as

\[ \Delta S_1 = m_1 C_1 \ln \frac{T_{f,1}}{T_{ini}} \]  

(29)

\[ \Delta S_2 = m_2 C_2 \ln \frac{T_{f,2}}{T_{ini}} \]  

(30)
\[ \Delta S_3 = m_3 \left[ C_\beta \ln \frac{T_{in}}{T_{out}} + C_\gamma \ln \frac{T_{f,3}}{T_{in}} - \frac{L}{T_{in}} \right] \]  

(31)

\[ S_{in} - S_{out} = M C_i \ln \frac{T_{out}}{T_{in}} \]  

(32)

Here, we use the total mass \( M \) of HTF used to charge the capsules, as well as the average outlet temperature. It is interesting to discuss the amount of entropy generated solely as a function of viscous dissipation within the fluid, assuming a bulk temperature as the average HTF temperature within the domain:

\[ S_{gen, diss} = \frac{M (T_{in} - T_{out})}{\rho_b T_b} \]  

(33)

\[ T_b = T_{in} + \frac{\Delta E_{sys}}{2MC_3} \]  

(34)

3. Simulation Description

The present work involved the simulation of seven different geometries, listed in Table 2. All capsules were chosen to have equal inner volume, corresponding to that of geometry “A”. In addition, Table 2 lists only inner dimensions, noting that we use a 5mm capsule shell thickness for the computational geometries.

Table 2: Capsule geometry descriptions (AR denotes Aspect Ratio).

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Type</th>
<th>Aspect Ratio</th>
<th>Inner Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Spherical</td>
<td>N/A</td>
<td>Radius 4.0cm</td>
</tr>
<tr>
<td>B</td>
<td>Slab</td>
<td>2</td>
<td>8.1cm × 8.1cm × 4.1cm</td>
</tr>
<tr>
<td>C</td>
<td>Slab</td>
<td>5</td>
<td>11.0cm × 11.0cm × 2.2cm</td>
</tr>
<tr>
<td>D</td>
<td>Slab</td>
<td>8</td>
<td>12.9cm × 12.9cm × 1.6cm</td>
</tr>
<tr>
<td>E</td>
<td>Cylindrical</td>
<td>2</td>
<td>Radius 2.7cm; length 11.1cm</td>
</tr>
<tr>
<td>F</td>
<td>Cylindrical</td>
<td>5</td>
<td>Radius 2.0cm; length 20.4cm</td>
</tr>
<tr>
<td>G</td>
<td>Cylindrical</td>
<td>8</td>
<td>Radius 1.7cm; length 28.0cm</td>
</tr>
</tbody>
</table>

More discussion is warranted in order to describe the computational domains, since they have not been explicitly defined thus far. In order to save computational costs, only one capsule is simulated in a bed of identical capsules, and the simulation domains are taken similar to that seen in Fig. 2. It should be noted that entrance and far-field effects, model validations, grid size and time step effects have been avoided through the same process described in [12].

Figure 2: Simplification of domains for a) spherical, b) cylindrical and c) rectangular capsule geometries.
In addition to a variable capsule geometry, we also choose three flow rates: $Q_1 = 0.87 \text{ l/s}$, $Q_2 = 1.74 \text{ l/s}$ and $Q_3 = 2.61 \text{ l/s}$, which are chosen to be similar to that experienced by a moderately sized storage tank for encapsulated ice TES. We also vary inlet temperatures from 267K to 271K in increments of 1K, meaning that we perform 105 total simulations to gain insight into what combinations of geometry and HTF characteristics give the best efficiency. As mentioned earlier, the PCM is assumed to be deionized water, with a solidification temperature of $T_{sf} = 273K$, latent heat $L = 334kJ/kg$, and initial temperature of $T_{ini} = 275K$. Residual tolerances for velocity and energy are set to $10^{-3}$ and $10^{-6}$, respectively, and all simulations concluded once a complete solidification of the capsule was reached. The reference temperature is $T_o = 298K$.

4. Results and Discussion

The most important results to discuss are the charging times, energy efficiencies, and exergy efficiencies, accompanied by a discussion of the exergy losses (which are directly related to entropy generation). Firstly, we present the charting times for all simulations as seen in Table 3. When compared across geometries, the fastest geometries to charge/freeze were the cylindrical and rectangular capsules with highest aspect ratios. This is due to the higher surface areas which enhance heat transfer.

Not surprisingly, those simulations conducted with lower HTF temperatures realized lower charging times, and there was a small amount of difference in charging times when compared by HTF flow rate.

Table 3: Charging times (in seconds) for all simulations.

<table>
<thead>
<tr>
<th>Flow Rate [l/s]</th>
<th>$T_{ini}$ [K]</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_3$ [2.61]</td>
<td>267</td>
<td>1035</td>
<td>1264</td>
<td>662</td>
<td>661</td>
<td>1051</td>
<td>728</td>
<td>591</td>
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<td></td>
<td>268</td>
<td>1156</td>
<td>1455</td>
<td>760</td>
<td>760</td>
<td>1189</td>
<td>822</td>
<td>667</td>
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<tr>
<td></td>
<td>269</td>
<td>1326</td>
<td>1729</td>
<td>900</td>
<td>893</td>
<td>1384</td>
<td>957</td>
<td>775</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>1586</td>
<td>2155</td>
<td>1113</td>
<td>1104</td>
<td>1686</td>
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<td>942</td>
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<tr>
<td></td>
<td>271</td>
<td>2045</td>
<td>2877</td>
<td>1472</td>
<td>1469</td>
<td>2214</td>
<td>1522</td>
<td>1231</td>
</tr>
<tr>
<td>$Q_2$ [1.74]</td>
<td>267</td>
<td>1039</td>
<td>1274</td>
<td>668</td>
<td>667</td>
<td>1079</td>
<td>748</td>
<td>608</td>
</tr>
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<td>268</td>
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<td>768</td>
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<td>687</td>
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<td>2278</td>
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<td>681</td>
<td>1130</td>
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<td>1494</td>
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<td>780</td>
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<td>893</td>
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<td>1774</td>
<td>925</td>
<td>919</td>
<td>1493</td>
<td>1041</td>
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<tr>
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<td>1514</td>
<td>2397</td>
<td>1662</td>
<td>1349</td>
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</table>

We next discuss the energy efficiency $\eta$ from (18). From (18), it is apparent that the only losses in the system are a result of viscous dissipation, which results in a lowered pressure at the outlet. It was found that these losses are inconsequential to the energy efficiency, and all energy efficiencies were calculated to be above 99.9%. This solidifies the notion that second law (exergy) efficiency is required in order to properly address the actual performance of the charging process.

These exergy efficiencies are shown in Table 4, and range from 78-92%. The scenarios which achieved the highest exergy efficiencies were those with an inlet HTF temperature closer to that of the solidification temperature. Exergy efficiencies did not appear to vary much across geometry type and even flow rate. This suggests that the temperature of the inlet HTF is the most important factor in charging an encapsulated ice TES storage tank. It also suggests that viscous dissipation, discussed next, does not markedly affect performance of the charging of capsules.
Table 4: Exergy efficiency (in percent) for all case studies

<table>
<thead>
<tr>
<th>Flow Rate [l/s]</th>
<th>$T_{in}$ [K]</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q₃ [2.61]</td>
<td>267</td>
<td>78.98</td>
<td>78.91</td>
<td>79.01</td>
<td>79.01</td>
<td>78.94</td>
<td>78.94</td>
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<td></td>
<td>268</td>
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<td>81.83</td>
<td>81.91</td>
<td>81.91</td>
<td>81.84</td>
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<td>91.91</td>
<td>91.90</td>
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<td>Q₁ [0.87]</td>
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<td>92.14</td>
<td>92.14</td>
<td>92.02</td>
<td>92.10</td>
<td>92.15</td>
</tr>
</tbody>
</table>

In order to properly address the affect of viscous dissipation, we calculate the total entropy generated in each simulation, and compare that with the entropy generated through viscous dissipation. Table 5 gives this information by means of the calculated total percent of generated entropy through viscous dissipation. It is immediately apparent that viscous dissipation, although important in sizing such equipment as pumps and piping, is not detrimental to the charging of capsules.

Table 5: Entropy generated, both total and through viscous dissipation.

<table>
<thead>
<tr>
<th>Flow Rate [l/s]</th>
<th>$T_{in}$ [K]</th>
<th>$S_{gen}$ [J/K]</th>
<th>$S_{gen, diss} / S_{gen} \times 100$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q₃$ [2.61]</td>
<td>267</td>
<td>7.4</td>
<td>7.3 7.3 7.3 7.3 7.4 7.4 0.1 0.0 0.0 0.0 0.2 0.5 0.8</td>
</tr>
<tr>
<td></td>
<td>268</td>
<td>6.1</td>
<td>6.0 6.1 6.1 6.1 6.1 6.1 0.1 0.0 0.0 0.1 0.2 0.6 1.1</td>
</tr>
<tr>
<td></td>
<td>269</td>
<td>4.9</td>
<td>4.8 4.8 4.8 4.8 4.9 4.9 0.2 0.0 0.1 0.1 0.3 0.9 1.6</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>3.6</td>
<td>3.6 3.6 3.6 3.6 3.6 3.7 3.7 0.3 0.1 0.1 0.1 0.5 1.5 2.6</td>
</tr>
<tr>
<td></td>
<td>271</td>
<td>2.4</td>
<td>2.4 2.4 2.4 2.4 2.4 2.5 2.5 0.5 0.1 0.2 0.3 1.0 2.9 5.0</td>
</tr>
<tr>
<td>$Q₂$ [1.74]</td>
<td>267</td>
<td>7.3</td>
<td>7.3 7.3 7.3 7.3 7.3 7.3 0.0 0.0 0.0 0.0 0.1 0.2 0.3</td>
</tr>
<tr>
<td></td>
<td>268</td>
<td>6.1</td>
<td>6.0 6.0 6.0 6.1 6.1 6.0 0.0 0.0 0.0 0.0 0.1 0.3 0.5</td>
</tr>
<tr>
<td></td>
<td>269</td>
<td>4.8</td>
<td>4.8 4.8 4.8 4.8 4.8 4.8 0.1 0.0 0.0 0.0 0.1 0.4 0.7</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>3.6</td>
<td>3.6 3.6 3.6 3.6 3.6 3.6 0.1 0.0 0.0 0.1 0.2 0.6 1.1</td>
</tr>
<tr>
<td></td>
<td>271</td>
<td>2.4</td>
<td>2.4 2.4 2.4 2.4 2.4 2.4 0.2 0.1 0.1 0.1 0.4 1.2 2.1</td>
</tr>
<tr>
<td>$Q₁$ [0.87]</td>
<td>267</td>
<td>7.2</td>
<td>7.2 7.1 7.1 7.2 7.2 7.1 0.0 0.0 0.0 0.0 0.0 0.0 0.1</td>
</tr>
<tr>
<td></td>
<td>268</td>
<td>6.0</td>
<td>5.9 5.9 5.9 6.0 5.9 5.9 0.0 0.0 0.0 0.0 0.0 0.1 0.1</td>
</tr>
<tr>
<td></td>
<td>269</td>
<td>4.8</td>
<td>4.7 4.7 4.7 4.8 4.7 4.7 0.0 0.0 0.0 0.0 0.0 0.1 0.2</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>3.5</td>
<td>3.5 3.5 3.5 3.6 3.5 3.5 0.0 0.0 0.0 0.0 0.0 0.1 0.3</td>
</tr>
<tr>
<td></td>
<td>271</td>
<td>2.4</td>
<td>2.4 2.3 2.3 2.4 2.3 2.3 0.0 0.0 0.0 0.0 0.1 0.3 0.5</td>
</tr>
</tbody>
</table>

To gain a better understanding of the effects that each variable (geometry, inlet HTF temperature and HTF flow rate) has on the exergy efficiency, Figure 3 shows the average $\psi$ holding only one of the three variables constant.
5. Conclusions

The solidification process for an encapsulated ice TES system is investigated herein, using Fluent software. In all, 105 simulations were run, varying capsule geometry, HTF flow rate and HTF temperature. In all cases, the energy efficiency, exergy efficiency and entropy generated were calculated, as well as entropy generated through viscous dissipation.

The first main finding of the study was that the energy efficiency was unrealistically high in all cases. Due to the assumptions used in the study, heat penetration and wall effects from the storage tank walls were ignored, thus the only source of energy loss was due to viscous dissipation. However, when compared to the thermal energy stored in each capsule, these losses were extremely small, and resulted in energy efficiencies of over 99.9% in all cases. For this reason, second law (exergy) efficiencies were sought, in order to gain better insight into the actual performance of the charging process.

Exergy efficiencies were much more reasonable, and varied from 78-92%. It was found that, most interestingly, the variable with the most impact on exergy efficiencies was the inlet HTF temperature, with those temperatures closer to the solidification temperature experiencing the highest efficiency. Another interesting finding was the relatively little effect viscous dissipation had on exergy efficiency, as well as entropy generated. In contrast, during calculation of energy efficiency equation viscous dissipation was the only mode of loss.

The findings illustrate two main points. Firstly, that energy analyses alone are not sufficient in analyzing the performance of cold TES systems. Secondly, the results show that although pressure loss developed in a storage tank is important in terms of equipment sizing, of much more importance is the temperature of the HTF used to charge the tank. In other words, much more thought must be given in order to size the HTF chiller than the method of moving the HTF.

Acknowledgements

The authors acknowledge support from the National Sciences and Engineering Research Council of Canada.

Nomenclature

\[ A \quad \text{Area [m}^2\text{]} \]
\[ C \quad \text{Specific heat [J/kg·K]} \]
E  Energy [J]
H  Enthalpy [J]
h  Specific Enthalpy [J/kg]
k  Thermal conductivity [W/m·K]
L  Latent heat [J/kg]
M  Total Mass [kg]
m  mass [kg]
n  Outward pointing unit normal [m]
P  Average Pressure [Pa]
p  Pressure [Pa]
Q  Flow rate [m³/s]
S  Entropy [J/K]
T  Temperature [K]
t  Time [s]
u  Velocity [m/s]
X  Volume [m³]
x  Spatial Coordinate [m]

Greek symbols
\( \beta \)  Liquid fraction
\( \Gamma \)  Boundary
\( \Delta \)  Change in
\( \eta \)  Energy efficiency
\( \mu \)  Dynamic viscosity [Pa·s]
\( \Xi \)  Exergy [J]
\( \rho \)  Density [kg/m³]
\( \psi \)  Exergy efficiency
\( \Omega \)  Domain

Subscripts and superscripts
\( b \)  bulk
\( f \)  Final
\( fl \)  fluid
\( gen \)  Generated
\( i \)  Dummy index
\( in \)  Inlet
\( ini \)  Initial
\( l \)  Latent
\( o \)  Reference state
\( out \)  Outlet
\( s \)  solid
\( sf \)  Solidification
\( sys \)  system

Acronyms
References


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Abstract:
The nitrogen fertilizers production is an energy intensive industry branch. However, from a thermodynamic point of view, the basic reactions of the nitrogen fertilizers production processes are exothermic and the overall reactions of both process routes (ammonium nitrate and urea production routes) are also exothermic. This means that, if all these reactions could be performed in a thermodynamically ideal way and at the reference conditions, some heat and/or power could be obtained from these reactions, rather than consumed. However, most of the reaction stages are limited by the chemical equilibrium and reaction’s kinetics, which require high pressures and temperatures, hence, big quantities of shaft power and heat (steam) have to be consumed. In modern energy-integrated ammonia and nitric acid plants the heat of the exothermic chemical reactions is used to generate mechanical work (by a steam cycle or/and by a gas turbine cycle) to drive compressors and other machinery. If needed, an extra amount of fuel is burned to satisfy all the requirements of energy in the plant itself and/or in the overall fertilizers production complex. The problem is whether it would be more effective to burn some quantity of fuel to provide a chemical plant with power and/or steam in the energy-integrated chemical plant itself; in an utility boiler or in a CHP plant at the same industrial site.
The goal of this work is to analyse the efficiency of the energy integration in a nitrogen fertilizers production site, including ammonia and nitric acid plants. The main issue is how to distinguish the technological and energy conversion processes in order to estimate their efficiencies separately despite the strong integration of these processes and the complexity of modern energy-integrated chemical plants.
The approach presented in this work is to define a model of the ammonia production process that enables specifying separately the theoretical minimum of energy and feedstock consumption in the chemical process and in the energy conversion processes (especially shaft work generation). Then, using real data for efficiency indices of both groups of processes, the next step is to examine the influence of these indices on the energy (and exergy) consumption and to specify the sets of parameters corresponding to the more efficient kind of plant, energy integrated or non-integrated, respectively. In Part 1 of this work, ammonia production plants are selected as a subject of analysis.

Keywords:
Energy integration, Cogeneration, Ammonia, Efficiency, Environmental impact

1. Introduction

In power industry the Combined Heat and Power (CHP) is defined as a simultaneous generation of usable heat and power (electricity or mechanical energy) in a single process. CHP is also referred to as cogeneration [1].
For many years the CHP generation has been applied predominantly in the chemical industry, petroleum refineries and other large industrial sites. In 2005 about 50% of the steam and hot water demand in EU27 industry was satisfied by CHP [1].
In chemical industry an energy-integrated chemical plant is a well-fitted combination of a chemical and a power plant. The waste heat of the exothermic chemical reactions is used to generate mechanical energy (by a steam cycle or/and by a gas turbine cycle) to drive compressors, pumps, fans, etc. In some cases the term “cogeneration” is also used [2], but only if electricity is produced [3]. The energy-integration concept enables the chemical plants to be energetically self-sufficient and to consume only feedstock and fuel and rather less electricity.

A vigorous growth of cogeneration in the chemical industry began since the first large single-train energy-integrated ammonia plant was put into operation in 1965 [4]. For the last five decades the energy-integrated chemical plants have been commonly used in the bulk chemicals industry. Nearly all modern ammonia, methanol and ethylene plants over the world are energy-integrated [4,5]. The developing of high-pressure (up to 30 MPa) multi-stage centrifugal compressors enabled the use of steam- and gas-turbines to drive all machinery, which in turn enabled designing large capacity plants as single-train units.

However, in some integrated plants the available heat of reactions cannot satisfy all demands and its temperature is relatively low. To solve this problem, in earlier designs an extra amount of fuel was burned in an auxiliary boiler (or in the process furnace itself) to satisfy all the requirements for power and steam in the plant.

The main question that should be answered is whether it would be more effective to burn some quantity of fuel to provide a chemical plant with power and/or steam in the energy-integrated chemical plant itself, in a utility boiler or in a CHP plant at the same industrial site.

In many cases the answer depends mainly on the demand of steam and power in the overall production site, on the export / import opportunities of electric power, etc.

The relative efficiencies of energy-integrated and non-integrated plants depend strongly on the sign of the reaction heat of the main chemical processes. According to this, three kinds of chemical plants could be distinguished:

- main reactions are exothermic, i.e., the plant is an energy source; examples are nitric acid and sulphuric acid plants;
- main reactions are endothermic, i.e., the plant is an energy sink; examples are ethylene plants;
- some of the main reactions are exothermic and some are endothermic; the overall effect is near neutral, examples are ammonia and methanol plants.

The nitrogen fertilizers production is selected as an appropriate subject of analysis, as it includes two different kinds of plants: ammonia and nitric acid production processes, both existing in energy-integrated and non-integrated versions.

The goal of the present work is to analyse the efficiency of the energy integration in a nitrogen fertilizers production site, including production of intermediates: (ammonia and nitric acid) and final product (ammonium nitrate). The subject of the first part of the analysis is the energy integration in ammonia production plants.

The exergy method [8] is used in both parts of this work in order to compare the efficiency of energy-integrated and non-integrated ammonia and nitric acid plants, as well as to estimate the overall efficiency of a whole nitrogen fertilizers production site.

In some previous works [9-11] we have compared the efficiencies of energy integrated and non-integrated ammonia plants [9] and nitric acid plants [10] using some Second Law-based (exergy and cumulative exergy) indices and operational data from real plants. The results showed that non-integrated ammonia plants are definitely more efficient than energy integrated; the results for nitric acid plants are opposite. A generalized conclusion was made that the energy integration is more advantageous in the case when the efficiency of the energy conversion process (shaft work generation) is higher than the efficiency of the chemical process and vice versa. However, these results could be questionable to some extent because they were obtained by processing data for similar, but yet different plants, and the difference of some of the process parameters in the compared plants might have an effect on these results. The considerable recent achievements both in chemical technology and in energy conversion processes and machinery, which undoubtedly influence the efficiency of the energy integration, also motivated the present study.
The main problem is how to distinguish the technological and energy conversion processes in order to estimate their efficiencies separately despite the strong integration of these processes and the complexity of modern energy-integrated chemical plants. Hence, we need to define a model of the ammonia production process that enables specifying separately the theoretical minimum of energy and feedstock consumption in the chemical process and in the energy conversion processes (especially shaft work generation). Then, using real data about heat and exergy losses and efficiency indices of both groups of processes, the next step is to examine the influence of these indices on the energy and exergy consumption and to specify the sets of parameters corresponding to the more efficient kind of plant, energy integrated or non-integrated, respectively.

2. Ammonia production background: basic reactions and heat effects

The commercial manufacture of ammonia since its beginning in 1913 is based on the catalytic synthesis of ammonia from a highly purified mixture of hydrogen and nitrogen. Although the synthesis of ammonia is an exothermic reaction, to obtain this mixture, especially hydrogen, a lot of energy is necessary to split a molecule of water, which is the main hydrogen-containing source. If a part of the hydrogen is supplied by another hydrogen-containing feedstock, like hydrocarbons, energy requirements are lower. Thus the most favourable feedstock for ammonia production is the natural gas (CH₄) because in this case only a half of the hydrogen is obtained from water. However, the hydrogen production from hydrocarbons and water is a strongly endothermic process, hence a considerable amount of high temperature heat is necessary to be introduced into the process, usually obtained by burning of some quantity of fuel with air.

The combination of both steam reforming and burning processes enables to obtain the hydrogen-nitrogen mixture directly, avoiding the air separation as a preliminary step. Thus the two-step steam and air reforming of hydrocarbons became the best industrial process of the hydrogen-nitrogen mixture preparing for more than 60 years [4,5].

Assuming approximately the oxygen and nitrogen content in air as 20% and 80% respectively, the following basic reactions of ammonia production from natural gas (CH₄) could be written:

\[
\begin{align*}
3/8 \text{CH}_4(g) + 3/8 \text{H}_2\text{O}(g) &= 3/8 \text{CO}(g) + 9/8 \text{H}_2(g) - 77.3 \text{kJ} \quad (1) \\
3/8 \text{CO}(g) + 3/8 \text{H}_2\text{O}(g) &= 3/8 \text{CO}_2(g) + 3/8 \text{H}_2(g) + 15.5 \text{kJ} \quad (2) \\
1/8 \text{O}_2 + 4/8 \text{N}_2 + 1/16 \text{CO}_2 &= 1/16 \text{H}_2\text{O} + 4/8 \text{H}_2\text{O} + 50.1 \text{kJ} \quad (3) \\
12/8 \text{H}_2 + 4/8 \text{N}_2 &= \text{NH}_3 + 46.2 \text{kJ} \quad (4)
\end{align*}
\]

Summarising reactions (1), (2), (3) and (4), the total ammonia production process could be expressed by the formal reaction:

\[
3.5/8 \text{CH}_4(g) + 5/8 \text{H}_2\text{O}(g) + 1/8 \text{O}_2 + 4/8 \text{N}_2 = \text{NH}_3(g) + 3.5/8 \text{CO}_2(g) + 34.5 \text{kJ} \quad (5)
\]

Thus the overall heat of reactions in ammonia production is slightly positive. But if water enters into the process as a liquid, the overall reaction is near thermally neutral:

\[
3.5/8 \text{CH}_4(g) + 5/8 \text{H}_2\text{O}(l) + 1/8 \text{O}_2 + 4/8 \text{N}_2 = \text{NH}_3(g) + 3.5/8 \text{CO}_2(g) + 6.98 \text{kJ} \quad (6)
\]

The theoretical minimum energy consumption in natural gas-based production of ammonia calculated on the basis of the reactions (1) – (6) is shown in Table 1. No heat losses are included.

3. Energy integration in ammonia plants

3.1. Theoretical and actual minimum energy consumption in ammonia production – the model of the chemical processes, methodology and calculations

As was shown in section 2, the overall heat of reactions of methane-based ammonia production is slightly positive, i.e., a small surplus of heat exists.
However, this is a mere theoretical thermochemical calculation, First Law-based, using the heat quantities only, not the heat potential (exergy).

As it is shown in Table 1, the heat of the exothermic reactions (2) and (4) is released at relatively medium and low temperatures, but the heat consumed by the endothermic reaction (1) must be put into the process at very high temperature, which can be only obtained by burning of some kind of fuel. Thus two separate heat balances must be fitted: a high temperature (HT) heat balance (Table 2) and a balance of the middle- and low-temperature (MT&LT) heat (Table 3).

Table 2 shows that the balance of the high-temperature heat sources and sinks is not fitted. The heat released from the exothermic reaction of methane burning (3) by the process air is not sufficient to supply all the heat necessary for the endothermic steam reforming of methane by reaction (1). Thus an additional quantity of methane must be burnt in order to fit the high temperature heat balance of the process no matter if the released heat is introduced directly or indirectly in the steam reforming process. The problem is where this methane could be burnt without introducing some additional nitrogen into the reaction mixture.

In the commercial ammonia technology, the reaction (1) is partly (up to 50%) going simultaneously with the reaction (3) in an autothermal reactor as a second step (known as “secondary reforming”) of the hydrogen-nitrogen mixture generation process (Fig. 1).

The first step (steam reforming of methane, or “primary reforming”) is carried out in a reactor of heat exchanger type, heated indirectly either by the hot effluent (up to 1000°C) of the second step autothermal reactor or by combustion of natural gas in a “reforming furnace”. The former case is the relatively new design known as “gas-heated-reactor“ or GHR, but the latter is the traditional and still the most common design. In this case the natural gas burned in the reforming furnace, is much more than the theoretical quantity, shown in Table 1, calculated to meet the heat balance of the process. After the radiation heat transfer in the furnace, the remainder flue gas heat is used partly for HP steam generation and superheating and then for preheating of the process flows (natural gas, steam and air) in the convection section.

The advantage of the GHR steam reforming design is the elimination of the furnace and combustion process, but the major problem of the ammonia plants with GHR is how to meet the high temperature heat balance of the reforming and of the overall ammonia production process. Although various designs are approved, the common approach is the rejection of the basic principle of modern ammonia technology to produce ammonia using stoichiometric air quantity, without any form of air separation. The most used approach is to burn the additional methane using surplus of air in the second step autothermal reforming reactor and obtain a non-stoichiometric hydrogen-nitrogen mixture. Then a new problem arises how to remove the surplus nitrogen from the mixture. The alternative is to add some oxygen to the air, but the air separation is a highly energy intensive process.

As it is clear from Table 2, the theoretical minimum of energy consumption for the process itself (represented by LHV of methane) is 22.2 GJ/t NH₃, corresponding to 620 Nm³ CH₄/t NH₃. Not all real stages of the modern ammonia technology are included in this model. Nevertheless, reactions (1) – (6) are quite enough to present the ammonia production process. The methanation reactions of CO and CO₂ are combinations of the reverse steam reforming (1) and CO conversion (3) reactions, hence they are included in the model indirectly. The average methane concentration in the make-up hydrogen-nitrogen mixture is 0.6-0.8%, corresponding to about 4% of the methane feedstock entering the steam reforming. As all this methane is recovered and returns back to the reforming furnace, but as a fuel, the overall heat balance (Table 1) remains unchanged and the total methane consumption is nearly the same, only its distribution between feedstock and fuel is slightly changed. Really, the total methane consumption is slightly higher, as the high temperature heat balance requires 4% more heat to be put into the reforming furnace; simultaneously the methanation reactions (250-300°C) increase the heat supply into the medium and low temperature heat balance.

Another process, included indirectly in the model, is the CO₂ removal, which is an energy consuming process. The theoretical minimum separation energy consumption depends on the
concentrations of the components only. Thus, the theoretical (isothermal) work consumption for the separation of an ideal mixture of CO\textsubscript{2} and hydrogen/nitrogen mixture (known as synthesis or make-up gas), based on the stoichiometric concentrations of the products of the reactions (1), (2) and (3), is included in the theoretical heat and work balance of the ammonia production, shown in Table 1.

The real energy consumption in separation processes is much higher than the theoretical work consumption. However, the exergy consumption is not so high, because in the most used CO\textsubscript{2} separation processes the energy input is as medium or low temperature heat. The actual heat consumption for CO\textsubscript{2} separation in ammonia plants dropped dramatically in the last 30 years from about 5000 kJ/Nm\textsuperscript{3} to about 1200 -1400 kJ/Nm\textsuperscript{3}CO\textsubscript{2}.

**Table 1. Overall balance of exothermic and endothermic heat of reactions in ammonia production**

<table>
<thead>
<tr>
<th>Production process</th>
<th>Standard heat of reaction ((-\Delta H, 25^\circ\text{C}, 101325 \text{ Pa}))</th>
<th>CH\textsubscript{4} consumed</th>
<th>Average reaction temperature, °C</th>
<th>Exergy of heat (\text{GJ}/t \text{NH}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ/mol product of reaction</td>
<td>kJ/mol NH\textsubscript{3}</td>
<td>GJ/t NH\textsubscript{3} (LHV)</td>
<td>GJ/t NH\textsubscript{3}</td>
</tr>
<tr>
<td>Exothermic reactions – available heat</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water gas shift reaction (2)</td>
<td>41.17</td>
<td>15.44</td>
<td>0.907</td>
<td>-</td>
</tr>
<tr>
<td>Methane burning reaction (3)</td>
<td>802.34</td>
<td>50.15</td>
<td>2.945</td>
<td>2.945</td>
</tr>
<tr>
<td>Ammonia synthesis reaction (4)</td>
<td>46.19</td>
<td>46.19</td>
<td>2.712</td>
<td>-</td>
</tr>
<tr>
<td>Total heat from exothermic reactions</td>
<td>-</td>
<td>111.78</td>
<td>6.564</td>
<td>2.945</td>
</tr>
<tr>
<td>Endothermic reactions – consumed heat</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam reforming of methane</td>
<td>206.10</td>
<td>77.29</td>
<td>4.539</td>
<td>-</td>
</tr>
<tr>
<td>Water (stoichiometric) evaporation heat</td>
<td>44.01</td>
<td>27.51</td>
<td>1.615</td>
<td>-</td>
</tr>
<tr>
<td>Total heat for endothermic processes</td>
<td>-</td>
<td>104.80</td>
<td>6.154</td>
<td>-</td>
</tr>
<tr>
<td>Theoretical work consumption for CO\textsubscript{2} removal from H\textsubscript{2}/N\textsubscript{2} mixture</td>
<td>-</td>
<td>2.84</td>
<td>0.167</td>
<td>-</td>
</tr>
<tr>
<td>Total heat and work consumption</td>
<td>-</td>
<td>107.64</td>
<td>6.321</td>
<td>-</td>
</tr>
<tr>
<td>Surplus total</td>
<td>-</td>
<td>4.14</td>
<td>0.243</td>
<td>-</td>
</tr>
<tr>
<td>Methane consumption as feedstock in steam reforming by reaction (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total theoretical minimum methane consumption (feedstock and fuel)</td>
<td>20.612</td>
<td>575.5</td>
<td>21.690*</td>
<td></td>
</tr>
</tbody>
</table>

*Exergy of consumed CH\textsubscript{4}(25^\circ\text{C}, 3.0 MPa)*

**Table 2. Theoretical high temperature (>8000°C) heat balance: available and consumed heat of reactions**

<table>
<thead>
<tr>
<th>Production process</th>
<th>Standard heat of reaction ((-\Delta H, 25^\circ\text{C}, 101325 \text{ Pa}))</th>
<th>CH\textsubscript{4} consumed</th>
<th>Average reaction temperature, °C</th>
<th>Exergy of heat (\text{GJ}/t \text{NH}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ/mol product of reaction</td>
<td>kJ/mol NH\textsubscript{3}</td>
<td>GJ/t NH\textsubscript{3} (LHV)</td>
<td>GJ/t NH\textsubscript{3}</td>
</tr>
<tr>
<td>Endothermic reactions – consumed heat</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam reforming of methane</td>
<td>206.10</td>
<td>77.29</td>
<td>4.539</td>
<td>-</td>
</tr>
<tr>
<td>Methane burning by reaction (3)</td>
<td>802.34</td>
<td>50.15</td>
<td>2.945</td>
<td>2.945</td>
</tr>
<tr>
<td>Heat supply by additional methane burning</td>
<td>802.34</td>
<td>27.14</td>
<td>1.594</td>
<td>1.594</td>
</tr>
<tr>
<td>Total heat supply by methane burning</td>
<td>802.34</td>
<td>77.29</td>
<td>4.539</td>
<td>4.539</td>
</tr>
<tr>
<td>Surplus total</td>
<td>-</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>Methane consumption as feedstock in steam reforming by reaction (1)</td>
<td>17.667</td>
<td>493.3</td>
<td>18.595*</td>
<td></td>
</tr>
<tr>
<td>Total theoretical minimum methane consumption (feedstock and fuel)</td>
<td>22.206</td>
<td>620.0</td>
<td>23.367*</td>
<td></td>
</tr>
</tbody>
</table>

*Exergy of consumed CH\textsubscript{4}(25^\circ\text{C}, 3.0 MPa)*
Fig. 1. Flowsheet of an energy integrated ammonia production plant

Table 3. Medium and low temperature (MT&LT) heat balance: available and consumed heat

<table>
<thead>
<tr>
<th>Production process</th>
<th>Standard heat of reaction (-ΔH, 25°C, 101325 Pa)</th>
<th>CH₄ consumed</th>
<th>Average reaction temperature, °C</th>
<th>Exergy of heat GJ/t NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ/mol product of reaction</td>
<td>kJ/mol</td>
<td>GJ/t NH₃</td>
<td>GJ/t NH₃ (LHV)</td>
</tr>
<tr>
<td>MT&amp;LT heat consumption in process steam generation for reactions:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stoichiometric for reactions (1) and (2)</td>
<td>44.01</td>
<td>27.51</td>
<td>1.615</td>
<td>-</td>
</tr>
<tr>
<td>Excess steam (over stoichiometric)</td>
<td>44.01</td>
<td>16.50</td>
<td>0.969</td>
<td>-</td>
</tr>
<tr>
<td>Total for process steam generation</td>
<td>-</td>
<td>44.02</td>
<td>2.588</td>
<td>-</td>
</tr>
<tr>
<td>Minimum actual MT&amp;LT heat consumption for CO₂ removal from H₂/N₂ mixture</td>
<td>-</td>
<td>12.24</td>
<td>0.719</td>
<td>-</td>
</tr>
<tr>
<td>Total MT&amp;LT heat consumption</td>
<td>-</td>
<td>56.25</td>
<td>3.307</td>
<td>-</td>
</tr>
<tr>
<td>Heat losses 10% from heat supply</td>
<td>-</td>
<td>7.81</td>
<td>0.459</td>
<td>-</td>
</tr>
<tr>
<td>Total actual MT&amp;LT heat consumption</td>
<td>-</td>
<td>64.06</td>
<td>3.766</td>
<td>-</td>
</tr>
<tr>
<td>Exothermic reactions – available heat</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water gas shift reaction (2)</td>
<td>41.17</td>
<td>15.44</td>
<td>0.907</td>
<td>-</td>
</tr>
<tr>
<td>Ammonia synthesis reaction (4)</td>
<td>46.19</td>
<td>46.19</td>
<td>2.712</td>
<td>-</td>
</tr>
<tr>
<td>Total MT&amp;LT heat supply from exothermic reactions</td>
<td>-</td>
<td>61.63</td>
<td>3.619</td>
<td>-</td>
</tr>
<tr>
<td>Excess steam condensation heat</td>
<td>-</td>
<td>16.50</td>
<td>0.969</td>
<td>-</td>
</tr>
<tr>
<td>Total MT&amp;LT heat supply</td>
<td>-</td>
<td>78.13</td>
<td>4.588</td>
<td>-</td>
</tr>
<tr>
<td>MT&amp;LT heat surplus for export steam generation</td>
<td>-</td>
<td>14.07</td>
<td>0.822</td>
<td>-</td>
</tr>
</tbody>
</table>

Thus, in Table 3 the value 1250 kJ/Nm³CO₂ is used, as typical in modern low energy ammonia plants [4]. The preferable temperature range of the heat sources is rather narrow for many reasons,
typically 170-140°C, hence, the heat available from the excess steam condensation and other low temperature sources is used mainly for this purpose.

In the real reforming process not liquid water, but steam is used as a reagent in reactions (1) and (2). Thus some heat is necessary to evaporate the water and this heat must be included in the balance [4]. Moreover, the steam reforming of methane by reactions (1) and (2) requires some surplus of steam above the stoichiometric ratio in order to obtain higher methane and CO conversion and to prevent carbon formation [4,5]. A 50 to 100% surplus is commonly used with a trend towards the minimum of 50% surplus in new plants. Thus, the total heat necessary for the water evaporation is about 2.6 GJ/t NH₃. A part of the available middle- and low-temperature heat from reactions (2) and (4) is consumed to evaporate the water for the process (Table 3). Indeed, the heat consumed for the evaporation of the overstoichiometric water is recovered back as the excess steam is condensed in the next stages of the process. But the exergy of this heat is much lower, because the condensation proceeds at gradually decreasing temperature from about 170°C down to ambient temperature and this heat can’t be entirely used.

It is clear that some heat losses are present in all thermal processes. In the most common design, the heat of the flue gas released into the atmosphere from the convection section of the reforming furnace, is the major source of the losses; in the newest GHR design these losses are eliminated. Some heat losses through the insulation and in the end coolers are unavoidable. The industrial practice shows that, depending on the design, the heat losses in modern ammonia plants are in the interval 10-15%, i.e., a thermal efficiency 85-90% could be reasonable. Assuming a minimum heat losses value equal to 10% of the exothermic reactions heat, this means that 10% more methane has to be burnt to close the high temperature heat balance.

Thus, the **actual minimum energy consumption for the ammonia process itself could be estimated as 22.7 GJ/t NH₃**, corresponding to 634 Nm³ CH₄/t NH₃, including the minimum feedstock (17.7 GJ/t) and fuel (5.0 GJ/t) consumption, respectively (Table 4).

### Table 4. Actual high temperature (>800°C) heat balance: available and consumed heat of reactions

<table>
<thead>
<tr>
<th>Production process</th>
<th>Standard heat of reaction (−ΔH, 25°C, 101325 Pa)</th>
<th>CH₄ consumed</th>
<th>Average reaction temperature, °C</th>
<th>Exergy of heat CH₄ consumed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ/mol product of reaction</td>
<td>kJ/mol NH₃</td>
<td>GJ/t NH₃</td>
<td>Nm³/t NH₃</td>
</tr>
<tr>
<td><strong>Endothermic reactions – consumed heat</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam reforming of methane by reaction (1)</td>
<td>206.10</td>
<td>77.29</td>
<td>4.539</td>
<td>-</td>
</tr>
<tr>
<td>Heat losses 10% from heat supply</td>
<td>-</td>
<td>8.59</td>
<td>0.504</td>
<td>-</td>
</tr>
<tr>
<td><strong>Total high temperature heat consumption</strong></td>
<td>-</td>
<td>85.88</td>
<td>5.043</td>
<td>-</td>
</tr>
<tr>
<td><strong>Exothermic reactions – available heat</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High temperature heat available</td>
<td>802.34</td>
<td>50.15</td>
<td>2.945</td>
<td>2.945</td>
</tr>
<tr>
<td>Heat supply by additional methane burning</td>
<td>802.34</td>
<td>27.14</td>
<td>2.098</td>
<td>2.098</td>
</tr>
<tr>
<td><strong>Total heat supply by methane burning</strong></td>
<td>802.34</td>
<td>77.29</td>
<td>5.043</td>
<td>5.043</td>
</tr>
<tr>
<td>Surplus total</td>
<td>-</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>Methane consumption as feedstock in steam reforming by reaction (1)</td>
<td>17.667</td>
<td>493.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Total minimum methane consumption (feedstock and fuel)</strong></td>
<td>22.710</td>
<td>634.1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Exergy of consumed CH₄ (25°C, 3.0 MPa)

Note: In most ammonia plants, the typical **real methane consumption**, marked as **feedstock only**, is very close to the value 22.7 GJ/t [4]. Indeed, this value includes, except the methane, converted by reaction (1), also the methane burned in the secondary air reforming by reaction (3).
3.2. Theoretical and actual energy consumption for shaft work generation in ammonia production plants

In some references, values about 22 GJ/t are specified as the practical minimum methane consumption for ammonia production, in contrast to the value 17 GJ/t (LHV of ammonia), marked as a theoretical minimum [4].

However, the theoretical (22.2 GJ/t) and practical (22.7 GJ/t) minimum energy consumption values, shown in Tables (2) and (4), include the methane consumed in reactions (1) – (6), if they are performed at atmospheric pressure. Energy for the reagents compression is not taken into account.

As the ammonia synthesis equilibrium is unfavourable at low pressure and the degree of conversion of the hydrogen-nitrogen mixture to ammonia is low even at high pressures, significant additional energy is required to compress the hydrogen-nitrogen mixture (synthesis gas) to high pressure (8 – 30 MPa), to drive the recirculation compressor and also to remove ammonia from the unreacted gaseous mixture.

Thus, the value 22.7 GJ/t can’t be seen as a practical minimum energy consumption measure.

In the old non-integrated and multiple-trains ammonia plants, designed before 1965, electric motors were used to drive the reciprocating compressors used at the time. In most modern single-train energy integrated ammonia plants, both make-up synthesis gas and air compressors are driven by steam turbines. In plants designed in the 60-ties and 70-ties nearly all pumps and fans are also turbine – driven. The complicated HP (10 – 14 MPa) steam generation system is precisely fitted to the chemical processes in order to use most effectively the heat of all reactions. However, as the reactions heat is not sufficient, significant quantities of fuel were burned in these plants for HP steam generation and superheating.

The fuel consumption depends strongly on the compressors and turbines efficiency (Table 5, Figure 2). As the efficiency of the first generation high pressure 3 or 4 cases centrifugal compressors was rather low, the steam and, accordingly, the fuel consumption, were rather high. In these plants about 2/3 of the natural gas was used as feedstock and 1/3 and even more – as fuel. Auxiliary boilers were included in ammonia plants in order to generate huge quantities of HP steam, about 5 to 7 times the produced ammonia and the total natural gas consumption was about 40 GJ/t ammonia. Ammonia plants from that epoch are facetiously described amongst professionals as “a steam power plant, which produces also some ammonia as a by-product” [4].

After 1973, the growing energy prices pressure stimulated the energy saving in ammonia plants in the next 20 years, mainly by reduction of the fuel burning, having as a result a total energy consumption drop down to 28 – 29 GJ/t.

Besides the substantially improving of the technological processes, some return back to the electric motors, especially for driving pumps and fans, contributed slightly to the energy saving, due to the low efficiency of small steam turbines. However, in most modern plants both compressors are still driven by steam turbines. Various options were tested in last 20 years: to drive the air compressor by a gas turbine or the make-up syngas compressor by an electric motor. Some attempts are made to integrate ammonia and CHP power plants in the same site by shifting the superheating the HP steam (generated in the ammonia plant) to the CHP plant.

However, last year’s industrial experience shows no substantial advantages for any of these versions. It is clear, that the situation is changing over the years due to the improving of the compressors, turbines, as well as the electricity generation in power plants (Fig. 2). Thus the minimum energy consumption point is gradually shifting across the parameters space roaming between electrical motors and steam turbines driving (Fig. 2 - 4).

The steam generation system structure and the basic steam system parameters of all single-train ammonia plants are nearly the same: HP steam 10-14 MPa, superheated to 510 ± 20°C; MP steam extraction for process at 4-4.5 MPa [4].

Hence, specifying a set of basic parameters of the technological process, it is possible to calculate the minimum value of total feedstock and energy (heat and shaft work) consumption, then to add
the values of the heat and/or exergy losses and thus to approximate step by step the real consumption values. As a result we obtain the real values of the shaft work, necessary to drive the production process and the primary energy (methane) consumed for the shaft work generation. Then the dependence of the methane consumption for shaft work generation on the basic parameters can be examined and compared with the fuel consumption in a power plant. The goal of the comparison is to specify the set of parameters where the steam turbine drivers are more preferable than electric motors and vice versa.

To estimate a minimum of the shaft work needed for an ammonia production plant, at least two major gas compression processes have to be taken into consideration: compression of the process air from atmospheric pressure to the pressure in the reforming process, which is about 3.0 MPa, and compression of the purified hydrogen-nitrogen gaseous mixture (make-up gas) from the reforming pressure to the ammonia synthesis pressure, which in modern plants is specified in a rather wide interval. The lowest value, used in commercial designs, is 8.0 MPa, the highest about 30.0 MPa, but the most used in modern designs are synthesis pressures between 12 to 22 MPa, which represent a flat optimum of total energy consumption [12]. To explain the existence of this optimum, two other compression processes have also to be considered: the circulation (recycle) compressor, and the refrigeration compressor, both related to the ammonia synthesis section of the plant. The shaft work consumption for refrigeration and circulation is much lower than for the make-up gas compression and depends conversely on the synthesis pressure. Thus the sum of the shaft work consumption of the three compressors is nearly constant in the optimum pressures interval [12].

At the upper limit of this interval, the work, consumed by the circulation and refrigeration compressors, is rather low and only shaft work consumed by the make-up gas and air compressors could be included in the model.

### Table 5. Shaft work consumption in ammonia production plants

<table>
<thead>
<tr>
<th>Process</th>
<th>Shaft work</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Theoretical shaft work (isothermal)</strong> for driving:</td>
<td></td>
</tr>
<tr>
<td>• H₂/N₂ compressor 3–20 MPa</td>
<td>0.553 153.6</td>
</tr>
<tr>
<td>• Air compressor 0.1-3 MPa</td>
<td>0.309 85.8</td>
</tr>
<tr>
<td>• Ammonia synthesis recycle compressor 19-20 MPa</td>
<td>0.076 21.1</td>
</tr>
<tr>
<td><strong>Total theoretical shaft work generated in steam turbines</strong></td>
<td>0.938 260.5</td>
</tr>
<tr>
<td>• Refrigeration compressor</td>
<td>0.030 8.3</td>
</tr>
<tr>
<td>• Others (BFW pump, CO₂ removal solution pumps, fans, etc.)</td>
<td>0.070 19.5</td>
</tr>
<tr>
<td><strong>Total theoretical shaft work (isothermal)</strong></td>
<td>1.038 288.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process</th>
<th>Shaft work</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Minimum actual shaft work (η_{th} = 0.7) for driving:</strong></td>
<td></td>
</tr>
<tr>
<td>• H₂/N₂ compressor 3–20 MPa</td>
<td>0.789 219.4</td>
</tr>
<tr>
<td>• Air compressor 0.1-3 MPa</td>
<td>0.442 122.6</td>
</tr>
<tr>
<td>• Ammonia synthesis circulation compressor 19-20 MPa</td>
<td>0.109 30.3</td>
</tr>
<tr>
<td><strong>Total minimum actual shaft work generated in steam turbines</strong></td>
<td>1.340 372.3</td>
</tr>
<tr>
<td>• Refrigeration compressor</td>
<td>0.043 11.9</td>
</tr>
<tr>
<td>• Others (BFW pump, CO₂ removal solution pumps, fans, etc.)</td>
<td>0.100 27.8</td>
</tr>
<tr>
<td><strong>Total minimum actual shaft work consumed</strong></td>
<td>1.483 412.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process</th>
<th>Shaft work</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Maximum actual shaft work (η_{th} = 0.4) for driving:</strong></td>
<td></td>
</tr>
<tr>
<td>• H₂/N₂ compressor 3–20 MPa</td>
<td>1.383 384.2</td>
</tr>
<tr>
<td>• Air compressor 0.1-3 MPa</td>
<td>0.772 214.4</td>
</tr>
<tr>
<td>• Ammonia synthesis circulation compressor 19-20 MPa</td>
<td>0.190 52.8</td>
</tr>
<tr>
<td><strong>Total maximum actual shaft work generated in steam turbines</strong></td>
<td>2.345 651.3</td>
</tr>
<tr>
<td>• Refrigeration compressor</td>
<td>0.075 20.8</td>
</tr>
<tr>
<td>• Others (BFW pump, CO₂ removal solution pumps, fans, etc.)</td>
<td>0.175 48.6</td>
</tr>
<tr>
<td><strong>Total maximum actual shaft work consumed</strong></td>
<td>2.595 720.8</td>
</tr>
</tbody>
</table>
Fig. 2. Dependence of the fuel consumption for shaft work generation on the efficiency of the main compressors in ammonia plants and energy efficiency of power plants (PP). 1-6 - compressors driven by electric motors; 7-8 – compressors driven by steam turbines (ST), steam generated in ammonia plant.

However, in all energy integrated modern ammonia plants, the circulation and make-up gas compressors are fitted together and driven by a joint driver (steam turbine). The air compressor is driven also by a steam turbine. The refrigeration compressor and other machinery (pumps, fans, etc.) could be driven by small steam turbines or by electric motors. In most modern plants electric motors are preferable as drivers of small machines, due to the relatively low efficiency of small steam turbines. So, in this work the main three compressors are assumed to be driven by steam turbines, other machinery – by electric motors.

The isothermal shaft work values shown in Table 5, represent the theoretical minimum work necessary to run the ammonia synthesis reaction at 20 MPa. In order to have actual values, the efficiency of the compressors should be known. In Tables 5 and 8 two examples are shown, representing the minimum and maximum actual shaft work consumed by the compressors at boundary values of the isothermal efficiency (0.7 and 0.4, respectively). For the first example, the heat balances and overall methane consumption in ammonia plants with steam-turbines driven and with electric motors-driven main compressors are shown in Tables 6 and 7, respectively.

A comparison of the fuel (methane) consumption for shaft work generation in ammonia plants (without and with heat losses in the steam system) and in power plants (First Law efficiencies from 0.28 to 0.38) at isothermal efficiencies of the main compressors from 0.4 to 0.7, is shown in Figure 2. The dependence of the fuel (methane) consumption for shaft work generation on the efficiency of the compressors in ammonia plants and energy efficiency of power plants is shown in Figure 3. The
Figure 4 presents the influence of the heat losses in the steam generation system of ammonia plants over the fuel (methane) consumption for shaft work generation.

The results show that the fuel consumption values for the shaft work generation in ammonia and power plants are comparable and depend strongly on the machinery efficiency in ammonia plants and on the energy efficiency of power plants, respectively. Due to the utilization of a part of the available MT&LT heat from the chemical processes in the steam cycle, the fuel consumption for the work generation in ammonia plants is lower than in power plants working at equal steam parameters.

Table 6. Heat and fuel (methane) consumption for shaft work generation in ammonia production
(Main compressors driven by steam turbines)

<table>
<thead>
<tr>
<th>Process</th>
<th>Shaft work to be generated in ammonia plant – main compressors driven by steam turbines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total minimum actual theoretical shaft work generated in steam turbines $n_d=0.7$</td>
<td></td>
</tr>
<tr>
<td>HP steam (10 MPa, 500°C) to MP steam 4 MPa</td>
<td>0.422</td>
</tr>
<tr>
<td>MP steam (4 MPa) to condensation</td>
<td>0.918</td>
</tr>
<tr>
<td>Total shaft work generated</td>
<td>1.340</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heat consumption for HP steam generation in ammonia plant</th>
<th>Shaft work $\text{GJ/t NH}_3$</th>
<th>Steam $\text{kg/t NH}_3$</th>
<th>$\text{CH}_4$ consumed $\text{LHV GJ/t NH}_3$</th>
<th>$\text{Nm}^3/\text{t NH}_3$</th>
<th>Exergy of work or heat $\text{GJ/t NH}_3$</th>
<th>Exergy of $\text{CH}_4$ $\text{GJ/t NH}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total heat for HP steam generation</td>
<td>7.268</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.985</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Actual medium and low temperature (MT&amp;LT) heat balance</th>
<th>Shaft work $\text{GJ/t NH}_3$</th>
<th>Steam $\text{kg/t NH}_3$</th>
<th>$\text{CH}_4$ consumed $\text{LHV GJ/t NH}_3$</th>
<th>$\text{Nm}^3/\text{t NH}_3$</th>
<th>Exergy of work or heat $\text{GJ/t NH}_3$</th>
<th>Exergy of $\text{CH}_4$ $\text{GJ/t NH}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total MT&amp;LT heat available from reactions (2) and (4)</td>
<td>3.619</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.982</td>
<td>-</td>
</tr>
<tr>
<td>Excess steam condensation heat</td>
<td>0.969</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.220</td>
<td>-</td>
</tr>
<tr>
<td>Total MT&amp;LT heat supply</td>
<td>4.588</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.202</td>
<td>-</td>
</tr>
<tr>
<td>Minimum actual MT&amp;LT heat consumption for CO$_2$ removal from H$_2$/N$_2$ mixture</td>
<td>0.719</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.224</td>
<td>-</td>
</tr>
<tr>
<td>Heat losses (10% from heat supply)</td>
<td>0.459</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.220</td>
<td>-</td>
</tr>
<tr>
<td>MT&amp;LT heat available for BF water preheating and water evaporation</td>
<td>3.410</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.758</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>High temperature (HT) heat balance</th>
<th>Shaft work $\text{GJ/t NH}_3$</th>
<th>Steam $\text{kg/t NH}_3$</th>
<th>$\text{CH}_4$ consumed $\text{LHV GJ/t NH}_3$</th>
<th>$\text{Nm}^3/\text{t NH}_3$</th>
<th>Exergy of work or heat $\text{GJ/t NH}_3$</th>
<th>Exergy of $\text{CH}_4$ $\text{GJ/t NH}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total HT heat consumed for HP steam generation</td>
<td>3.858</td>
<td>2244</td>
<td>3.858</td>
<td>107.7</td>
<td>1.799</td>
<td>4.060</td>
</tr>
<tr>
<td>Heat losses (10% from methane burning heat)</td>
<td>0.429</td>
<td>-</td>
<td>0.429</td>
<td>12.0</td>
<td>-</td>
<td>0.452</td>
</tr>
<tr>
<td>Total HT heat supply by additional methane burning</td>
<td>4.287</td>
<td>-</td>
<td>4.287</td>
<td>119.7</td>
<td>1.799</td>
<td>4.512</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total actual minimum methane consumption in ammonia plant</th>
<th>Shaft work $\text{GJ/t NH}_3$</th>
<th>Steam $\text{kg/t NH}_3$</th>
<th>$\text{CH}_4$ consumed $\text{LHV GJ/t NH}_3$</th>
<th>$\text{Nm}^3/\text{t NH}_3$</th>
<th>Exergy of work or heat $\text{GJ/t NH}_3$</th>
<th>Exergy of $\text{CH}_4$ $\text{GJ/t NH}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual minimum methane consumption as feedstock and fuel for process (from Table 4)</td>
<td>-</td>
<td>-</td>
<td>22.711</td>
<td>634.1</td>
<td>-</td>
<td>23.902</td>
</tr>
<tr>
<td>Total actual minimum methane consumption for HP steam generation</td>
<td>-</td>
<td>-</td>
<td>4.287</td>
<td>119.7</td>
<td>1.799</td>
<td>4.512</td>
</tr>
<tr>
<td>Total actual minimum methane consumption in ammonia plant</td>
<td>-</td>
<td>-</td>
<td>26.998</td>
<td>753.8</td>
<td>-</td>
<td>28.415</td>
</tr>
<tr>
<td>Electricity from power plant for driving other machinery</td>
<td>0.143</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.143</td>
<td>-</td>
</tr>
<tr>
<td>Fuel (methane) consumption in power plant for electricity generation ($\eta=0.32$)</td>
<td>-</td>
<td>0.447</td>
<td>12.5</td>
<td>-</td>
<td>0.472</td>
<td>-</td>
</tr>
<tr>
<td>Total actual minimum methane consumption in ammonia plant (ind. electricity generation)</td>
<td>-</td>
<td>-</td>
<td>27.445</td>
<td>766.3</td>
<td>-</td>
<td>28.886</td>
</tr>
</tbody>
</table>
Table 7. Total methane consumption in ammonia plant and for electricity production in power plant
(All compressors in ammonia plant driven by electric motors)

<table>
<thead>
<tr>
<th>Process</th>
<th>Shaft work (GJ/t NH₃)</th>
<th>CH₄ consumed (LHV)</th>
<th>Exergy of CH₄ (GJ/t NH₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual minimum methane consumption as feedstock and fuel for process (from Table 4)</td>
<td>-</td>
<td>22.711</td>
<td>634.1</td>
</tr>
<tr>
<td>Minimum electricity from power plant for driving all machinery</td>
<td>1.483</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Minimum fuel (methane) consumption in power plant for electricity generation (η=0.32 [4])</td>
<td>-</td>
<td>4.634</td>
<td>129.4</td>
</tr>
<tr>
<td>Total minimum methane consumption in ammonia and power plants</td>
<td>-</td>
<td>27.345</td>
<td>763.5</td>
</tr>
<tr>
<td>Maximum electricity from power plant for driving all machinery</td>
<td>2.595</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Maximum fuel (methane) consumption in power plant for electricity generation (η=0.32 [4])</td>
<td>-</td>
<td>8.109</td>
<td>226.4</td>
</tr>
<tr>
<td>Total maximum methane consumption in ammonia and power plants</td>
<td>-</td>
<td>30.820</td>
<td>860.5</td>
</tr>
</tbody>
</table>

Table 8. Theoretical and actual energy consumption and CO₂ emissions in natural gas-based production of ammonia

<table>
<thead>
<tr>
<th>Methane consumption and CO₂ emissions in ammonia production plants</th>
<th>Methane consumption</th>
<th>CO₂ emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GJ/t NH₃</td>
<td>Nm³/t NH₃</td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>Methane as feedstock for steam reforming reaction (1)</td>
<td>17.667</td>
<td>493.3</td>
</tr>
<tr>
<td>Methane burning reaction (3)</td>
<td>2.945</td>
<td>82.2</td>
</tr>
<tr>
<td>Additional methane burning</td>
<td>1.594</td>
<td>44.5</td>
</tr>
<tr>
<td>Theoretical minimum consumption for chemical process</td>
<td>22.206</td>
<td>620.0</td>
</tr>
<tr>
<td>Heat losses in methane burning (10%)</td>
<td>0.505</td>
<td>14.1</td>
</tr>
<tr>
<td>Actual minimum consumption for chemical process</td>
<td>22.711</td>
<td>634.1</td>
</tr>
<tr>
<td>Actual consumption for work generation:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• in ammonia plants</td>
<td>4.287</td>
<td>8.031</td>
</tr>
<tr>
<td>• in power plants</td>
<td>0.447</td>
<td>0.781</td>
</tr>
<tr>
<td>Total actual consumption in BAT new plants:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Main compressors driven by steam turbines</td>
<td>27.445</td>
<td>31.523</td>
</tr>
<tr>
<td>Total actual consumption in BAT new plants:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>All machinery driven by electric motors</td>
<td>27.345</td>
<td>30.820</td>
</tr>
<tr>
<td>CO₂ benchmark allowances for ammonia production for 2013-2014; carbon leakage exposure is in consideration (EC Decision 27.4.2011, [13])</td>
<td>29.522</td>
<td>824.2</td>
</tr>
<tr>
<td>CO₂ benchmark allowances for ammonia production for 2020 if carbon leakage exposure would be not in consideration (factor 0.8 for 2013 down to 0.3 for 2020).</td>
<td>11.071</td>
<td>309.1</td>
</tr>
</tbody>
</table>
Fig. 3. Dependence of the fuel (methane) consumption for shaft work generation on the efficiency of the compressors in ammonia plants and energy efficiency of power plants.

Fig. 4. Dependence of the fuel (methane) consumption for shaft work generation on the efficiency of the compressors and heat losses in ammonia plants.
3.3. Theoretical and actual minimum CO₂ emissions estimation

The proposed model of the ammonia production process enables specifying separately also the theoretical and actual CO₂ emissions from the chemical process itself and from the shaft work generation. The first conclusion is that the CO₂ emissions couldn’t be made lower than 1218 kg/t, corresponding to the theoretical minimum methane consumption for the chemical process (Table 8). Moreover, extra emissions must be added from the shaft work generation processes in the ammonia plant or in a power plant. In case the main compressors are driven by steam turbines (HP steam generated in the ammonia plant), the CO₂ emissions would be in the range from 236 to 483 kg/t, depending on the turbines and compressors efficiency. In this case the total actual minimum of the CO₂ emissions would be from 1482 to 1729 kg/t (Table 8). In case the main compressors are driven by electric motors, the total actual minimum of the CO₂ emissions would be from 1500 to 1690 kg/t, depending on the power plant efficiency.

The comparison of these values with the CO₂ benchmark allowances for ammonia production, established by the European Commission [13] for years 2012 and 2013, shows that the value 1619 kg/t is within the range of the actual minimum values for both shaft work generation options. The fulfilment of this regulation requires the application of the best available ammonia technology as well as the high efficient compressors and turbines.

However, if the proposed in the same EC decision [13] further CO₂ emissions reduction (linear decrease by factor of 0.8 for 2013 down to 0.3 for 2020) would be implemented for ammonia plants as well, the corresponding value of 607 kg/t would be unfeasible since it would be twice lower even than the theoretical minimum of 1218 kg/t for the chemical process only.

4. CONCLUSIONS

- A simplified, but generalized model of the overall ammonia production process, presented by reactions (1) – (6), is used to distinguish the methane consumption for the chemical process and for the energy transformation processes (shaft work generation). The model is applicable to all types of modern ammonia plants with conventional reforming, advanced reforming and gas-heated reforming, as the model parameters for methane consumption and heat balance of the plant are independent from the features of the specific plant design. The model is used to find the theoretical minimum and actual methane consumption of the chemical processes in ammonia production. The dependence of the actual consumption on the heat losses is examined.

- The dependence of the additional fuel consumption for shaft work generation in ammonia plants on the isothermal efficiency of the compressors and thermal efficiency of the steam generation is investigated and compared with the fuel consumption in power plants with different energy efficiencies.

- The results show that the fuel consumption values for the shaft work generation in ammonia and power plants are comparable and depends strongly on the machinery efficiency in ammonia plants and on the energy efficiency of power plants, respectively. Due to the utilization of a part of the available MT&LT heat from the chemical processes in the steam cycle, the fuel consumption for the work generation in ammonia plants is lower than in power plants working at equal steam parameters.

- At higher machinery and thermal efficiencies, the generation of the shaft work in the ammonia plants itself is preferable than in old power plants with typically lower efficiencies. However, as the power plants offer more opportunities for improvements than ammonia plants, in the future electric motors could become again preferable for compressors driving.

- The theoretical and the actual minimum of the CO₂ emissions from the chemical process itself and from the shaft work generation are specified and compared for both cases of the main compressors drivers: steam turbines and electric motors.
Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFW</td>
<td>Boiler Feed Water</td>
</tr>
<tr>
<td>CHP</td>
<td>Combined Heat and Power</td>
</tr>
<tr>
<td>GHR</td>
<td>Gas-Heated Reforming</td>
</tr>
<tr>
<td>HP</td>
<td>High Pressure, MPa</td>
</tr>
<tr>
<td>HHV</td>
<td>High Heating Value, kJ</td>
</tr>
<tr>
<td>LHV</td>
<td>Low Heating Value, kJ</td>
</tr>
<tr>
<td>LP</td>
<td>Low Pressure, MPa</td>
</tr>
<tr>
<td>LT</td>
<td>Low temperature, °C</td>
</tr>
<tr>
<td>MP</td>
<td>Middle Pressure, MPa</td>
</tr>
<tr>
<td>MT</td>
<td>Middle Temperature, °C</td>
</tr>
<tr>
<td>η</td>
<td>efficiency</td>
</tr>
</tbody>
</table>

References


Evaluation of the Oil and Gas Processing at a Real Production day on a North Sea Oil Platform Using Exergy Analysis

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Abstract:
Industry may benefit from knowledge about the 2nd law of thermodynamics and exergy analysis. The motivation for this study is to explore the applicability of exergy analysis as an evaluation and monitoring tool for an offshore platform. A particular oil producing platform located in the North Sea is analysed. We use exergy analysis to indicate the potential for reduction in power consumption of the oil and gas processes on the platform, and present the exergetic efficiency as a useful performance parameter. The exergetic efficiency says something about improvement potential, while current performance parameters only focus on power consumption. We analyse the oil and gas processing at the particular platform for a real production day. A mix of water and reservoir petroleum is separated into oil, gas and water. The produced oil is stabilized and pumped 18 km to a nearby platform, the water is treated and discharged to the sea and the produced gas is compressed and reinjected into the reservoir. The oil and gas processing is driven by gas turbines, and produced gas that is treated in the fuel gas system is used as fuel. The oil and gas processing can be divided into five sub-processes; the separation train, the recompression train, the reinjection train, the export oil pumping section and the fuel gas section. A flowsheet for these processes is simulated using measured process data, and the exergy loss in each process unit is calculated. In addition to a real production day (Case 1), we have looked at the same data but with all adiabatic compressor efficiencies increased by 2 percentage points (Case 2) as well as absence of anti-surge recycling (Case 3). In Case 1 the specific power consumption was 180 kWh/Sm\textsuperscript{3} while the exergetic efficiency was 0.32. The highest losses were related to compression of gas. In Case 2 the specific power consumption was reduced with 3 \% while the exergetic efficiency of the process increased to 0.33. In Case 3 the specific power consumption was reduced with 15 \% and the energetic efficiency increased to 0.38. Clearly, efficient gas compression is important. We see the advantage of considering destructed exergy and exergetic efficiency in addition to the industry’s own measures of performance, as these parameters show different features of the processes.

Keywords:
Exergy, Efficiency, Compressor Efficiency, Anti-Surge Control, Oil Platform.

1. Introduction
In 2008, gas turbines and diesel engines on oil and gas platforms were responsible for 21 \% of Norway’s total CO\textsubscript{2}-emissions [1]. Most platforms generate their own power with gas turbines, and the typical power consumption at a Norwegian continental shelf platform is between 10 MW and several 100 MW. There is a general agreement that the world’s CO\textsubscript{2} emissions should be reduced and that the world’s resources should be utilised in sustainable way. Improvement of energy efficiency is a challenge in the petroleum sector, as in the industry in general. The sector is therefore in need for a tool to monitor the energy performance of the platform processes.

Today, specific CO\textsubscript{2} emissions (CO\textsubscript{2} emission per barrel produced oil) is often used as a performance parameter by the oil and gas industry. This parameter reflects the aim of reducing the world’s CO\textsubscript{2} emissions - it encourages energy efficiency and use of renewable energy sources. However, it does not account for the varying operating conditions for different platforms.
Obtaining a sustainable resource management in the petroleum sector can be complex. In Norway, as well as in a number of other countries, the industry has to pay tax for CO$_2$ and NO$_x$ emissions. At the same time increased recovery and extended lifetimes in mature fields is encouraged. However, measures designed to improve recovery often require significant amounts of energy and may entail additional emissions to air [2]. The taxes do then punish measures that are encouraged by the authorities [3].

We want to explore the use of exergy analysis as a tool for platform performance benchmarking and as an everyday tool to evaluate performance. The exergetic efficiency compares the work used in a process with the work needed for the same process if it were reversible. We also want to calculate the destructed exergy in different parts of the process to indicate possibilities for improvement. We therefore analyse the oil and gas separation processes on a specific North Sea oil platform. Exergy analysis is a thermodynamic method which is not yet systematically used by the oil and gas industry.

The oil and gas produced at the platform are subject to certain specifications. The oil must meet the pressure required for 18 km transportation through a pipeline, and it must have a specified vapor pressure. The gas must meet the pressure required to be injected into the reservoir for pressure maintenance.

Specific CO$_2$ emissions accounts for both fuel gas consumption and flaring. The CO$_2$ emissions associated with the part of the platform studied is proportional to the fuel gas consumption, and thus the power consumption. We choose to look at specific power consumption when we compare with exergy analysis in the rest of this paper.

Oliveira et al [4] did in 1997 an exergy analysis of the petroleum separation processes on a Brazilian offshore platform. On this platform exergy is consumed in order to heat petroleum before separation, to compress natural gas and to pump oil to the coast. There is recovery of exhaust gases for heating purposes. The analysis showed that exergy destruction on this platform is dominated by heating of oil, despite the heat recovery system, and by compression of gas.

This paper is a continuation of a work presented earlier [5], where an exergy analysis was performed using a process flowsheet that was considered representative for the processes on the platform we look at. Adiabatic efficiencies were assumed to be 75 % in all compressors and pumps. It was pointed out that the highest losses took place in the reinjection trains where gas is compressed before it is reinjected into the reservoir. The calculated destructed exergy at the process plant was 12 MW and the exergetic efficiency 0.36.

In the current work we analyse a real production day for the same platform. However, the process flowsheet has now been established using measured temperatures, pressures, flow rates and power consumption throughout the process for a specific production day. We have also included fuel gas treatment, and recycling of gas due to anti-surge protection of the compressors. This will give results that are more realistic - especially for the gas compression processes. We have done a case-study where in addition to the real production day (Case 1), we have looked at the same day, but with all adiabatic compressor efficiencies increased with 2 pp (percentage points) (Case 2) and the same day but without need for anti-surge recycling (Case 3).

2. Theoretical background

2.1. Exergy

The basic principles of exergy and exergy relations relevant for this study are presented. For a comprehensive introduction to exergy analysis, see [6] or [7]. The exergy of a system is defined as the maximum theoretical work obtainable when the system interacts with the environment to equilibrium [7]. This maximum theoretical work is obtained when all processes involved are reversible. In all real processes some exergy will be destructed. In an exergy analysis of a process,
thermodynamic inefficiencies can be identified. Important quantities in exergy analysis are defined by [8] as follows:

- The *product exergy*, $E_P$, represents the desired result expressed in terms of exergy.
- The *fuel exergy*, $E_F$, represents the resources in terms of exergy used to provide the product exergy.
- *Exergy loss*, $E_L$, represents thermodynamic inefficiencies of a system associated with the transfer of exergy with energy and material streams to the surroundings.
- *Exergy destruction*, $E_D$, represents thermodynamic inefficiencies of a system associated with the irreversibilities (entropy generation) within the system boundaries.

For a system in steady state the destructed exergy, $E_D$, for a certain time period is the exergy entering the system minus the exergy leaving the system:

\[ E_D = W + \sum_k \int_{t_k} \left( 1 - \frac{T_0}{T_k} \right) \beta Q_k + \sum_j n_j e_j, \]  

where $W$ is work added, $Q$ is heat transferred at temperature $T_k$, $T_0$ is the temperature of the environment, $n$ is number of moles in a material stream, and $e$ is molar exergy. Subscript $j$ denotes material stream $j$. Some of the terms in (1) will correspond to fuel exergy rate, some will correspond to product exergy rate and some will correspond to rate of exergy loss, depending on the system considered:

\[ E_D = E_P - E_F - E_L. \]  

### 2.2. Process performance parameters

There exists a variety of ways to define performance parameters for industrial processes based on energy and exergy. We present some parameters that are useful for oil and gas processing:

- The *specific power consumption* we define as consumed power per oil produced. As long as all power comes from the same fossil power source, this is proportional to specific CO$_2$.
- The *exergetic efficiency*, $\varepsilon$, as defined in [8]:

\[ \varepsilon = \frac{E_P}{E_F}. \]

This parameter takes into account the minimum theoretical work that has to be done for the given process.

- The *efficiency defect*, $\delta_i$, of subsystem $i$, presented in [6] as the fraction of the input exergy to the whole system which is lost through irreversibilities in the subsystem. In our notation:

\[ \delta_i = \frac{E_{D,i}}{E_F}. \]

This parameter shows how different subsystems contribute to reduction in the exergetic efficiency.

### 3. System description

#### 3.1. Process overview

A schematic overview of the oil and gas processing at the studied platform is given in Fig. 1. Details for the simulated process flowsheet for the processes are given in Appendix A with set-up of the process units, compositions of feed streams and temperatures, pressures, efficiencies and flow rates throughout the process.
The feed stream of the process consists of reservoir fluids with 78 mol% gas. It comes from a production manifold and enters a separation train. Here gas and water are separated from the crude oil using gravitational separators and an electrostatic coalescer. The train consists of three stages where in the first two stages there are three-phase separators, and in the third stage there are a two-phase separator and an electrostatic coalescer. For each separator, the pressure is reduced, so that more gas is released from the oil. The oil shall meet specifications of basic sediment content, water content and vapour pressure, which is why the separation process is performed in several stages at different pressures. In total the pressure is reduced from 71 to 2.8 bar during this section. Fuel gas for the gas turbines is supplied from high pressure gas from the 1st-stage separator. Oily water from the separators is sent to a water treatment process where traces of oil are removed. The water treatment process is neglected here. A water pump pumps water from the electrostatic coalescer back to the 2nd separator.

The remaining, stabilised oil is pumped 12 km to a nearby platform via two pumps with cooling of the oil in between. A minimum flow is required through the pumps, and to achieve this, some of the oil is recycled back right after the 2nd-stage separator.

The gas that is released in each stage in the separation train is sent to a recompression train. The train consists of three stages, each with a cooler, a scrubber and a compressor. The cooler cools the gas in order to get a low inlet temperature for the compressor and by this way get a more efficient compression. The scrubber is a separator that removes small amounts of condensed liquid. Scrubbing of the gas protects the compressor and allows more optimal compression. In each stage, the gas is compressed to the pressure of the previous stage of separation. A minimum flow of gas is required through the compressors to prevent compressor surging, and to achieve this some of the gas is recycled around each stage (anti-surge recycling). Approximately $15 \times 10^3$ Sm$^3$/h, $21 \times 10^3$ Sm$^3$/h and $22 \times 10^3$ Sm$^3$/h is recycled in the 1st, 2nd and 3rd recompression stages, respectively. In the end, the pressure has reached the 1st-stage separation pressure.

**Fig. 1. Schematic overview of the mass streams in the oil and gas processing.** First the feed stream enters the separation train where it is separated into gas, oil and water. The water is sent out of the process, the oil is sent to the export pumping section where it is pumped for export, high pressure gas is sent to the reinjection trains and low pressure gas is sent to the recompression train where it is compressed before it is sent to the reinjection train. In the reinjection train the gas is further compressed before it is reinjected into the reservoir. Fuel gas is taken from the high pressure gas from the separation train, and treated in the fuel gas system. It is used in the power turbines and in pilot flames in the flare. There is a drain system where small amounts of liquid from the different sub-processes are collected and pumped back to the separation train. It consists of several units, but for simplicity it is represented by only mass streams in the figure. The pressure of some of the process streams are given to show the pressure variations through the process.
After the recompression, the gas enters three parallel reinjection trains. Here it is compressed up to injection well pressure, which is 233 bar. In each of these trains there are two stages, each with a cooler, a scrubber and a compressor, the same way as in the recompression train. The train is run at maximum capacity, so there is no need for anti-surge recycling. The resulting high pressure gas is injected back into the reservoir.

Fuel gas drawn from the 1st-stage separator is cooled and fed through a pressure reducing control valve to a scrubber for liquid removal. After the scrubber, the gas is heated with an electrical heater before a last chance liquid removal and then sent to the power turbines. Gas for a pilot flame at the flare is also taken from this section. For normal process conditions, the amount of gas to the flare from other parts of the processes is negligible.

Condensate from scrubbers throughout the processes is sent back to the 2nd separation stage, either directly or through a drain system.

3.2. Process characteristics – the real production day

The real production day we consider, is one out of a series of days from 2009 to 2011 with available measured process data. The selected day is normal in the sense that it is among the 85% of the days that give values closest to the median for selected process variables like pressures and temperatures in process streams. The process conditions were stable throughout the day: The standard deviation in measured produced oil flow rate is less than 10 Sm$^3$/h (for an average flow rate of 132.5 Sm$^3$/h) and the injected gas rate measured in each of the in total 5 injection wells is less than 10$^3$ Sm$^3$/h (for an average total flow rate of 370 $\cdot$ 10$^3$ Sm$^3$/h).

There are several parameters that vary from day to day, which are important for the performance of the oil platform. These parameters and process characteristics for the selected real production day are summarised in Table 1.

Table 1: Variation in process parameters important for the performance of the oil platform for all normal production days, together with process characteristics for the real production day analysed.

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>Variation</th>
<th>Real production day analysed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas injection flow rate, 10$^3$ Sm$^3$/h</td>
<td>332 – 391</td>
<td>370 (Median)</td>
</tr>
<tr>
<td>Oil production, Sm$^3$/h</td>
<td>121.6 – 302.6</td>
<td>132.5 (Low)</td>
</tr>
<tr>
<td>Gas injection pressure, bar</td>
<td>210 – 240</td>
<td>233 (High)</td>
</tr>
</tbody>
</table>

The adiabatic efficiencies calculated from measured inlet and outlet temperature and pressure for the real production day are given in Table 2.

Table 2: Adiabatic efficiencies for the compressors for the real production day analysed.

<table>
<thead>
<tr>
<th>Compressor</th>
<th>Adiabatic efficiency</th>
<th>Compressor</th>
<th>Adiabatic efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Recompression</strong></td>
<td></td>
<td><strong>Reinjection B</strong></td>
<td></td>
</tr>
<tr>
<td>1st stage</td>
<td>47 %</td>
<td>1st stage</td>
<td>64 %</td>
</tr>
<tr>
<td>2nd stage</td>
<td>69 %</td>
<td>2nd stage</td>
<td>57 %</td>
</tr>
<tr>
<td>3rd stage</td>
<td>56 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Reinjection A</strong></td>
<td></td>
<td><strong>Reinjection C</strong></td>
<td></td>
</tr>
<tr>
<td>1st stage</td>
<td>64 %</td>
<td>1st stage</td>
<td>69 %</td>
</tr>
<tr>
<td>2nd stage</td>
<td>54 %</td>
<td>2nd stage</td>
<td>64 %</td>
</tr>
</tbody>
</table>

For the selected real production day, we studied three cases:

- **Case 1: Real production day.** Temperatures, pressures and flow rates throughout the process based on historical data.
- **Case 2: Increased compressor efficiencies.** The same process flowsheet as in Case 1 was used, except for that adiabatic efficiencies were increased with 2 pp for all gas compressors.
• **Case 3: No anti-surge recycling.** The same process flowsheet as in Case 1 was used, except for that all anti-surge flows around compressors in the recompression section were set to zero.

4. **Methodology**

4.1 **Simulation of the process flowsheet**

The platform processes were simulated using Aspen HYSYS [9]. We chose to use the Peng-Robinson property package, where the Peng-Robinson (PR) equation of state is used to calculate thermodynamic properties. This package is the recommended property package for oil and gas applications [10]. Liquid densities were calculated with the COSTALD method, since this generally gives better results than the equation of state. The HYSYS PR option was chosen. This option has several enhancements to the original PR equation [10]. Interaction coefficients were set to values from the HYSYS library and the interaction parameters unavailable from the library were set as estimated by HYSYS. Hypothetical components were used to simulate the heavy oil fractions. Details about the hypothetical components used, together with the composition of the feed streams, and process variables set throughout the process for Case 1 are given in Appendix A. For Case 2 and 3 the same simulated process flowsheet were used, except for the modifications described in Section 3.2.

4.2 **Exergy analysis**

The exergy destruction in each process unit was found from the exergy balance of the unit. Thermodynamic properties like enthalpy and entropy were taken as calculated by HYSYS. Contributions to the exergy from kinetic energy were neglected, while a contribution from potential energy was included where head differences lead to a pressure increase in an oil stream. This was taken into account by introducing a dummy pump that increased the pressure in the simulated process flowsheet.

We chose to define \( E_P \) as the exergy difference between process streams leaving and entering the system and \( E_F \) as power delivered to the process units (after electrical losses and mechanical losses in gears etc.). The simulated power delivered to the dummy pressure increase pump was not included in the fuel exergy, as this exergy was not delivered by the power turbines.

Exergy lost with cooling water is mixed irreversibly with the sea, and this was therefore regarded as destructed exergy, \( E_D \). This means in practice that the control volume boundaries around these units were extended and drawn around the points where cooling water and sea water are mixed. There are no other streams considered as exergy loss, giving \( E_L = 0 \).

5. **Results and discussion**

In Table 3 the efficiency defects for each sub-process for the three cases studied are presented. The destructed exergy in each subsystem distributed over type of process unit is presented for each case in Fig. 2, while performance parameters are presented for the three cases in Table 4.

**Table 3. Efficiency defect for each sub-process in the oil and gas processing at the platform for the three cases analysed.**

<table>
<thead>
<tr>
<th>Sub-process</th>
<th>Case 1: Real production day</th>
<th>Case 2: Increased compressor efficiencies</th>
<th>Case 3: No anti-surge recycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separation train</td>
<td>0.04</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Export section</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Recompression train</td>
<td>0.17</td>
<td>0.17</td>
<td>0.03</td>
</tr>
<tr>
<td>Reinjection trains</td>
<td>0.44</td>
<td>0.43</td>
<td>0.51</td>
</tr>
<tr>
<td>Fuel gas system</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Fig. 2. Destructed exergy distributed on type of process unit in the different sub-processes of the oil and gas processing at the platform, for a real production day, for the same day but with all adiabatic compressor efficiencies increased with 2 pp and for the same day but without anti-surge recycling.

Table 4. Performance parameters for the oil and gas processing at the platform for the three cases analysed. ‘Power consumption’ is power added to the process units, after electric losses and mechanical losses in gears etc.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Case 1: Real production day</th>
<th>Case 2: Increased compressor efficiencies</th>
<th>Case 3: No anti-surge recycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power consumption ($E_P$), MW</td>
<td>23.9</td>
<td>23.1</td>
<td>20.3</td>
</tr>
<tr>
<td>Destructed exergy ($E_D$), MW</td>
<td>16.1</td>
<td>15.5</td>
<td>12.6</td>
</tr>
<tr>
<td>Product exergy ($E_P$), MW</td>
<td>7.7</td>
<td>7.7</td>
<td>7.7</td>
</tr>
<tr>
<td>Specific power consumption, kWh/Sm$^3$</td>
<td>180</td>
<td>174</td>
<td>154</td>
</tr>
<tr>
<td>Exergetic efficiency</td>
<td>0.32</td>
<td>0.33</td>
<td>0.38</td>
</tr>
</tbody>
</table>

5.1. Case 1: Real production day

In Table 3 we see that losses take place mainly in the reinjection trains and the recompression train, which have efficiency defects of 0.44 and 0.17 respectively. The pressure is raised significantly in these sections, and this is where the largest part of the power is consumed. Figure 2 shows that the losses in the reinjection trains consist almost exclusively of losses in compressors and losses with the cooling water. The losses in the recompression train consist of losses in the compressors, losses with the cooling water and losses due to anti-surge recycling of gas around the compression stages. It is clear that to improve the exergy efficiency and reduce the power consumption of the process one should focus on the gas compression, which is as expected.

The current result shows considerably more losses associated with gas compression compared to results in [5]. The results in the previous paper correspond to efficiency defects of 0.24 and 0.04, for the reinjection and recompression trains, respectively. The large difference is mainly due to the use of adiabatic efficiencies of 75 % in the previous paper, while the efficiencies simulated based on
measured inlet and outlet temperatures and pressures were lower. Furthermore, anti-surge recycling was not taken into account in the previous paper.

5.2. Case 2: Increased compressor efficiencies
With 2 pp higher adiabatic efficiencies in all gas compressors, we see a reduction in destructed exergy of 0.5 MW in the compressors in the reinjection train, 0.1 MW in the coolers in the reinjection train and 0.1 MW in the compressors in the recompression train. Reduction of exergy destruction in the compressors is a direct effect of the increased efficiencies. The reduction of exergy destruction in coolers is due to a lower outlet temperature from the compressors, so that less heat has to be removed with the cooling water in the following cooler. The improvements result in a specific power consumption reduced with 3 % (cf. Table 4). We see that the efficiency defect in the reinjection trains is reduced. Since less power is now needed for the whole process, other efficiency defects are slightly increased, which is observed for the separation train. The exergetic efficiency of the whole process increases from 0.32 to 0.33.

5.3. Case 3: No anti-surge recycling
Without anti-surge recycle flow around the compressors in the recompression train, the destructed exergy of 1.6 MW due to pressure loss in recycle streams is eliminated. We also obtain a reduction in destructed exergy of 1.1 MW in the compressors and 0.8 MW in the coolers. This is due to a lower amount of gas compressed and cooled. The efficiency defect of the recompression train is reduced from 0.17 to 0.03. The improvements reduce the specific power consumption with 15 % (cf. Table 4). Since no exergy is saved in the other sections and the total power consumption is reduced, the efficiency defects in the other sections are increased. The exergetic efficiency of the whole process increases from 0.32 to 0.38.

5.4. Perspectives on exergy analysis in the oil industry
The oil and gas industry is well aware of the large losses related to gas compression. Furthermore it is well known that a lot of thermal energy is released with the cooling water to the sea. The thermal energy discharge cannot however well represent the thermodynamic losses, as the temperatures of the discharges are relatively low compared to the ambient temperatures. Exergy analysis is a systematic approach that localises thermodynamic losses and quantifies theoretical saving potential. It makes it possible to compare the magnitude of different types of losses. This is more useful, the more complex the system is.

The destructed exergy is for our system equal to the power consumption minus the theoretical minimum work needed for the process. This is valuable information and gives a wider picture of the situation. The exergetic efficiency is the ratio between this minimum work and the power consumption. Both these parameters can add to the industry’s own measures of performance, like the specific CO\textsubscript{2} emissions. The exergetic efficiency can be used to both quantify as well as justify best practices. It can also be used by the public sector to set standards for performance, that all should adhere to. Such standards may eventually lead to developments of more energy efficient technologies and to the best operation of these.

Under the introduction of other power sources for offshore platforms, for instance electric power from land or power from offshore windmills [11], specific CO\textsubscript{2} emissions is no longer proportional to specific power consumption. Specific CO\textsubscript{2} emissions encourages the use of renewable power sources, but once such a source is taken into use, this parameter do not say anything about the performance of the process anymore. Exergetic efficiency, however, will always evaluate the process.

We have now only looked at the oil and gas processing at one platform. We propose that more platforms should be analysed, to explore the applicability of exergy analysis when comparing different platforms. We also propose that one platform should be monitored over time, to see how
exergy analysis can be used to evaluate efforts on adapting to changing process conditions or on increasing the process efficiency.

6. Conclusion

An exergy analysis has been performed for a real production day on a North Sea oil platform. The specific power consumption was 180 kWh/Sm³ while the exergetic efficiency was 0.32. The highest losses were related to compression of gas. By increasing all adiabatic compressor efficiencies with 2 pp the specific power consumption was reduced with 3 % while the exergetic efficiency of the process increased to 0.33. By eliminating need for anti-surge recycling of gas, the specific power consumption was reduced with 15 % and the exergetic efficiency increased to 0.38. It has been shown that exergy analysis is useful for the oil industry both for location and quantification of thermodynamic losses. Destructed exergy and exergetic efficiency give useful information in addition to the industry’s own measures of performance.

Appendix A

We present the set-up of the flowsheet that was simulated for the real production day using HYSYS in Section A.1. In Section A.2 we give the process variables and the feed streams set in the simulation.

A.1. Set-up for process flowsheet

Figs. A.1 – A.6 show the set-up for each sub-process. A short overview of the whole system is already given in Section 3.

Fig. A.1. Simulated process flowsheet for the separation train. The separation train has three separation stages. In the 1st stage there are two three-phase separators; one normal and one test-separator (both are continuously in use). For simplicity they are merged into one separator in the simulated process flowsheet. In the 2nd stage there is one three-phase separator. In the 3rd separation stage there are one two-phase separator and one electrostatic coalescer. The feed stream enters the 1st separation stage. The pressure is reduced between each stage. A water pump pumps water from the electrostatic coalescer back to the 2nd three-phase separator. Coolers are added on the gas streams to simulate heat losses to the environment. A dummy pump is included after the two-phase separator to simulate pressure increase due to height difference in the liquid stream.
Fig. A.2. Simulated process flowsheet for the export pumping section. The oil is first pumped in a booster pump, then cooled, and then pumped in a main export pump. To ensure a minimum flow in the pumps, there are liquid recycle streams that recycle oil to the separation train. Parallel standby pumps and coolers are not included in the simulation.

Fig. A.3. Simulated process flowsheet for the recompression train. The gas is compressed in three stages, with a cooler, a scrubber and a compressor in each stage. Gas is recycled around each stage to keep a minimum flow through the compressors.

Fig. A.4. Simulated process flowsheet for the reinjection trains. The gas is compressed in three parallel trains with two stages each. Each stage consists of a cooler, a scrubber and a compressor. Only train A is shown in detail, since the three trains have the same set-up. The mass streams of train B and C have the same numbers as shown in train A, but the numbers end with B and C instead of A.
Fig. A.5. Simulated process flowsheet for the fuel gas system. The gas is cooled and depressurised, before it is scrubbed and heated. Some gas is split off to the pilot flames in the flares, and the rest is split into two, scrubbed, filtered and depressurised before it is sent to the power turbines. In the simulated flowsheet, the last two scrubbers and filters are merged into one scrubber.

Fig. A.6. Simulated process flowsheet for the drain system. In the drain system small amounts of liquid from knock out drums in the flare system and from scrubbers with low liquid flow rates in the oil and gas processes are collected in a reclaimed oil sump. When the liquid in the reclaimed oil sump reaches a certain level, it is pumped to the 2nd separation stage. For simplicity this is replaced by a small pump that continuously pumps liquid from scrubbers to the 2nd separation stage in the simulated process flowsheet. Since we look at a normal production day with a stable production, liquid from the flare system is neglected.
A.2.1. Temperatures, pressures and efficiencies

Temperatures and pressures throughout the system were set to the average measured value for the real production day (24 h), see Table A.1. For some process units efficiency and pressure drop were set to values found in documentation from the contractors of the equipment, see Table A.2. For some small pumps efficiencies were assumed, see Table A.3.

Table A.1. Process variables set as average measured value in process streams for the real production day (24 h). The measured pressures, \( P \), have uncertainties of 1 % while the temperatures, \( T \), have \( 1.0 \, ^\circ\text{C} \) where the uncertainties are expressed as 95 % confidence intervals.

<table>
<thead>
<tr>
<th>Sub-process and stream number</th>
<th>Variable</th>
<th>Value</th>
<th>Sub-process and stream number</th>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separation</td>
<td></td>
<td></td>
<td>C234</td>
<td>( P, \text{bar} )</td>
<td>12.81</td>
</tr>
<tr>
<td>C181</td>
<td>( P, \text{bar} )</td>
<td>70.4*</td>
<td>C243</td>
<td>( P, \text{bar} )</td>
<td>32.1</td>
</tr>
<tr>
<td>C211B</td>
<td>( P, \text{bar} )</td>
<td>8.50</td>
<td>C234</td>
<td>( T, , ^\circ\text{C} )</td>
<td>48.1</td>
</tr>
<tr>
<td>C213oB</td>
<td>( P, \text{bar} )</td>
<td>2.80</td>
<td>Re injection A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C541</td>
<td>( P, \text{bar} )</td>
<td>8.77</td>
<td>C3220A</td>
<td>( P, \text{bar} )</td>
<td>68.8</td>
</tr>
<tr>
<td>C181</td>
<td>( T, , ^\circ\text{C} )</td>
<td>76.5*</td>
<td>C3520A</td>
<td>( P, \text{bar} )</td>
<td>137.4</td>
</tr>
<tr>
<td>C331</td>
<td>( T, , ^\circ\text{C} )</td>
<td>73.6*</td>
<td>C3225A</td>
<td>( P, \text{bar} )</td>
<td>137.4*</td>
</tr>
<tr>
<td>C333</td>
<td>( T, , ^\circ\text{C} )</td>
<td>59.2</td>
<td>C3525A</td>
<td>( P, \text{bar} )</td>
<td>236</td>
</tr>
<tr>
<td>C335</td>
<td>( T, , ^\circ\text{C} )</td>
<td>46.9</td>
<td>C3320A</td>
<td>( T, , ^\circ\text{C} )</td>
<td>28.0*</td>
</tr>
<tr>
<td>Recompression</td>
<td></td>
<td></td>
<td>C3520A</td>
<td>( T, , ^\circ\text{C} )</td>
<td>94.0</td>
</tr>
<tr>
<td>C3205</td>
<td>( P, \text{bar} )</td>
<td>2.41</td>
<td>C3325A</td>
<td>( T, , ^\circ\text{C} )</td>
<td>28.0</td>
</tr>
<tr>
<td>C3505</td>
<td>( P, \text{bar} )</td>
<td>5.72</td>
<td>C3525A</td>
<td>( T, , ^\circ\text{C} )</td>
<td>77.1</td>
</tr>
<tr>
<td>C3210</td>
<td>( P, \text{bar} )</td>
<td>5.20</td>
<td>Re injection B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3510</td>
<td>( P, \text{bar} )</td>
<td>18.75</td>
<td>C3220B</td>
<td>( P, \text{bar} )</td>
<td>68.9</td>
</tr>
<tr>
<td>C3215</td>
<td>( P, \text{bar} )</td>
<td>18.29</td>
<td>C3520B</td>
<td>( P, \text{bar} )</td>
<td>139.8</td>
</tr>
<tr>
<td>C3515</td>
<td>( P, \text{bar} )</td>
<td>70.0</td>
<td>C3225B</td>
<td>( P, \text{bar} )</td>
<td>139.1</td>
</tr>
<tr>
<td>C7305</td>
<td>( T, , ^\circ\text{C} )</td>
<td>39.9</td>
<td>C3525B</td>
<td>( P, \text{bar} )</td>
<td>236</td>
</tr>
<tr>
<td>C3505</td>
<td>( T, , ^\circ\text{C} )</td>
<td>104.9</td>
<td>C3320B</td>
<td>( T, , ^\circ\text{C} )</td>
<td>28.0</td>
</tr>
<tr>
<td>C3310</td>
<td>( T, , ^\circ\text{C} )</td>
<td>21.0</td>
<td>C3520B</td>
<td>( T, , ^\circ\text{C} )</td>
<td>95.6</td>
</tr>
<tr>
<td>C3510</td>
<td>( T, , ^\circ\text{C} )</td>
<td>111.8</td>
<td>C3325B</td>
<td>( T, , ^\circ\text{C} )</td>
<td>28.0</td>
</tr>
<tr>
<td>C3315</td>
<td>( T, , ^\circ\text{C} )</td>
<td>24.0</td>
<td>C3525B</td>
<td>( T, , ^\circ\text{C} )</td>
<td>74.4</td>
</tr>
<tr>
<td>C3515</td>
<td>( T, , ^\circ\text{C} )</td>
<td>146.5</td>
<td>Re injection C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel gas system</td>
<td></td>
<td></td>
<td>C3220C</td>
<td>( P, \text{bar} )</td>
<td>66.1</td>
</tr>
<tr>
<td>C6692</td>
<td>( P, \text{bar} )</td>
<td>38.8</td>
<td>C3520C</td>
<td>( P, \text{bar} )</td>
<td>131.9</td>
</tr>
<tr>
<td>C6695</td>
<td>( P, \text{bar} )</td>
<td>38.4</td>
<td>C3225C</td>
<td>( P, \text{bar} )</td>
<td>129.2</td>
</tr>
<tr>
<td>C6697</td>
<td>( P, \text{bar} )</td>
<td>38.0</td>
<td>C3525C</td>
<td>( P, \text{bar} )</td>
<td>236</td>
</tr>
<tr>
<td>C6696</td>
<td>( P, \text{bar} )</td>
<td>9.3</td>
<td>C3320C</td>
<td>( T, , ^\circ\text{C} )</td>
<td>30.0*</td>
</tr>
<tr>
<td>C6699</td>
<td>( P, \text{bar} )</td>
<td>18.25</td>
<td>C3520C</td>
<td>( T, , ^\circ\text{C} )</td>
<td>93.4</td>
</tr>
<tr>
<td>C6693</td>
<td>( T, , ^\circ\text{C} )</td>
<td>35.0</td>
<td>C3325C</td>
<td>( T, , ^\circ\text{C} )</td>
<td>30.0*</td>
</tr>
<tr>
<td>C6695</td>
<td>( T, , ^\circ\text{C} )</td>
<td>63.0</td>
<td>C3525C</td>
<td>( T, , ^\circ\text{C} )</td>
<td>80.7</td>
</tr>
<tr>
<td>Export pumping</td>
<td></td>
<td></td>
<td>Drain system</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C217</td>
<td>( P, \text{bar} )</td>
<td>4.25</td>
<td>C441</td>
<td>( P, \text{bar} )</td>
<td>8.52*</td>
</tr>
<tr>
<td>C241</td>
<td>( P, \text{bar} )</td>
<td>13.30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The weighted mean based on mass flow rate for the measured values in the gas flow from the two separators that in the simulated flowsheet is merged into one, see Fig. A.1.
*Temperature is assumed to be as measured in test manifold.
*The measured pressure is 137.5 bar, but since it cannot be higher than the pressure in C3528A, it is set to 137.4 bar.
*This temperature is not measured for the real production day, so the set point for the cooler upstream is used.
*This temperature is not measured for the real production day, and the set point for the cooler upstream is not known for the specific day, so the set point a few weeks earlier is used.
*The pressure is set to the highest measured pressure in the closest pumping period.
Table A.2. Efficiencies, $\eta$, and pressure drop, $\Delta P$, given for process equipment in documentation from the contractors.

<table>
<thead>
<tr>
<th>Sub-process</th>
<th>Process unit</th>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Export pumping</td>
<td>Booster pump</td>
<td>$\eta$, %</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Main export pump</td>
<td>$\eta$, %</td>
<td>48</td>
</tr>
<tr>
<td>Fuel gas system</td>
<td>Fuel gas cooler</td>
<td>$\Delta P$, bar</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Table A.3. Assumed efficiencies, $\eta$, for small pumps. The efficiency for the dummy pump has no practical meaning.

<table>
<thead>
<tr>
<th>Sub-process</th>
<th>Process unit</th>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separation</td>
<td>Water pump</td>
<td>$\eta$, %</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>Dummy pump</td>
<td>$\eta$, %</td>
<td>100</td>
</tr>
<tr>
<td>Drain system</td>
<td>Drain system pump</td>
<td>$\eta$, %</td>
<td>75</td>
</tr>
</tbody>
</table>

A.2.2. Feed streams and flow rates

The feed entering the system consists of fluid coming from two different parts of the reservoir. The compositions of the gas, oil and water phases from each of the two feed types are set as predicted by the operator for 2009. It is assumed that they are unchanged until the day we look at, which is in 2011. The heavy oil fractions are simulated using hypothetical components in HYSYS. They are defined by setting molecular weight, normal boiling point and ideal liquid density, see Table A.4. Other properties are estimated by HYSYS. The hypothetical components are developed by the operator, and are representative for the well streams at this specific platform.

The flow rates of oil, gas and water vary from day to day. The flow rates of the feed streams are set to fit the simulated flow rates of exported oil, injected gas and produced water with measurements, see Table A.5. For each phase, it is assumed that the ratio between flow rates from the two reservoir parts is the same as the ratio between the flow rates that were predicted for 2011 in 2007 for the two parts. The resulting molar flow rate for each component in the feed is given in Table A.6.

Molar flow rates for streams that are split off from the main stream throughout the process are given in Table A.7. They are set to fit with measured volumetric flow rates. In the reinjection trains the volumetric flow rates are measured several places. Then the molar flow rate of each of the train is set to make the simulation fit as good as possible with all the measurements and so that the simulated volumetric flow rates are within the uncertainty limits (95 % confidence interval) of the measured values.

Table A.4. Molecular weight, $M$, normal boiling point, $T_b$, and ideal liquid density, $\rho_{id, liq}$, for the hypothetical components used to describe the heavy oil fractions.

<table>
<thead>
<tr>
<th>Name</th>
<th>$M$, g/mol</th>
<th>$T_b$, °C</th>
<th>$\rho_{id, liq}$, kg/m$^3$</th>
<th>Name</th>
<th>$M$, g/mol</th>
<th>$T_b$, °C</th>
<th>$\rho_{id, liq}$, kg/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HypoA-1</td>
<td>81</td>
<td>73</td>
<td>721.2</td>
<td>HypoC-1</td>
<td>94</td>
<td>69</td>
<td>707.5</td>
</tr>
<tr>
<td>HypoA-2</td>
<td>108</td>
<td>99</td>
<td>740.1</td>
<td>HypoC-2</td>
<td>119</td>
<td>133</td>
<td>781.7</td>
</tr>
<tr>
<td>HypoA-3</td>
<td>125</td>
<td>152</td>
<td>774.6</td>
<td>HypoC-3</td>
<td>172</td>
<td>215</td>
<td>821.3</td>
</tr>
<tr>
<td>HypoA-4</td>
<td>171</td>
<td>230</td>
<td>817.1</td>
<td>HypoC-4</td>
<td>238</td>
<td>293</td>
<td>860.3</td>
</tr>
<tr>
<td>HypoA-5</td>
<td>247</td>
<td>316</td>
<td>859.3</td>
<td>HypoC-5</td>
<td>383</td>
<td>405</td>
<td>900.7</td>
</tr>
<tr>
<td>HypoA-6</td>
<td>388</td>
<td>437</td>
<td>906.2</td>
<td>HypoC-6</td>
<td>636</td>
<td>567</td>
<td>963.7</td>
</tr>
<tr>
<td>HypoA-7</td>
<td>640</td>
<td>618</td>
<td>988.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A.5. Measured flow rates in process streams leaving the platform.

<table>
<thead>
<tr>
<th>Produced fluid</th>
<th>Stream number</th>
<th>Flow rate, Sm$^3$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil export</td>
<td>C2491</td>
<td>132.5 ± 0.4</td>
</tr>
<tr>
<td>Injection gas</td>
<td>C3692</td>
<td>$370 \cdot 10^3 \pm 40 \cdot 10^3$</td>
</tr>
<tr>
<td>Produced water</td>
<td>C5191 + C5193</td>
<td>67 ± 5</td>
</tr>
</tbody>
</table>
Table A.6. Molar flow rates for each component in the feed stream of the simulated process flowsheet.

<table>
<thead>
<tr>
<th>Component</th>
<th>Molar flow rate, kmol/h</th>
<th>Component</th>
<th>Molar flow rate, kmol/h</th>
<th>Component</th>
<th>Molar flow rate, kmol/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>151.67</td>
<td>H₂O</td>
<td>3777.38</td>
<td>HypoA-7</td>
<td>25.03</td>
</tr>
<tr>
<td>Methane</td>
<td>13608.28</td>
<td>N₂</td>
<td>148.82</td>
<td>HypoC-1</td>
<td>3.96</td>
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<td>Ethane</td>
<td>1117.99</td>
<td>HypoA-1</td>
<td>181.30</td>
<td>HypoC-2</td>
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<td>Propane</td>
<td>615.70</td>
<td>HypoA-2</td>
<td>117.12</td>
<td>HypoC-3</td>
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<td>i-Butane</td>
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<td>114.99</td>
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<td>1.70</td>
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<tr>
<td>n-Butane</td>
<td>221.74</td>
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<td>90.01</td>
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<td>1.10</td>
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<td>i-Pentane</td>
<td>72.66</td>
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<td>65.67</td>
<td>HypoC-6</td>
<td>0.71</td>
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<tr>
<td>n-Pentane</td>
<td>94.61</td>
<td>HypoA-6</td>
<td>38.06</td>
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</table>

Table A.7. Molar flow rates for streams that are split off from main stream throughout the process. They are set to fit with measured volumetric flow rates.

<table>
<thead>
<tr>
<th>Sub-process and stream number</th>
<th>Molar flow rate, kmol/h</th>
<th>Sub-process and stream number</th>
<th>Molar flow rate, kmol/h</th>
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<tr>
<td>Export pumping</td>
<td></td>
<td>Re-injection</td>
<td></td>
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<tr>
<td>C261</td>
<td>270.5</td>
<td>C3625B</td>
<td>4366</td>
</tr>
<tr>
<td>C263</td>
<td>203.0</td>
<td>C3625C</td>
<td>7631</td>
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<tr>
<td>Recompression</td>
<td></td>
<td>Fuel gas system</td>
<td></td>
</tr>
<tr>
<td>C7605i</td>
<td>623.7</td>
<td>C6690</td>
<td>428.1</td>
</tr>
<tr>
<td>C7610i</td>
<td>879.2</td>
<td>C6696</td>
<td>14.2</td>
</tr>
<tr>
<td>C7615i</td>
<td>922.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

References
Exergetic and economic analysis of Kalina cycle for low temperature geothermal sources in Brazil

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\textsuperscript{d} Gênera Serviços e Comércio LTDA; vernei@generatech.com.br

Abstract:
This paper deals with the thermodynamic analysis (of both the first and second law of thermodynamic) of the Kalina cycle to find the optimum ammonia-water concentration and evaporation pressure at turbine inlet for different low temperatures geothermal sources on the basis of an exergy analysis. In this work, the Aspen-HYSYS software was used to simulate the Kalina cycle and to calculate the thermodynamic properties based on Soave-Redlich-Kwong (SRK) Equation of State (EoS). The influence of these parameters over the power generation and over the first and second efficiency laws, were calculated. The exergy losses of each component were also studied, pointing the ammonia-water concentration and pressure influence over the power generation and cycle efficiency. Finally the size of the component for the different configurations of the plant and the costs of heat exchanger, turbine and pump were evaluated for the condition of the real geothermal source in Brazil. Lower values of US$/kW (888 US$/kW) were obtained for the configuration of 84% of ammonia and 16% of water mass fraction in the composition of the working fluid at an evaporation pressure of 2500 kPa, producing 923.98 kW with 5.86% of thermal efficiency.

Keywords:
Thermodynamic analysis, Kalina cycle, ammonia-water mixture, equation of state, exergy, costs of investment, energy output, geothermal energy.

Introduction

One of the pillars for sustainable development is based on the use of renewable energy sources. In Brazil, during the last years the demand for energy has increased significantly, and this growth trend will be maintained in the coming years. So it is essential that reliable sources of renewable energy are included in the national energy matrix. However, the use of alternative energy sources is always complementary to the use of traditional fossil sources. Currently some alternative renewable energy sources are already technical and economically feasible. The processes and equipment used have a significant degree of efficiency and reliability. The new renewable energy also increases the diversity of the energy supply, ensures the sustainability of the energy generation. In the long terms, reduces atmospheric emissions of greenhouse gases and air pollutants, creates new employment opportunities in remote rural areas and promotes stability and reliability of the energy system. More traditional renewable energy sources are: solar, wind, geothermal, hydropower and biomass.

Renewable energy sources such as solar, low-enthalpy geothermal sources and large amounts of heat from the industrial wastes are potentially promising sources of energy, able to supply a large share of global electric energy demand. However, low and moderate temperatures of these sources cannot be efficiently converted into electricity through conventional power generation, which is why a lot of this energy is simply wasted.
Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>pressure, (kPa)</td>
</tr>
<tr>
<td>T</td>
<td>(absolute) temperature, (K)</td>
</tr>
<tr>
<td>t</td>
<td>temperature, (°C)</td>
</tr>
<tr>
<td>R</td>
<td>gas constant, (J/kg K)</td>
</tr>
<tr>
<td>V</td>
<td>specific volume, (m³/kg)</td>
</tr>
<tr>
<td>w</td>
<td>acentric factor of the working fluid</td>
</tr>
<tr>
<td>a</td>
<td>coefficient of the Soave-Redlich-Kwong equation of state (J/kg)</td>
</tr>
<tr>
<td>b</td>
<td>coefficient of the Soave-Redlich-Kwong equation of state (J/kg)</td>
</tr>
<tr>
<td>U</td>
<td>global heat transfer coefficient, (W/m²K)</td>
</tr>
<tr>
<td>A</td>
<td>area (m²)</td>
</tr>
<tr>
<td>C</td>
<td>cost (US$)</td>
</tr>
<tr>
<td>(\dot{m})</td>
<td>mass flow rate (kg/s)</td>
</tr>
<tr>
<td>(\dot{Q})</td>
<td>heat rate (kW)</td>
</tr>
<tr>
<td>(\dot{W})</td>
<td>power rate (kW)</td>
</tr>
<tr>
<td>h</td>
<td>enthalpy (kJ/kg)</td>
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<tr>
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<td>specific exergy (kJ/kg)</td>
</tr>
<tr>
<td>s</td>
<td>entropy (kJ/kg K)</td>
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<tr>
<td>(\dot{E})</td>
<td>exergy (kW)</td>
</tr>
<tr>
<td>(\eta)</td>
<td>efficiency (%)</td>
</tr>
<tr>
<td>q</td>
<td>total heat transfer</td>
</tr>
</tbody>
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Subscripts

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>critical</td>
</tr>
<tr>
<td>r</td>
<td>reduced temperature (r = \frac{T}{T_c})</td>
</tr>
<tr>
<td>in</td>
<td>inlet</td>
</tr>
<tr>
<td>out</td>
<td>outlet</td>
</tr>
<tr>
<td>0</td>
<td>dead state</td>
</tr>
<tr>
<td>t</td>
<td>turbine</td>
</tr>
<tr>
<td>p</td>
<td>pump</td>
</tr>
<tr>
<td>d</td>
<td>destruction</td>
</tr>
<tr>
<td>w</td>
<td>geothermal fluid</td>
</tr>
<tr>
<td>th</td>
<td>thermal</td>
</tr>
<tr>
<td>e</td>
<td>exergy</td>
</tr>
<tr>
<td>eq</td>
<td>equipment</td>
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<tr>
<td>h</td>
<td>hot</td>
</tr>
<tr>
<td>c</td>
<td>cold</td>
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Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT</td>
<td>high temperature</td>
</tr>
<tr>
<td>LT</td>
<td>low temperature</td>
</tr>
</tbody>
</table>

For low-temperature geothermal reservoirs, the common type of plants used for the conversion of heat into electrical energy, are binary plants. Up to December 2010, there was not an installed capacity of electricity generation from geothermal energy reported in Brazil. Right now, the main use of geothermal resources in Brazil is in direct use as spas and heating.

The Kalina cycle, originally conceived by Kalina [1] is potentially viable for efficiently generating energy from low temperature sources. The first geothermal plant of this type was built in Husavik, Iceland [2]. Currently, the Kalina cycle is of great interest in different applications [3-6]. Indeed, there are several different configurations of the Kalina cycle, depending, essentially, on the characteristics of the heat source. Various studies had been published about the thermodynamic properties of ammonia-water mixtures [7-10]. The design studies for the use of Kalina cycle, for electric generation from geothermal resources with low temperature indicate different compositions of ammonia-water mixtures, being the most common one about 70% ammonia – 30% water [11-13].

Water-Ammonia mixture

The ammonia-water mixture is non-azeotropic. The characteristic of nonazeotropic mixtures is that the composition and temperature changes during boiling for all possible compositions of the mixture. Ammonia-water mixture differ of pure water or pure ammonia, the four main differences of the mixture and pure water are listed below.

1. The ammonia-water mixtures have variable boiling and condensation temperatures. Conversely, pure ammonia and pure water have constant boiling and condensation temperatures.
2. The physical properties of the mixture can be altered by changing the concentration of ammonia. Since the thermophysical properties remain constants.
3. These mixtures have thermophysical properties that lead to increases or decreases the fluid temperature without changing its energy content.

4. Another important characteristic is about the freezing point of the fluid. The pure water freezes at (0 °C), pure at (-78 °C). Solutions of ammonia and water have lower freezing temperature. Because of the above points, the ammonia-water solutions are appropriate to be used in Kalina cycle applications for low temperatures geothermal electric generation systems.

**Phase diagram**

Ammonia has a lower boiling temperature compared with water, and so is the most volatile component of the ammonia-water solution. This means that when the temperature of the mixture increases, the ammonia will boil first. Contrary, when the mixture is cooled, water will condense first. This unique feature is shown in Fig 1. This diagram plots the temperature versus the concentration of ammonia in the mixture at 550 kPa.

![Phase diagram](image)

**Figure 1: Equilibrium temperature-concentration curve for NH$_3$- H$_2$O at constant pressure.**

In figure 1, the lower curve is the curve of saturated liquid, which happen the start of boiling when the mixture is heated or complete condensation occurs when cooling. While, the upper curve shows the saturated vapour line, or point where there is the complete vaporization of the mixture or the onset of condensation.

When a mixture of ammonia-water is vaporized, a phase diagram conveys much information about the process. For example, when the mixture begins to boil at the boiling point temperature, given by point 3, the % of ammonia in mass is 70% and 30% of water.

As the mixture continues boiling, the temperature increases and point 4 is achieved, wherein the concentration of the remaining liquid and the vapour formed are given by points 6 and 5 respectively. Eventually, the line 7 is reached, where the mixture is saturated vapour at a temperature above the dew point and the vapour concentration is the same as the concentration of the liquid to the beginning of the evaporation process.

In figure 2 is shown an evaporation process in a Kalina Cycle. This non-constant temperature in an evaporation/condensation process permits, if comparing whit pure working fluids cycles, lower values of irreversibilities and higher power output of the cycle.

**Kalina cycle modelling**

In the process flow diagram given in Fig 3, the main components of the Kalina cycle plant are: evaporator, separators, low and high temperature recuperator, circulation pump, condenser and
The ammonia-water mixture is heated in the high-temperature recuperator and evaporator; ammonia-rich vapor is separated in the separator and sent to the turbine-generator. After passing through the turbine-generator, the expanded ammonia-rich liquid is mixed in the low-temperature recuperator with the cool ammonia-poor liquid from the separator and sent to the condenser, whence it is recirculated to the evaporator to complete the cycle.

**Figure 3. Schematic representation of Kalina cycle with AspenPlus software**

**Method**

The study of the Kalina cycle requires knowing the thermodynamic properties of the ammonia-water mixture which acts as the working fluid.

The property packages available in Aspen-HYSYS allow you to predict properties of mixtures ranging from well defined light hydrocarbon systems to complex oil mixtures and highly non-ideal (non-electrolyte) chemical systems.

These properties can be obtained from cubic equations of state (EoS). The cubic equations of estate SRK (Soave-Redlich-Kwong) packages contain enhanced binary interaction parameters for all library hydrocarbon-hydrocarbon pairs (a combination of fitted and generated interaction parameters), as well as for most hydrocarbon-nonhydrocarbon binaries.

\[ P = \frac{RT}{V - b} - \frac{\alpha a}{V(V + b)} \]  \hspace{1cm} (1)

The parameters of the SRK EOS are calculated from the following equations:

\[ a = 0.42747 \frac{R^2T^2_c}{P_c} \]  \hspace{1cm} (2)

\[ b = 0.08664 \frac{RT_c}{P_c} \]  \hspace{1cm} (3)

\[ \alpha = \left[1 + m\left(1 - \sqrt{T_c}\right)\right]^2 \]  \hspace{1cm} (4)

\[ m = 0.48508 + 1.55171w - 0.1561w^2 \]  \hspace{1cm} (5)
Assumptions used in the analysis
1. Pressure drop and heat loss in pipe lines are neglected.
2. Ambient temperature 25 °C.
3. The ammonia-water mixture at the turbine inlet is saturated vapour.
4. The condensing temperature, lower temperature of the system was set at 36 °C.
5. The isentropic efficiency of the turbine is 85%.
6. The pump efficiency is assumed to be 55%.
7. The pinch point was set at 3 °C at the evaporation start, (see fig. 2)
8. The terminal temperature differential (TTD), between inlet geothermal source temperature and outlet working fluid temperature in evaporator was set in 10 °C, (see fig. 2).

Thermodynamics analysis
Mass and energy balances for each component of the heating system can be calculated using equations (6-7).

\[
\sum \dot{m}_{in} = \sum \dot{m}_{out} \quad (6)
\]
\[
\dot{Q} - \dot{W} = \sum \dot{m}_{in} h_{in} - \sum \dot{m}_{out} h_{out} \quad (7)
\]

The objective of the exergy analysis is to determine the operating conditions of a system which destroys the least available work. The exergy of the ammonia-water mixture can be calculated from the following relation:

\[
e = (\dot{Q} - \dot{W}) - T_0 (s - s_g) \quad (8)
\]

Where the properties in the dead state are evaluated at \(T_0\) and \(P_0\). When the fluid is in the liquid phase at the dead-state conditions, it is sufficiently accurate to take the dead-state enthalpy and entropy values as if the fluid were a saturated liquid at the dead-state temperature, for this case, 25 °C.

The exergy destruction rate can be calculated for each component of the cycle from the following exergy balance equation:

\[
\dot{E}_{dl} = \sum \dot{m}_{in} e_{in} - \sum \dot{m}_{out} e_{out} - W \quad (9)
\]

Finally, the previous energy and exergy analysis makes it possible to calculate the respectively thermal and exergetic efficiency of the cycle from the followings equations:

\[
\eta_{th} = \frac{\dot{W}_t - \dot{W}_p}{\dot{Q}_{in}} \cdot 100 \quad (10)
\]
\[
\eta_e = \frac{\dot{W}_t - \dot{W}_p}{\dot{m}_{in} e_{in}} \cdot 100 \quad (11)
\]

Based on (6–9), the balance of first and second law of the thermodynamic of the most important cycle components has been developed.

Results and discussion
The following analysis was performed for 1 Kg/s and temperature between 90 °C to 140 °C of a geothermal source. In order to obtain the optimum performance for the Brazilian conditions of the cycle the concentrations of ammonia-water and the operation pressure were varied.
First, the optimum working pressure was evaluated, in order to obtain a maximum power output, at saturated conditions in the turbine inlet at different composition of the working fluid, that vary from ammonia 65% - water 35%, ammonia 75% - water 25%, to 84% ammonia – water 16% as shown in Figure 4. It can be observed that the power output varies with the working pressure, temperature and composition of the ammonia-water mixture. At each concentration and temperature, we obtain a maximum power output under a determinate working pressure.

For Brazilians condition, where the condensation temperature of the cycle is approximately 36 °C due to the ambient temperature of 25 °C, different condensation pressure is required for the different composition of the working fluid. At lower condensation pressures, which theoretically would render higher values of power output and efficiency, is not possible to work at, because the fluid will not get totally condensed at the end of the condenser and would cause damages to the circulation pump. Moreover, to vary the condensation pressure of the cycle by decreasing the concentration of ammonia in the working mixture was also analyzed and shown in Figure 4, where the evaporation pressure was plotted against the power output at different temperature and composition of the working mixture. Different condensation pressure was assumed for each ammonia-water composition in order to reach maximum power output and cycle efficiency. Condensation pressure of 800 kPa was used for 65%-35% of ammonia-water solution, 1000 kPa for 75%-35% and 1200 kPa for 84%-16%.

Figure 4. Cycle maximum power achieved for different temperatures of the geothermal source and evaporation pressures. (a) 65% of ammonia fraction (b) 75% of ammonia fraction (c) 84% of ammonia fraction.
Figure 5. Mass flow rate for different temperatures of the geothermal source and evaporation pressures. (a) 65% of ammonia fraction (b) 75% of ammonia fraction (c) 84% of ammonia fraction.
Figure 6. Vapor mass flow rate for different temperatures of the geothermal source and evaporation pressures. (a) 65% of ammonia fraction (b) 75% of ammonia fraction (c) 84% of ammonia fraction.

From figure 4, 5 and 6, it can be conclude that exist a value of pressure in which power output is greatest, pressure below this optimal value the cycle is able to evaporate more working fluid but the variation of the enthalpy in the turbine is lower, that result in lower power output of the cycle. By other hand, higher pressure than optimal produce higher variation of enthalpy in the turbine, but the cycle is able to evaporate less mass flow rate, that result in lower power output too. Then, is possible to determine, what is the evaporation pressure of the Kalina Cycle for a given mass flow rate and temperature of the geothermal source in which is obtained higher cycle performance.

The energy efficiencies of the Kalina cycle plants vary between 5.5 and 10.6% while the exergetic efficiency vary from 32.3 to 46.7%. The variations of thermal and exergetic efficiency are shown in Fig. 7. The maximum thermal efficiency is 10.6%, when geothermal fluid temperature is 140 °C and 84% of ammonia mass fraction in the composition of the working fluid mixture. Higher values of exergy efficiency were obtained under the same working conditions.

In practice, 90% ammonia fraction is the break point of this curve beyond which efficiency start to decrease sharply as the plant approaches a standard binary cycle [2].

Figure 7. Influence of the temperature of the geothermal source and ammonia-water composition over the thermal and exergetic efficiency of the cycle.

In figure 8 is shown the exergy destruction of each component of the cycle for the different ammonia-water composition as a working fluid. The exergy destruction in the cycle behaves as follow: the condenser is responsible for the biggest irreversibility, following by the evaporator, turbine HT and LT recuperator and finally the pump.

Figure 8. Exergy destruction by components of the Kalina Cycle.
Economic Evaluation

Table 1 is shown some operation parameters for a Kalina Cycle of the geothermal source found in Brazil [17], (100 °C and 100 kg/s of geothermal water), working at different composition of the working fluid.

An economic evaluation to find a lower cost per kW was carried out for the different percent of ammonia in mass in the composition of the working fluid, taking to account the costs of the components of the cycle.

Table 1. Operation parameters of the cycle at different ammonia-water compositions of the working fluid.

<table>
<thead>
<tr>
<th>Operation parameters</th>
<th>65</th>
<th>75</th>
<th>84</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of ammonia mass fraction</td>
<td>65</td>
<td>75</td>
<td>84</td>
</tr>
<tr>
<td>Power output (kW)</td>
<td>861.62</td>
<td>914.81</td>
<td>923.98</td>
</tr>
<tr>
<td>Evaporator heat consumption (kW)</td>
<td>13071.11</td>
<td>12447.78</td>
<td>14666.94</td>
</tr>
<tr>
<td>Circulation pump (kW)</td>
<td>79.86</td>
<td>83.48</td>
<td>64.8</td>
</tr>
<tr>
<td>Thermal efficiency (%)</td>
<td>5.98</td>
<td>6.68</td>
<td>5.86</td>
</tr>
<tr>
<td>Exergetic efficiency (%)</td>
<td>35.52</td>
<td>39.29</td>
<td>35.67</td>
</tr>
<tr>
<td>Evaporation pressure (kPa)</td>
<td>2000</td>
<td>2500</td>
<td>2500</td>
</tr>
<tr>
<td>Condensation pressure (kPa)</td>
<td>800</td>
<td>1000</td>
<td>1200</td>
</tr>
<tr>
<td>Mass flow rate (kg/s)</td>
<td>25.71</td>
<td>20.4</td>
<td>15.81</td>
</tr>
<tr>
<td>Vapor mass flow rate (kg/s)</td>
<td>8.27</td>
<td>8.8</td>
<td>8.91</td>
</tr>
<tr>
<td>Cooling water temperature (°C)</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Turbine efficiency (%)</td>
<td>85</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Pump efficiency (%)</td>
<td>55</td>
<td>55</td>
<td>55</td>
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</tbody>
</table>

Size of the Components and Operations Cost Estimation

Can be consider that the total cost of the equipments of the cycle (evaporator, pump, generator and condenser) contributes largely to the total system cost in a low-temperature geothermal power plant and is assumed to be representative of the complete system cost.

Heat exchanger sizing

The size of the main components (heat exchangers, pumps and turbine) can be estimated for the four different options fixed for the Kalina cycle. Basically, the size of the heat exchanger can be calculated using the LMTD methods (log Mean Temperature Difference), [20]

The total heat transfer rate per unit of time \(q\), can be expressed in the following equations:

\[
q = UA\Delta T_{m} = UA \left[ \left( T_{h2} - T_{c2} \right) - \left( T_{h1} - T_{c1} \right) \right] \ln \left[ \frac{ T_{h2} - T_{c2} }{ T_{h1} - T_{c1} } \right]
\] (12)

The determination of the overall heat transfer coefficient \(U\) is often tedious and needs data not yet available at the preliminary stages of the design. As a first approximation, for preliminary
calculations, the values shown below were used. Since the heat exchangers can be built according to varies geometrical design, there are corrections factors that must be used with the equations (12) depending on the configuration [22].

Therefore, typical values of $U$ are useful for quickly estimating the required exchange area [18, 21, 22]. Thus, $U$ is given as a conventional value of 1 kW/m$^2$ K to estimate the sizes of the HT and LT recuperators. Values of 0.9 and 1.1 kW/m$^2$ K were used for size estimation of the vaporizer and the condenser. The value for the vaporizer is the lowest one, for a steam in the shell and liquid in the tubes of the heat exchanger, running under forced circulation. The value for the condenser is based on ammonia in the shell and cooling water in the tubes.

Estimated heat transfer areas of the heat exchangers in the Kalina cycle are listed in Table 2 for the different configurations.

Table 2: Estimated sizes of the heat exchangers for different ammonia fractions in Kalina Cycle.

<table>
<thead>
<tr>
<th>Components</th>
<th>% of ammonia mass fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65</td>
</tr>
<tr>
<td>Size (m$^2$)</td>
<td>65</td>
</tr>
<tr>
<td>Vaporizer</td>
<td>490.4</td>
</tr>
<tr>
<td>Condenser</td>
<td>860.68</td>
</tr>
<tr>
<td>HT recuperator</td>
<td>104.63</td>
</tr>
<tr>
<td>LT recuperator</td>
<td>223.86</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1679.57</strong></td>
</tr>
</tbody>
</table>

Costs estimation of the equipments

To determine the purchase costs of the equipments an approach estimation of the costs was used, based on costs values from past purchase orders, and quotations from experienced professional of cost estimations [18-19].

In the estimation of the purchase cost of the heat exchangers, the base cost $C_o=588$ US$ per square meter of heat transfer surface area was used. Thus:

$$C_{eq} = C_o(Eq_{size})^n \quad (13)$$

Where the exponent $n$ is a constant decimal number, in this case 0.8, and $Eq_{size}$ stands for the heat transfer surface area of the heat exchanger, available in table 2 for the different configurations. Using these data the costs of the heat exchangers have been estimated by the relationship in Equation 13 and are presented in Table 3.

Table 3: Costs estimation of the heat exchangers for different ammonia fractions in Kalina Cycle

<table>
<thead>
<tr>
<th>Components</th>
<th>% of ammonia mass fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65</td>
</tr>
<tr>
<td>Cost, US$</td>
<td></td>
</tr>
<tr>
<td>Vaporizer</td>
<td>83,525.23</td>
</tr>
<tr>
<td>Condenser</td>
<td>130,993.79</td>
</tr>
<tr>
<td>HT recuperator</td>
<td>24,271.82</td>
</tr>
<tr>
<td>LT recuperator</td>
<td>44,602.43</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>283,393.27</strong></td>
</tr>
</tbody>
</table>

The cost for the other main components (turbine and pump) has been estimated. Considering in these cases, the power capacity of each component:
\[ C_{eq} = C_0 (\text{Power})^{n} \]  

(14)

where the base cost, \( C_0 \), for the pump is 1120 US$/kW, and for the turbine 4405 US$/kW. The exponents 0.8 and 0.7 were used for size estimation of the pump and turbine. Estimated values of purchased equipment cost for the turbine and the pump are listed in Table 4.

Table 4: Capacities and costs of the turbine and pump for different ammonia fractions in Kalina Cycle

<table>
<thead>
<tr>
<th>Components</th>
<th>% of ammonia mass fraction</th>
<th>65%</th>
<th>75%</th>
<th>84%</th>
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<tbody>
<tr>
<td>Turbine</td>
<td>861.62</td>
<td>499,651.22</td>
<td>914.81</td>
<td>521,047.77</td>
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<tr>
<td>Pump</td>
<td>79.86</td>
<td>37,246.16</td>
<td>83.48</td>
<td>38,590.82</td>
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</table>

So, in figure 9, the increase of the total costs of the equipment was plotted with the power output of the turbine and the ammonia-water solution of the working fluid. Just taking to account the capital cost of equipment of the cycle, was obtain a rate of US$/kW of power output of the plant as shown in figure 10.

Figure 9. Increase of the total purchase costs of equipment with the power output for different ammonia-water solution of the working fluid.

Figure 10. Variation of the costs of a kW with the total purchase cost of equipment for different ammonia-water solution of the working fluid.
Conclusions
The present study analyze the Kalina cycle from the point of view of the first and second law of thermodynamic and the costs of the kW produced, taking to account the equipment costs of the system. Considering the key parameters, which affect the cycle as a whole, and they were identified for this analyze as: the ammonia-water composition, the evaporation/condensation pressures and the temperature of the heat source, identifying the operation point where the plant provides higher power output with the best efficiency.
1. The maximum performance of the cycle, for the analyzed conditions, is reached with 84% of ammonia mass fraction.
2. When increasing the percent of ammonia mass fraction in the composition of the working fluid, the mass flow rate decrease and increases the percentage of mass that can be evaporated. It impact in lower size of heat exchangers and higher power output of the cycle for this composition of the mixture.
3. The lower value of 888 US$/kW of the investment was obtained at 84% of ammonia mass fraction and a power output of 923.98 kW.

Acknowledgments
The authors want to thanks the Coordination of Improvement of Higher Education (CAPES), The National Council of Technological and Scientific Development (CNPq) and The Foundation for Research Support of Minas Gerais State (FAPEMIG) for their collaboration and financial support in the development of the research work. Also want to thanks AES Tietê Company for funding the Project: “Technological Alternatives for the Implantation of Hybrid Geothermal Energy in Brazil from Low-Temperature Sources”.

References


Exergy analysis and comparison of CO₂ heat pumps

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Abstract:
Carbon dioxide (CO₂, R744), being a natural refrigerant with extraordinary beneficial properties found everywhere in our ambiance, can provide answer to the environmental problems caused by the use of other refrigerants. The intention of this work is to outline the variation of exergy efficiency factor, COP and exergy flow related to the use of carbon dioxide in two stage and single stage CO₂ cycle heat pumps. To conjure up the relevant mathematical models for the thermodynamic cycles were developed and an attempt was made for our efficiency and exergy losses results to be displayed. Moreover, fundamental process and system design issues of the applicable CO₂ heat pumps cycles were inaugurated, along with their properties and characteristics comparing CO₂ use to that of R22 and its substitutes R407C and R410A applied to relevant conditions. Since exergy analysis is of importance to provide theoretical basis for optimization of the systems operation and the minimization of losses, the results of this paper will advance the systems’ design and performance. For some conditions R744 may seem to fall short in comparison to the rest refrigerants, nevertheless it signifies a more eco-friendly epoch for the field. The downside of the very high discharge pressure associated with transcritical cycles is counterbalanced by adopting staging in compression. There is a significant increase in COP for the two-stage R744 system compared to the single stage one, with the COP ranging between 3.40 and 2.70 depending on the temperature ratio, that is the gas cooler outlet temperature to the evaporator temperature.

Keywords:
Exergy, Carbon Dioxide, Heat pumps, Exergy Analysis, Single Stage Cycle, Two Stage Cycle.

1. Introduction
Carbon dioxide is one of the most feasible answers to the contribution of the fluorocarbon refrigerants to global warming and ozone depletion, being a natural refrigerant with zero ODP (Ozone depletion potential), negligible GWP (Global warming potential), and very low cost. Global warming effect is considered to be the most prominent problem of the world climate. Refrigerants that are utilized in the heat and cooling systems have quite higher GWP than CO₂. Even refrigerants that were considered ozone layer friendly, such as HFC-134a, have GWP of many times greater than CO₂’s (in HFC-134a is 1300 times)[1, 2]. In addition carbon dioxide (CO₂) is not toxic, flammable or corrosive. It is inexpensive and readily available. After the Montreal Protocol the interest for CO₂ cycles was so great that a large number of research developments have been commenced for the production of carbon dioxide’s refrigeration system components.

1.1 - CO₂ Properties
Carbon dioxide furthermore has two exceptional properties, its most remarkable one being its low critical temperature Tₖᵣᵢₜ of 31.1°C, compared to conventional refrigerants and working close or even above the critical pressure Pₖᵣᵢₜ of 73.8 bar in vapour compression systems functioning in normal ambient temperatures [3, 4].

In a subcritical heat pump cycle, such low critical temperature is considered an inconvenience as heat cannot be delivered at temperatures greater than the critical temperature limiting consequently
the operating temperature range. Additionally, heating capacity and the performance of the system are relegated at temperatures inferior but close to $T_{\text{crit}}$, since the enthalpy of vaporization then is reduced [5], making the operation of a conventional heat pump avoidable at a heat rejection temperature near $T_{\text{crit}}$. Carbon dioxide’s low critical temperature provides the opportunity to operate in a transcritical manner. In a transcritical heat pump, heat rejection (gas cooler) is operated above the critical pressure, heat delivery temperatures are no longer limited by $T_{\text{crit}}$ and the evaporator is operated below that and for this reason the cycle is identified as transcritical.

The other unique property of CO$_2$ is the high working pressure required to use under typical heat pump conditions. Heat pump systems, both sub and transcritical, using CO$_2$, work at greater pressures than with the majority of other refrigerants. The operational pressures of subcritical CO$_2$ heat pumps reach as high as 60–70 bar, whereas for the transcritical pressures vary from 80 to 110 bar or even more. Although high pressure defies compressors’ capability and components’ robustness, it presents some benefits as well, providing to CO$_2$ a relatively high vapor density and an equally high volumetric heating capacity. This attribution offers the option for CO$_2$ to have a smaller working volume cycled in order to attain the same heating demand which permit the use of smaller components and more compact systems [3].

Nevertheless, the most important disadvantage of CO$_2$ cycle is that owing to huge expansion loss compared to conventional refrigerants’ cycle it presents lower COP making the modifications of the cycle crucial [6]. Lorentzen [4] described more than a few customized cycles comprising of two-stage internal ‘subcooling’ and expansion options. By modifying the basic single-stage transcritical cycle a lot can be achieved. Some adaptations that are promising are dividing of flows, expansion via work generation instead of throttling, staging compression and expansion and the use of internal heat exchange. Trying to obtain higher efficiency values, we will employ the modification of the two-stage compression of the CO$_2$ with intercooling. Then we will compare these results to the equivalents of the single stage CO$_2$ and conventional vapour compression cycles. In order to model the total systems, and thereby investigate the possible operating conditions with replacement refrigerant mixtures, a computer code was created.

1.2 - First and Second Law analysis

Studying the inefficiencies of existing systems our work focuses on the understanding of heat pumps cycles, their efficiencies and potentials for improvement, based on First and Second Laws of Thermodynamics. COP is used to evaluate performance of air-conditioning or heat pump from the viewpoint of the First Law of Thermodynamics. Exergy, being presented in an amount of works [7-13] corresponds quantitatively to the useful part of energy, the maximum possible amount of work a system, a flow of matter or energy can produce as it comes to equilibrium with an appointed reference environment. Exergy analysis combines the conservation of mass and energy principles with the second law of thermodynamics for the design of more efficient and environmental friendly systems. While efficiencies using energy are ambiguous for not being measures of “an approach to an ideal”, exergy efficiencies are considered as such, measuring, in a way, the potential of the system for improvement [11].
2. Modelling of Operation

2.1 - Conventional Heat pump’s model

Fig. 1. Schematic diagram of the single stage heat pump cycle.

Figure 1 shows the heat pump’s vapour / transcritical CO\textsubscript{2} compression cycle flow chart. The working fluid moves from the evaporator, which is connected to the low-temperature heat source into the compressor as a superheated vapour. Following, the compressed vapour, flows into the condenser which is connected to the high-temperature heat sink and respectively to the gas cooler for the CO\textsubscript{2}. Here it condenses and afterwards, as a liquid, it undergoes expansion in the throttling valve. The throttled two-phase mixture, which is liquid for the most part, moves into the evaporator from which ensues the vapour that is then superheated and directed to the compressor to complete the flow cycle.

2.2 - Transcritical two-stage CO\textsubscript{2} cycle with intercooling.

Fig. 2 Schematic diagram of the two stage heat pump cycle with intercooling.

Figure 2 shows the two stage CO\textsubscript{2} transcritical heat pump cycle with intercooling used. Here the saturated working fluid of state 2 moves from the evaporator into the low pressure (LP) compressor where it’s compressed to state 3 before it enters the intercooler. There takes place the cooling, by external fluid, of the vapour which increases the mass of CO\textsubscript{2} vapour entering the high pressure
(HP) compressor. Ambient air is taken as the external fluid. The saturated vapour from the intercooler at state 4 is compressed to state 5 and afterwards the super-critical vapour is cooled in the gas cooler to state 6. CO$_2$ vapour is further cooled in the internal heat exchanger to state 7. CO$_2$ then expands in the expansion device to state 8 and evaporates to state 1 producing cooling effect. The internal exchanger in the system exists for system thermal efficiency improvement [14].

2.3 - Thermodynamic analysis

2.3.1 - Single stage cycle

Based on the known equations for the exergy and energy analysis [16-18] of a heat pump cycle, as the one shown in Figure 1, we have:

The exergy efficiency factor is

$$\zeta = \text{COP} \left( \frac{T_w - T_a}{T_w} \right).$$  \hspace{1cm} (1)

with the coefficient of performance (COP) of the system being

$$\text{COP} = \frac{q}{\Delta e_{\text{abs}} + \sum \Delta e_{\text{loss}}} = \frac{(h_2 - h_4)}{(h_2 - h_4) \left(1 - \frac{T_a}{T_w}\right) + \sum \Delta e_{\text{loss}}}.$$  \hspace{1cm} (2)

Exergy losses, for each component of the system are:

- Compression losses:

$$\Delta e_{\text{comp}} = T_a (s_2 - s_1)$$ \hspace{1cm} (3).

- Additional losses due to the compressor motor:

$$\Delta e_{\text{mot}} = w \frac{1 - \eta_{\text{mot}}}{\eta_{\text{mot}}} \frac{T_a}{T_w},$$ \hspace{1cm} (4)

where $\eta_{\text{mot}}$ is the compressor motor efficiency factor, $w$ the specific compression power demand ($h_2 - h_1$) and the heat from the heat pump motor absorbed by the heated substance [17].

- Condensation / gas cooler losses:

$$\Delta e_{\text{cond}} = (h_2 - h_4) \frac{T_a}{T_w} - T_a (s_2 - s_4).$$ \hspace{1cm} (5)

- Evaporation losses:

$$\Delta e_{\text{evap}} = T_a (s_i - s_3) - (h_1 - h_5).$$ \hspace{1cm} (6)

- Throttling (isenthalpic process) losses:

$$\Delta e_{\text{thr}} = T_a (s_5 - s_4).$$ \hspace{1cm} (7)

Therefore, summing up we obtain the total exergy loss:
\[ \sum \Delta e_{\text{kins}} = \Delta e_{\text{comp}} + \Delta e_{\text{mot}} + \Delta e_{\text{cond}} + \Delta e_{\text{evap}} + \Delta e_{\text{thr}} = (h_3 - h_1) + \left[ (h_2 - h_4) + (h_2 - h_1) \frac{1 - \eta_{\text{mot}}}{\eta_{\text{mot}}} \right] \frac{T_a}{T_w} \]  

(8)

The exergy efficiency factor is consequently given by the equation (1):

\[ \zeta = \frac{(h_2 - h_4)(1 - \frac{T_a}{T_w})}{(h_2 - h_1) \left(1 + \frac{1 - \eta_{\text{mot}}}{\eta_{\text{mot}}} \frac{T_a}{T_w} \right)}. \]  

(9)

The refrigerants compared to R74 are R407C and R410A and R22.

A variety of sources were used [19-25] to ensure the consistent application of property. The differences observed were minimal. It is taken into consideration in all relevant calculations the fact that R407C and R410A are non-azeotropic, since they show a different behaviour from pure substances as it is presented by Smith and Van Ness [26].

Firstly, due to different evaporator and condenser inlet/outlet temperatures, we have to select condenser inlet temperature in opposition to the warm space temperature taking care of the condenser inlet and outlet temperatures to be sufficient so as to reject heat and finally liquid enthalpy at the expansion device and related property data being in position to achieve the suitable evaporator inlet temperature. The fluid behaves normally in all other points. Undeterred by the fact that this method of evaluation occupied in this study is not fully representative of a dynamic operation of a heat pump system, yet it sets up the foundations for understanding its thermodynamic performance.

3.2.2 - Two stage cycle

The two-stage CO2 transcritical heat pump cycle with intercooling is modelled modularly incorporating each individual process of the cycle. The state points in Figure 2 are defined as the conditions of the refrigerant characterized by its temperature, mass flow rate and quality.

Exergy losses, for each component of the system are:

- **Compression losses:**
  \[ \Delta e_{\text{comp}} = \Delta e_{\text{comp1}} + \Delta e_{\text{comp2}} = T_a (s_3 + s_5 - s_2 - s_4) \]  
  \[ \quad \text{(10).} \]

Additional losses due to the compressors motors:

\[ \Delta e_{\text{mot}} = w \frac{1 - \eta_{\text{mot}}}{\eta_{\text{mot}}} \frac{T_a}{T_w}, \]  

where \( \eta_{\text{mot}} \) is the compressors motor efficiency factor, \( w \) the specific compression power demand \( (h_5 - h_4 + h_3 - h_2) \) and the heat from the heat pump motor absorbed by the heated substance.

- **Intercooler losses**
  \[ \Delta e_k = (h_3 - h_s) \frac{T_a}{T_w} - T_a (s_3 - s_4). \]  
  \[ \quad \text{(12).} \]

- **Gas cooler losses**
  \[ \Delta e_c = (h_5 - h_6) \frac{T_a}{T_w} - T_a (s_5 - s_6). \]  
  \[ \quad \text{(13).} \]
Evaporation losses:
\[ \Delta e_{\text{evap}} = T_s (s_1 - s_8) - (h_1 - h_8). \]  

Expander valve (isenthalpic process) losses:
\[ \Delta e_{\text{ex}} = T_s (s_8 - s_7). \]

Internal heat exchanger:
\[ \Delta e_{\text{he}} = T_s [(s_7 - s_6) - (s_1 - s_2)]. \]

Therefore, summing up we obtain the total exergy loss:
\[ \sum \Delta e_{\text{loss}} = \Delta e_{\text{comp}} + \Delta e_{\text{mot}} + \Delta e_{\text{ge}} + \Delta e_{\text{evap}} + \Delta e_{\text{he}} = (h_3 - h_1) + \left[ (h_3 - h_4 + h_5 - h_8) + (h_5 - h_4 + h_3 - h_2) \right] \frac{1 - \eta_{\text{mot}}}{\eta_{\text{mot}}} \frac{T_s}{T_w}. \]  

The exergy efficiency factor is consequently given by the equation (1):
\[ \zeta = \frac{(h_3 - h_4 + h_5 - h_8)(1 - \frac{T_s}{T_w})}{(h_5 - h_4 + h_3 - h_2) \left( 1 + \frac{1 - \eta_{\text{mot}}}{\eta_{\text{mot}}} \frac{T_s}{T_w} \right)}. \]

### 2.4 - Assumptions

It is renowned that CO2 refrigeration and air conditioning systems shows cooling COP more sensitive to ambient temperature variation than conventional systems, being therefore superior at sensible and low ambient temperature, and to some extent poorer at very high temperature. Consequently, it would be deceptive to base a comparison of CO2 with the other refrigerants on design point conditions, which typically are at an extreme ambient temperature while the use of average seasonal conditions is wiser [27].

Our exergy efficiency, COP and exergy losses diagrams of the mixtures under consideration are schematized in comparison with the CO2 and are plotted based on calculations, having taken into consideration the following assumptions:

- The environmental temperature (Ta) is equal to 273 K [17, 28], while the temperature of the warm place (T_w) is considered 308 K [29]. The temperatures Tcon and Te are taken: Tcon at the inlet of the condenser at the vapour saturation curve for R22, R407C and R410A and at the inlet of the gas cooler for R744, while Te at the exit of the evaporator in the superheat region. Pressure drops in evaporator are for R22 [30] and R407C [31, 32] 135 kPa, for R410A [33] 85 kPa and for R744 [34] 100kPa, while during condensation the pressure drop varies for R22 [30] from 46 to 52 kPa, for R407C [31,32] from 40 to 46 kPa and for R410A [32, 33] from 32 to 35 kPa, lessening with increasing condensation temperature; whereas correspondingly for R744 [29, 35] the already small (1 to 3 kPa as shown in [36]) pressure drop during cooling process of supercritical CO2 decreases as inlet pressure of gas cooler increases having a temperature glide of approximately 61K [29]. In addition the isentropic compressor efficiency factor is chosen as 0.75 and the compressor motor efficiency factor as 0.85 in an endeavor to maintain a logical price for the evaluation.
- The evaporator temperature (Te) is taken as 263K for all condensing temperatures whilst condensation temperature (Tcon) for the mixtures and the outlet temperature of the CO2 gas cooler is ranging from 313 to 328 K. Accordingly the temperature ratio \( \tau = (T_{\text{con}}/T_{\text{e}}) \) or \( \tau = (T_{\text{gc}}/T_{\text{e}}) \) varies within the range of 1.19 to 1.25.
The featured two-stage CO2 transcritical cycle configuration is solely a theoretical one to present the basis for performance comparison with other refrigerants. It is simulated and its performance is evaluated on the basis of maximum combined COP to obtain the optimum gas cooler and in-between pressures. These values are obtained for various operating conditions along with simultaneous variation of the compressors discharge pressure and intermediate pressure having a step size of 0.5 bar for each. The performance is evaluated on various evaporator temperatures Te from 223 K to 243 K) and gas cooler outlet temperatures Tgc (308 K to 333 K) [37].

3. Results and discussion

The results attained in this analysis are comparison of refrigerants for exergy efficiency, COP and exergy losses (Figures 3 to 5). Properties of R22 are illustrated in plots by bold continuous lines, while R407C by thin discontinuous lines, R410A by thin continuous lines, R744 (single stage) by dotted lines and R744 (two stage) bold dotted lines.

Figure 3 shows the exergy efficiency factor as a function of temperature ratio $\tau$. Exergy efficiency decreases when the temperature ratio $\tau$ increases. The curves’ hollows are facing upwards.

The single stage heat pump working with R744 has the least favourable exergy behaviour with an exergy efficiency of 13% at the temperature ratio of $\tau = 1.25$ and 28% at the temperature ratio of $\tau = 1.19$. While the R744 of the two-stage transcritical heat pump features far better exergy performance compared to the latter, with an exergy efficiency of 31% at a temperature ratio of $\tau = 1.25$ and 38% at a temperature ratio of $\tau = 1.19$, demonstrating less variation on its performance with the change of temperature ratio.

R22, on the other hand, presents the best exergy behaviour of all with an exergy efficiency of 42% at a temperature ratio of $\tau = 1.19$ and 33% at $\tau = 1.25$, followed by R407C ($\zeta = 41\%$ at $\tau = 1.19$ and $\zeta = 32\%$ at $\tau = 1.25$) and R410A ($\zeta = 40\%$ at $\tau = 1.19$ and $\zeta = 29.5\%$ at $\tau = 1.25$).

Figure 4 shows the disparity of COP of the heat pump system for each working refrigerant related to the temperature ratio $\tau$, decreasing while the latter lifting as exergy efficiency factor does. COP ranges from 1.05 at temperature ratio of $\tau = 1.19$ (for R744) to 3.77 (for R22) at $\tau = 1.19$. There is a pointed increase in COP for the two-stage R744 system compared to the single stage one. Here, the single stage working R744 has likewise the worst behaviour, with COP to vary between 2.48 (at $\tau = 1.19$) and 1.15 (at $\tau = 1.25$), whilst the R744 of the two-stage transcritical heat pump features once more better comportment, with COP fluctuating amid 3.40 (at $\tau = 1.19$) and 2.70 (at $\tau = 1.25$).

The optimum performance is displayed yet again by R22, with COP of 3.67 at a temperature ratio of $\tau = 1.19$ and 2.88 at $\tau = 1.25$, followed by R407C with COP of 3.70 at a temperature ratio of $\tau = 1.19$.
and 2.74 at $\tau=1.25$ and R410A with COP of 3.57 at a temperature ratio of $\tau=1.19$ and 2.58 at $\tau=1.25$. R22 may seem more attractive to use from the efficiency aspect, however we have to bear in mind that it constitutes a harmful effect on the ozone layer with the result of extreme UV levels conducing to further environmental damage and several deadlines have been arranged depending on the country for complete R22 replacement in accordance to the terms established by the Montreal Protocol meetings.

The prices for COP and exergy efficiency factor are in agreement with those of Robinson and Groll E.M. [39] at the equivalent conditions’ region.

![Fig.4 Variation of COP for various temperature ratios](image)

Figure 5 presents the percentage of the major exergy losses for the two CO$_2$ systems. These are of the gas cooler and of the compressor and we can conclude that for the two stage CO$_2$ transcritical cycle the losses lessen dramatically. For the single stage heat pump working with R744 the compressor accounts for approximately 49% of the total cycle irreversibility and the gas cooler for the 25%, while respectively the percentage of exergy losses in the two-stage transcritical heat pump is 32% for the compressor and 20% for the gas cooler.
Fig. 5 Exergy losses of the systems’ components

As pointed out by Dincer and Rosen [15] “Exergy efficiency weights energy flows by accounting for each in terms of availability. It stresses that both losses and internal irreversibilities need to be dealt with to improve performance” and by Moran and Shapiro [38] “Exergy analysis is particularly suited for furthering the goal of more efficient energy use, since it enables the locations, types, and true magnitudes of waste and lost to be determined”. Following the above described study the behaviour of the system can be improved, minimising individual exergy loss of each component and maximising efficiencies. Compressor efficiency is a major factor in enhancing the performance of the system, the smaller the compressor, the more prominent the compression losses. Generally speaking throttling losses can be reduced minimising the temperature difference before and after the throttling valve, as well as by decreasing the temperature differences in evaporator and condenser. This would also produce lower compression losses.

4. Conclusions

In this report we have made an effort to elucidate the diversity of the alternatively used refrigerant mixtures R407C and R410A replacing R22, and R744 replacing all of them in the field of exergy efficiency, COP and exergy losses depending on temperature ratio $\tau$, for constant warm place temperature. The best exergy behaviour of all is presented by R22, with an exergy efficiency of 42% at a temperature ratio of $\tau=1.19$. R744 may seem to fall short in comparison to the rest refrigerants for some conditions, nevertheless it is the most environment friendly of all and based on that and on its beneficial potentialities its use signifies a “new” ecological era for the field. As stated before, one of the downsides associated with transcritical cycles is that the system operates at a very high discharge pressure. There is a sharp reduction in optimum discharge pressure by adopting staging in compression. Inter-stage pressure is one of the most critical parameters for optimizing COP values. Moreover, by using highly efficient system components, the transcritical two-stage CO2 systems can be used more effectively. Two-stage transcritical heat pump working with R744 features far better exergy performance compared to the single stage cycle with a pointed increase in
COP for the two-stage R744 system. Furthermore for the two stage R744 transcritical cycle the losses lessen dramatically.

The evolution of exergy efficiency factor and COP are illustrated and collated in diagrams so as to clarify the differences of alternative refrigerants more accurately.

**Nomenclature**

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<th>Description</th>
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<td>Specific heat at constant pressure</td>
<td>(kJ kg$^{-1}$ K$^{-1}$)</td>
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<tr>
<td>$e$</td>
<td>Specific exergy</td>
<td>(kJ kg$^{-1}$)</td>
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<td>$h$</td>
<td>Enthalpy</td>
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<td>$w$</td>
<td>Specific compression power demand</td>
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**Greek symbols**

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<td>Compressor motor efficiency factor</td>
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<td>$\tau$</td>
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**Superscripts**

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**References**


Exergy Analysis of a CO2 Recovery Plant for a Brewery

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Abstract:
A large number of new and old breweries around the world experience increasing energy cost associated with the production of beer. Large heating and cooling demands in the brewing process and a wide use of utilities for assisting the processes necessitate a detailed analysis of individual efficiencies for processes and the different utility plants.

One considerable utility plant is the CO2 recovery plant, which purifies/purges the CO2 generated in the fermentation process in order to reuse it in the brewery site or sell it to customers who demand high quality CO2.

In the paper a detailed model of a 2000kg/h CO2 recovery plant for a brewery is presented, which is a typical plant capacity for a large CO2 self-sufficient brewery. The model includes all significant unit operation in the CO2 plant and a complete mass and energy balance of it.

In order to prevent hidden loads and misleading analysis; the system is modeled as a final supplier solution, which is initially considered without heat and recovery integration even though this is commonly used. The following steps are presented. First step introduces the process and the component appearance followed by the energy requirements and corresponding loads. Consumptions and loads are compared with an existing plant at a corresponding capacity and are validated.

Energy and exergy analysis are used in order to illustrate the performance of each individual system component of the CO2 recovery plant.

A schematic overview of all exergy flows including destruction is presented and proves a clear understanding of the exergy inefficiencies associated with the plant.

The highly detailed and validated model enables and prepares different holistic methodologies and analyses to be used, including thermoeconomic diagnosis and optimization of plant set points.

Keywords:
Exergy analysis, Grassmann diagram, CO2 recovery plant, utility plant.

1. Introduction

Many breweries all over the world contain a CO2 recovery system in order to collect the generated CO2 from the fermentation process and exploit it for the process use. Energy requirements have been investigated in several breweries in order to determine overall electric and thermal demands, e.g. using pinch analysis in order to design the optimal heat exchanger network [1]. Even manual power, such as physical human work has been converted into exergy and included in the analyses [2]. Further evaluations have presented data for exergetic inefficiencies in the various parts of the production lines and comparison with other production sites [1].

1.1 Process description

This study examines a CO2 recovery plant in the application of a brewery. The plant capacity is 2000 kg CO2 per hour, designed for a typical brewery in the size of 4 million hectoliter of beer per year.
The recovery process is composed of three parts: (1) compression and purification processes, (2) stripping and condensing process finally followed by (3) a pressure storage and evaporation of the CO$_2$ for use in the production. A cooling facility is assisting the CO$_2$ plant.

### 1.1.1 Compression and purification processes

A schematic diagram is shown in Figure 1. CO$_2$ is produced during fermentation of the beer and with a small overpressure it reaches the recovery plant first arriving in the foam trap which discards possible visible gas impurities such as foam generated during fermentation. Water soluble impurities (mainly alcohol) are removed in the water scrubber and the CO$_2$ is lead to the balloon as a buffer supplying the following two-step-compressors containing inter- and after cooler and dehumidifier. Here the CO$_2$ has reached a relatively high pressure close to 20bar. After the compression odours are removed in the carbon filters followed by drying the CO$_2$ to a dew point of -60°C in the dehydrator. The carbon filters and dehydrators are regenerated by an electric heating element and by CO$_2$ purge gas or air.

![Figure 1: CO$_2$ compression and purification processes followed by stripping and liquefaction.](image)

### 1.1.2 Stripping and liquefaction process

Purified CO$_2$ enters the reboiler for the stripping column in which it is precooled before liquefaction in the CO$_2$ condenser at temperature down to -25°C. Here the CO$_2$ is condensed to the reflux tank and inert gas is separated and discharged to the surroundings.

Liquid CO$_2$ is pumped to the top of the stripping column, where further reduction of oxygen and inert gas is obtained. From the bottom of the column liquid CO$_2$ is partly pumped to the storage tank and partly circulated through the reboiler which heats the column and herby ensure continuous evaporation. For the simplest plant setup the CO$_2$ is finally led through a steam heated evaporator before entering the production site, which means that the cooling potential is not utilized due to time constraints.

### 1.1.3 Low temperature cooling facility

Figure 2 shows how the cooling demand is supplied to the CO$_2$ plant. An ammonia cycle supplies the CO$_2$ condenser and dehumidifier with cooling at two different stages, which are separated in an economizer. Heat removal from the ammonia condenser is done by a water cycle assisted with a cooling tower that furthermore supplies the inter cooler and after cooler with cooling.
**Figure 2: Cooling facility for the CO₂ liquefaction.**

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<thead>
<tr>
<th>CO₂ process:</th>
<th>NH₃ cycle:</th>
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<td><strong>After component:</strong></td>
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<td>CO₂ compressor step 2</td>
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<td>Dehydrator</td>
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<td>Storage pump</td>
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<td>CO₂ expansion</td>
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<td>CO₂ evaporator</td>
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</table>

**Table 1: Operation states for the CO₂ recovery plant.**

### 2. Methodology

An exergy analysis has been performed on a CO₂ recovery plant. The process setup is shown in Figure 1, while states throughout the process is shown in Table 1.

#### Assumptions

The following studies have been done on basis of the following assumptions:

- The system operates steady state at maximum capacity.
- Electricity consumed due to regeneration of filters is included due to a time average approach.
- Component efficiencies and heat transfer coefficients do not vary with pressure, temperature or mass flow.
- Only pressure drops in heat exchangers and filters are taken into account, while remaining pressure drops and thermal losses are neglected. E.g. heat transfer to the storage tank is neglected. This loss will cause an extra load in the CO₂ condenser, due to the fact that CO₂ gas is rejected from the tank to the condenser supply line.
- All compressors are cooled by cooling water from the same stream as for the following coolers (inter cooler, after cooler, NH₃ condenser).
- The stripping column is regenerative. It is therefore assumed that the stream out of the reboiler is pure gas and corresponds (due to mass and state) to the evaporation from the stripping column.
It is estimated that the incoming CO$_2$ contains 4.2% gaseous water. Chemical exergy in the CO$_2$ is neglected due to the fact that its impact is less than 0.1%.

**Data validation and solution procedure**

Simulations have been made in DNA [3] (Dynamic Network Analysis) which is an open source simulation software [4]. It contains a list of standard components that in this case fulfills the modeling requirements.

Operating parameters, such as compressor isentropic and mechanical efficiencies, pressure drop in heat exchangers, operating states (temperatures and pressures) is all data from a specific plant setup. The simulation has been split into three parts. First part presents CO$_2$ containing water as a real gas in order to model the compression and condensing of water in the gaseous CO$_2$. Second part is a model for CO$_2$ as cooling media (R744) and it handles the condensing-, stripping- and evaporation process. Finally the cooling facility is modeled as an ammonia refrigeration cycle connected with a water cycle.

The stripping column is regenerative (not external heated), and therefore calculations are based on input and output data which is verified.

**Exergy analysis and entropy generation**

Exergy has the advantage that it valorizes energy as potential work and not only consider the mounts of energy available. An exergy analysis of the system will reveal component irreversibilities, which is an expression of entropy generation. This encourages determination of lost available work (or exergy destruction) for each component in the system and mapping of the disappearance of the work added to the system. This analysis provides a reasonable basis for optimizing the system design trough for example a thermoeconomic analysis [5].

For a system or a component only a given amount of work can be transferred to the output stream [6]. This originates in the entropy generation, of which the transferred work is given (1):

$$W = W_{rev} - T_0 \delta_{gen} \quad \text{(1)}$$

which leads to the relation of lost work (2) (the Guoy-Stodola Theorem) [6]:

$$W_{lost} = T_0 \delta_{gen} \quad \text{(2)}$$

Entropy generation may in some cases appear a bit abstract in order to understand and present lost work. The following representation of exergy is therefore used during the execution of an exergy analysis.

**Methodology for exergy analysis**

All exergy transfers in inlets and outlets, $E_i$ and $E_e$ are calculated in the model. The exergy of the given stream refer to the maximum theoretical work that can be obtained by bringing the stream to the dead state or environmental state ($T_0$, $p_0$). Exergy flow is determined on basis of the unit-of-mass exergy [kJ/kg], so called specific exergy (3) [5]. In the case we decide to neglect chemical exergy, because of its neglectable impact, this only represents the phisycal exergy.

$$e^{phys} = (h - h_0) - T_0(s - s_0) \quad \text{(3)}$$

Destruction of exergy is calculated by the exergy balance (4):

$$E_i = E_e + E_L + E_D \quad \text{(4)}$$
In which $E_L$ and $E_D$ describes the loss and destruction respectively. For the major part of the components in the respective model, lost streams are not utilized and therefore included as a part of the destruction according to the system.

Destruction will be considered for each component and can be expressed in different ratios. One useful ratio is of the total destruction in the plant (5):

$$y_D^* = \frac{E_D}{E_{D,tot}}$$  \hspace{1cm} (5)

Another representation of the destruction, which is used in this paper, is destruction as a ratio of total fuel input (6):

$$y_D = \frac{E_D}{E_{F,tot}}$$  \hspace{1cm} (6)

This is in order to have the same reference when comparing with exergy streams relatively. For example exergy losses are likewise determined as a rate of the total fuel input (7).

$$y_L = \frac{E_L}{E_{F,tot}}$$  \hspace{1cm} (7)

The final product leaves the plant as requested in the production site. The exergy content of the product stream leads to determine the overall exergy efficiency for the plant (8).

$$\eta_{II} = \frac{E_{product}}{E_{F,tot}}$$  \hspace{1cm} (8)

In cases where the exergy of the final product is equal to the ambient, it may be more evident to focus on the destruction in each component in order to reduce the overall efficiency.

**Grassmann diagram for CO$_2$ recovery plant**

A Grassmann diagram shows a graphical representation of the exergy development throughout the process. The so called exergy diagram illustrates all exergetic inputs and outputs for the entire plant – both the CO$_2$ recovery process and cooling facility.

Exergy inputs and outputs related to the product streams, power inputs, waste streams and exergy interactions due to heat exchangers determines the destructions. All these are shown for each incorporated component in the diagram.

This exergy flow representation provides a valuable overview of the plant details which energy considerations alone cannot accommodate. It locates/pinpoint destruction of exergy and may provide better knowledge in order to improve the overall performance in a CO$_2$ recovery plant [7]. A Grassmann diagram of the investigated CO$_2$ recovery plant is shown in Figure 7.

### 3. Results

**Energy demand for the isolated CO$_2$ recovery process**

Figure 1 shows the energy demands for the isolated CO$_2$ recovery process, i.e. without the cooling facility. It appears that the total energy consumption is 767kW, contributed by cooling, heating and electricity with a share of 51.6%, 24.6% and 23.8% respectively.

The majority of electricity is consumed in the CO$_2$ compressors, while a minor part is consumed due to pumps and regeneration of filters.

A little more than half of the consumption is related to a cooling demand. Apparent is the cooling needed for CO$_2$ condensing, which contributes with 25% of the total consumption. A similar
amount of cooling demand is needed in order to remove the heat generated due to the compression stages. Out of these 205kW it appears that 15% are expended on condensing water due to humidity. After the recovery process the CO₂ is delivered to the production as gas at a reduced pressure. This expansion generates a cooling effect that has to be removed corresponding to another 25% of the total energy demand.

![Energy demands for the isolated CO₂ recovery process.](image)

**Figure 3: Energy demands for the isolated CO₂ recovery process.**

*Exergy expenditure in the isolated CO₂ recovery process*

Converting the previous energy demand analysis into an exergy consideration of input and output exergy streams (cf. Figure 4), the following is observed:

- Total exergy input/output is 220kW.
- Electricity consumption remain unchanged, thus its share of the total consumption increases.
- The large cooling consumption for the CO₂ condenser (190.8kW) is strongly reduced to 20% (37.3kW) due to the exergy perspective.
- Cooling in the inter cooler, after cooler and dehumidifier are all above ambient temperature, which in the exergy perspective has been added to the output as a hot waste stream. Accordingly the energy flow (205kW) reduces to 9.6% (19.7kW) exergy.
- Evaporation of CO₂ is added as an output stream because of its cooling potential. This stream is also reduced (from 188.5kW energy) to 36% (67.3kW) when based on exergy.
- The CO₂ product appears to leave the plant containing 23.1% of the total exergy.
- Finally the exergy destruction occurs due to lost streams and other thermal irreversibilities. This share represent 58.9kW corresponding to 26.7% of the total output exergy.

![Exergy expenditure in the isolated CO₂ recovery process.](image)

**Figure 4: Exergy expenditure in the isolated CO₂ recovery process.**
Energy demand for the entire CO$_2$ recovery plant

Considering the demand in the existing CO$_2$ recovery plant setup (Figure 5) the supply of cooling facility increases the consumption by 30% which results in a total energy consumption of 991kW. The heating demand remains constant while the electricity consumption is extended by an ammonia compressor of 110kW. The cooling demand keeps its share of 51%. All 507kW cooling of the plant is placed in a cooling tower.

![Energy demand for the entire CO$_2$ recovery plant](image)

Figure 5: Energy demands for the entire CO$_2$ recovery plant.

Exergy expenditure for the entire CO$_2$ recovery plant

Figure 6 shows the input and output exergy streams for the entire plant and the following can be observed:

- Total exergy input/output is 358kW.
- Electricity still remains unchanged, but as a major part, 83% of the exergy input, while the heating demand (of 188.5kW) is replaced by steam consumption reduced to 32% (61.2kW) exergy.
- The exergy output of CO$_2$ remains unchanged and has a share of 14.2%.
- Cooling demand of 507kW is all rejected in the cooling tower as heat just above the ambient temperature, which reduces to 2.2% (7.7kW) exergy of waste heat and becomes a part of the exergy destruction.
- Due to the steam input a small amount of 2% exergy is leaving as return condensate.
- As much as 82.6% of the exergy output disappears as thermal irreversibilities and streams that are being discharged to the environments.

![Exergy expenditure for the entire CO$_2$ recovery plant](image)

Figure 6: Exergy expenditure in the entire CO$_2$ recovery plant.
The consumption of the pressurized CO\textsubscript{2} in the production site and return of condensate to a given boiler results in an overall exergy efficiency for the CO\textsubscript{2} recovery plant of 0.15. However utilization of the cooling potential due to the CO\textsubscript{2} evaporation would increase the exergy efficiency to 0.5.

Figure 7: Grassmann diagram of the exergy flows in a CO\textsubscript{2} recovery plant complemented by cooling facilities.

**Exergy appearance in CO\textsubscript{2} recovery plant in details**

Figure 7 shows the exergy formation throughout the recovery plant and Figure 8 describes the exergy destruction in each single component as a ratio of the total fuel input. The following observations are made:

**CO\textsubscript{2} process**

- As long as the cooling potential due to CO\textsubscript{2} evaporation and the waste heat streams are not utilized, the total exergy destruction associated with the recovery plant becomes 85% (303kW), of the total fuel exergy input of 357kW.
- 35% of the input exergy is destroyed due to the CO\textsubscript{2} evaporation, which is a result of using steam containing a high exergy value in order to heat the low temperature CO\textsubscript{2} that also has high exergy content as cooling potential.
Due to the compressor inefficiencies 10.1% of the total exergy input is destroyed. Waste heat after the two compression steps is generated, even though 11.2% of the exergy input is disposed by cooling water. The following dehumidifier causes another 0.4% of destruction. Temperature difference between NH3 and CO2 in the CO2 condenser carries 3% destruction of the input exergy. Minor exergy destruction is the CO2 expansion of 1.4%. Regeneration of carbon filter and dehydrator entails 1.9% and the reboiler 0.6%. Finally to be mentioned is the blow off loss stream that carry another 1.6% of the input exergy.

**Cooling facility**

Inefficiencies in NH3 compressor induces 7% destruction, while the heat generated and disposed in the NH3 condenser carries 8.4% of the total exergy input. Only 2.1% is destroyed in the cooling tower in spite of the relatively large heat disposal (Figure 5). The exergy destruction connected to this large amount of energy is placed in the local heat exchange such as NH3 condenser, inter cooler and after coolers. Finally some minor destructions are found due to expansion valves, pump inefficiencies and mixing of medias containing different temperature levels.

**Figure 8: Exergy destruction in each component as a ratio of the total fuel input.**

Evaluation of the cooling plant shows that the ammonia refrigeration cycle contributes with 200kW cooling of energy, in which 191kW and 9kW is located in the CO2 condenser and dehumidifier respectively.
The total electricity input is 110kW which gives a COP of 1.81. Reconfiguration of temperatures may lead to less exergy destruction and therefore higher energy efficiency. By increasing the evaporation temperature both COP will increase and less exergy destruction in the evaporator (CO₂ condenser) is obtained.

The total cooling load of the entire cooling system (including the water cycle) is 396kW of energy which lead to a COP of 3.5. What is relevant to notice is the introduction of circulation of water, which transports and disposes heat from above ambient temperature to the ambient through a cooling tower.

In order to reduce the exergy destruction the operating temperatures in the NH₃ cycle may be analyzed.

4. Discussion

The major sinner of the plant turns out to be the CO₂ evaporator that destroys 35% of the total exergy input. CO₂ should obviously not be evaporated by steam (according to an energy/exergy perspective). Apparently, the cooling potential associated with the CO₂ expansion has to be utilized. In order to exploit most of the refrigeration potential as possible, it is necessary to locate low temperature cooling demands. Since the condensing of the CO₂ involves the lowest temperature demands in the brewery the evaporation may be utilized in order to cool the CO₂ condenser – directly or indirectly. Due to time constraints between production and consumption of CO₂, it may be necessary to introduce thermal heat storage (sensible or latent).

Almost 10% of the total exergy input is destroyed due to thermal degradation in the ammonia condenser. A reduction of the condensing temperature or an exploitation of this excess heat may therefore be important in order to obtain a reduction in the total energy consumption of a brewery. Moreover, excess heat corresponding to 11.1% of the exergy input is destroyed in inter- and after cooler, of which 15% is due to condensing of water. A reduction of the water content in the incoming CO₂ will accordingly contribute in the reduction of cooling demand.

Compressor inefficiencies represent 17.1% destruction of the total exergy input, which encourage investigating the technical and economic feasibility in using more efficient compressors.

The analysis performed enables a thermoeconomic analysis on the system design and further evaluation of optimal operating set points.

5. Conclusion

An analysis of energy demands for the CO₂ recovery process has been made, which gives a good foundation for determining capacities/plant dimensions for cooling facilities, heat- and power supply. The analysis has been extended by an exergy analysis in which it turns out to be more representable to illustrate some demands, such as the waste heat and cooling potential (CO₂ expansion) as output streams rather than input streams. This enables a more detailed analysis of the energy consumption and utilization through the plant.

The same has been concluded in a corresponding analysis for the entire plant setup.

An exergy analysis has been performed on a complete CO₂ recovery plant setup and presented in a Grassmann diagram in which amounts of input and output exergies are shown graphically. This presentation improves the understanding of the exergy (or value of energy) appearance in the process.

A schematic overview of all exergy output including destructions has been presented as a ratio of the total exergy input. This provides a clear understanding of the exergy inefficiencies associated with the plant – in other words a description of where the valuable energy disappear in the system.
The major contributors to the exergy destruction constitute of the CO\textsubscript{2} evaporation (35% of the total exergy input), followed by the temperature degradation of generated heat due to compression of CO\textsubscript{2} and NH\textsubscript{3} and destruction associated with compression irreversibilities.

**Acknowledgement**

Union Engineering is acknowledged for sharing data for plant setup and operational states.

**Nomenclature**

- **$\tilde{e}_p****: physical specific exergy
- **$\tilde{E}_D$**: Exergy destruction
- **$\tilde{E}_{D,\text{tot}}$**: Total exergy destruction
- **$\tilde{E}_e$**: Exergy output
- **$\tilde{E}_{F,\text{tot}}$**: Total fuel exergy input
- **$\tilde{E}_i$**: Exergy input
- **$\tilde{E}_l$**: Exergy loss
- **$\tilde{E}_{\text{product}}$**: Exergy in product
- **$\tilde{S}_{\text{gen}}$**: Entropy generation
- **$\tilde{W}$**: Work
- **$\tilde{W}_{\text{rev}}$**: Reversible work
- **$\tilde{W}_{\text{lost}}$**: Lost work
- **$\gamma_D$**: Destruction ratio of the total input
- **$\gamma_{D'}$**: Destruction ratio of the total exergy destruction
- **$\gamma_L$**: Exergy loss as ratio of the total exergy input
- **$\eta_{II}$**: Second law efficiency

**References**


Exergy analysis of the silicon production process

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Abstract:
We present an exergy analysis of the theoretical silicon production process and for two cases of an industrial process. The theoretical process is a first effort to establish a reference case for the silicon production process.
In the theoretical process we consider the process with pure reactants and stoichiometric reactions. The industrial process is evaluated for the case of no power production and power production using a steam turbine and generator equipment in the off-gas system. For the theoretical process we find that the exergetic efficiency is 47.5% for a silicon yield of 1 while utilization of thermal exergy in the off-gas increases the exergetic efficiency to 58.6% and 67.4% for off-gas temperatures of 300\textdegree C and 800\textdegree C, respectively. The exergetic efficiency for the industrial process is estimated to 30.8% and 38.9% for the case of no power production and power production, respectively.

Keywords:
Exergy analysis, Exergetic efficiency, Silicon production process.

1. Introduction

According to the International Energy Agency [1], the industrial sector accounted for 40% of the total global power consumption in 2009. To increase the efficiency of resource utilization in industrial processes is thus a benign and substantial route to address environmental concerns and energy security.

Exergy analysis of a process as it is operated today is a first step towards a resource efficient process. The exergy analysis method combines the first law (conservation of energy) and second law of thermodynamics (degradation of energy) in the analysis of thermal, mechanical and chemical systems. It determines the locations, types and magnitudes of waste and losses and therefore it is particularly well suited for evaluating a process in terms of resource utilization. The exergy analysis method is an established method described in several textbooks, see e.g. [2, 3].

Silicon and its alloys (high in silicon content) are produced by carbothermic reactions in submerged arc furnaces which require high temperatures. Such are reached by adding large amounts of electric energy. Most plants use 11-13 kWh per kilogram of silicon metal produced [4]. An exergy analysis of a ferrosilicon furnace at an Elkem plant on Iceland published in 2009 [5] showed that 70% of the total exergy put into the furnace is lost. Thus, the \textit{exergetic efficiency}, defined as the ratio of the exergy in the product and the exergy used in the process, was 30%. The analysis showed that almost half of the total exergy input is lost in the furnace. Around one fifth is lost with the off-gas.

The theoretical upper limit for the exergetic efficiency is unity. In practice, lower limits apply as all real processes are associated with irreversibilities, e.g. uncontrolled chemical reactions. To explore
a practical limit of a process is of interest as it gives a more realistic figure on the real potential for process improvements.

We present an exergy analysis of the theoretical silicon production process and for two cases of an industrial process. The theoretical process is the process with pure reactants and stoichiometric reactions; it covers the main features of an industrial process and it is a first effort to establish a reference case for exergy analysis of the industrial process.

1.1 Production of silicon

Silicon is commercially prepared by reduction of silicon dioxide with carbon in a submerged arc furnace (SAF); a schematic drawing illustrating the process is given in Fig. 1. The illustration shows the furnace surrounded by raw material - and power supply system, off-gas removal - and heat recovery equipment, tapping, casting and crushing.

![Fig. 1. Schematic drawing illustrating a typical silicon production process [6]. Silicon is commercially prepared by reduction of silicon dioxide with carbon in a submerged arc furnace (SAF). The illustration shows the SAF surrounded by raw material and electrical power supply systems, off-gas and heat recovery equipment, tapping, casting and crushing of the product.](image)

The SAF is the heart of the silicon plant. The size of the furnace is characterized by the electrical power needed, which can be in the range from less than 10 MW to 45 MW. The raw materials, quartz and carbonaceous reduction materials (coke, coal, charcoal and woodchips), are fed to the furnace at the top, and are referred to as the charge material.

Production of silicon is an energy intensive process, requiring temperatures above 1800 °C. These temperatures are achieved by adding large amounts of electric energy. Liquid silicon is tapped from the bottom of the furnace. After tapping, the liquid is refined by slag treatment or gas purging. Then the liquid silicon is poured into suitable moulds, allowed to cool down and then crushed to the desired particle sizes.
The off-gas from the furnace reaction (SiO+CO) is mixed with excess air under the furnace hood and burned, captured into the gas-cleaning system and filtered. The off-gas temperature is controlled by the excess of air. Sometimes this parameter is shown as the ratio of the total off-gas volume and the furnace load ((Nm³/s)/MW load). The dust in the filter consists mainly of SiO₂ particles, also referred to as condensed silica fume, which can be used as filler material in concrete, ceramics, rubber etc. Since the off-gas escapes from the furnace hood at high temperatures (200 - 700 °C), it is suitable for electric energy production using a steam turbine and generator system.

2. Theory

2.2 Energy analysis

The energy balance for a control volume, assuming steady state and neglecting the contribution from kinetic and potential energy can be written as

\[ 0 = \dot{Q}_{cv} + \dot{W}_{cv} + \sum_i m_i h_i - \sum_e m_e h_e \]  

(1)

The first two terms on the right hand side is the heat and work added to the control volume and \( h \) is the specific enthalpy of the material stream \( m \). Subscripts \( i \) and \( e \) refer to inlet and outlet streams, respectively.

2.2 Exergy analysis

The exergy of a system is defined as the maximum work obtainable from the interaction between the system and an idealized system called the reference environment [3]. In this work, the reference environment takes the temperature and pressure \( T_0 = 25 \, ^\circ C \) and \( p_0 = 1 \, \text{atm} \) respectively. When doing an exergy analysis of a process, all energy streams entering and leaving the system are evaluated in terms of its exergy. The exergy balance for a control volume assuming steady state is

\[ 0 = \sum_j \left(1 - \frac{T_0}{T_j}\right) \dot{Q}_j + \dot{W}_{cv} + \sum_i m_i e_i - \sum_e m_e e_e - \dot{E}_D \]  

(2)

The first term on the right hand side can be interpreted as exergy accompanying transfer of thermal energy. The second term can be interpreted as exergy accompanying work. Further, \( e \) is the specific exergy of the stream of material \( m \) and \( \dot{E}_D \) is the exergy destruction.

The specific exergy of a stream of material (neglecting contributions from kinetic and potential energy) can be written as the sum of the physical and chemical exergy

\[ e = e^{PH} + e^{CH} \]  

(3)

The physical exergy is the maximum work obtainable as the system passes from its initial temperature and pressure, \( T \) and \( p \), to the temperature and pressure of the reference environment, \( T_0 \) and \( p_0 \). At \( T_0 \) and \( p_0 \), the system is said to be in the restricted dead state. The physical exergy is given by the expression

\[ e^{PH} = (h - h_0) - T_0(s - s_0) \]  

(4)

Here, \( h \) and \( s \) are the specific enthalpy and entropy at the system temperature and pressure, while \( h_0 = h(T_0, p_0) \) and \( s_0 = s(T_0, p_0) \).

The chemical exergy is the maximum work obtainable as the system at \( T_0 \) and \( p_0 \) comes into total equilibrium with the reference environment. The system is then said to be in the dead state.

Standard chemical exergy values based on standard exergy reference environment is tabulated, see e.g. [2]. The chemical exergy of a substance can be determined from:
\[ \overline{e}^{CH} = -\Delta G_0 + \sum_P n\overline{e}_P^{CH} - \sum_R n\overline{e}_R^{CH} \] (5)

Here \( \Delta G_0 \) is the change in the Gibbs energy for the reaction forming a substance from the reference substances at temperature \( T_0 \) and pressure \( p_0 \) and \( \overline{e} \) is the molar chemical exergy. The last two terms in (5) are evaluated from known standard chemical exergies. \( P \) and \( R \) refer to the products and reactants, respectively, and \( n \) is the number of moles.

The chemical exergy of an ideal mixture is determined from

\[ \overline{e}_{\text{mix}}^{CH} = \sum x_i \overline{e}_i^{CH} + RT_0 \sum x_i \ln x_i \] (6)

Here, \( x_i \) is the mole fraction of component \( i \) in the solution and \( R \) is the universal gas constant.

The exergetic efficiency, \( \varepsilon \), is used as a parameter for evaluating thermodynamic performance for the system [3]:

\[ \varepsilon = \frac{\text{exergy in product}}{\text{exergy used in the process}} \] (7)

3. Case studies

3.1 The theoretical silicon production process

The theoretical silicon production process is the process with pure reactants and stoichiometric reactions. It is described by Schei et.al in [4]. This simplified description covers the main features of the process as it is operated today. Therefore, it may be suitable as a reference case for the industrial process.

In the theoretical process, the overall process is divided into three subsystems; the submerged arc furnace, the gas treatment section and the product treatment section, see Fig. 2.

**Fig. 2.** A schematic diagram of the theoretical silicon production process showing the material and energy flows in the system. The theoretical silicon production process is described by Schei et.al in [4].
The submerged arc furnace:

Pure silicon dioxide and carbon (graphite) are added to the furnace together with electrical energy. The furnace reaction is described by the following equation

\[(1+x)\text{SiO}_2+(2+x)\text{C} = \text{Si} + x\text{SiO}_2 + (2+x)\text{CO}\]  

(8)

The enthalpy and the entropy of this reaction are positive. The theoretical amount of electrical energy needed to produce one mole of silicon is determined from the enthalpy of the furnace reaction. The amount of electrical energy added to the furnace is referred to as the furnace load.

There are no losses in the electrical supply system or thermal energy losses from the furnace to the surroundings. The gas leaving the top of the furnace consists of SiO and CO and it has a measured temperature of 1400 °C. Liquid silicon leaves the bottom of the furnace at a temperature of 1600 °C.

The silicon yield \(S\), where \(0 \leq S \leq 1\), is the amount of silicon in the quartz that goes to the silicon. It relates to the parameter \(x\) as

\[S = \frac{1}{1+x}\]  

(9)

Gas treatment section

The gas leaving the top of the furnace enters the gas treatment section where it is burned in excess air. The gas treatment section corresponds to the area under the furnace hood in a real furnace. The reaction in the gas treatment section can be described as

\[x\text{SiO}+(2+x)\text{CO}+m\text{O}_2+4m\text{N}_2 = x\text{SiO}_2 + (2+x)\text{CO}_2 + (m-x-1)\text{O}_2 + 4m\text{N}_2\]  

(10)

Here, \(m\) is the amount of oxygen introduced with air. The amount of excess air determines the temperature of the off-gas leaving the gas treatment section.

Product treatment section

In the product treatment section, liquid silicon at a temperature of 1600 °C and \(p = p_0\) solidifies and cools down to 25 °C. Silicon leaves the process at \(p = p_0\) and \(T_0 = 25°\text{C}\).

3.2 A submerged arc furnace operated at a Norwegian silicon plant

The industrial process is a 45 MW furnace operated at an Elkem Silicon plant in Norway. In 2010, Kamfjord et al. [7] published an energy balance for this furnace. We use their input data [8], scaled to a 10 MW furnace, to establish the energy balance (1) which we use to characterize the furnace. For this furnace, the control volume includes the furnace and the area under the furnace hood which is equivalent to the furnace and the gas treatment section for the theoretical process described above.

Energy enters the process as electrical energy and as enthalpy in the raw materials which is a mixture of coke, coal, charcoal, woodchips and quartz. Energy leaves the process as enthalpy in the product, cooling water and off-gas and by radiation and convection from the furnace, cf. (1). Typical composition of carbonaceous raw materials used in silicon production is given in Table 1.

In the calculations, we neglect the contributions from moisture and ash in the carbonaceous raw material and only take into account the contribution from fixed carbon, which is a measure of the solid combustion material in carbonaceous materials, and the volatile matter. The fixed carbon is pure graphite and we make a distinction between volatile matter contained in coke/coal/charcoal and woodchips. The product is taken to be pure silicon. Table 2 shows the amount of fixed carbon, volatile matter and silicon for the furnace evaluated.
Table 1. Typical composition of carbonaceous materials used as raw materials in the silicon production process, given on a wet basis [4].

<table>
<thead>
<tr>
<th>Type</th>
<th>Fixed Carbon (%)</th>
<th>Volatile (%)</th>
<th>Moisture (%)</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke</td>
<td>75</td>
<td>4</td>
<td>16</td>
<td>4</td>
</tr>
<tr>
<td>Coal</td>
<td>51</td>
<td>35</td>
<td>12</td>
<td>2</td>
</tr>
<tr>
<td>Charcoal</td>
<td>46</td>
<td>8</td>
<td>39</td>
<td>6</td>
</tr>
<tr>
<td>Woodchips</td>
<td>12</td>
<td>35</td>
<td>52</td>
<td>1</td>
</tr>
</tbody>
</table>

The enthalpy in the cooling water is determined from measured values of flow and the difference between inlet and outlet temperature. We estimate the heat lost by radiation and convection to be 5 % [4] of the total energy put into the process. The enthalpy in the off-gas is taken from difference between the total energy put into the process and the enthalpy in cooling water, heat lost by radiation and convection and enthalpy in the product. cf. (1).

Table 2. Material entering and leaving the submerged arc furnace operating at one silicon plant in Norway [8]. The numbers given refer to one hour of production in a 10 MW furnace. Volatile Matter (VM) type 1 refers to VM contained in coke, coal and charcoal while type 2 refers to VM contained in woodchips.

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed carbon</td>
<td>855</td>
</tr>
<tr>
<td>Volatile Matter type 1</td>
<td>235</td>
</tr>
<tr>
<td>Volatile Matter type 2</td>
<td>158</td>
</tr>
<tr>
<td>Si- metal</td>
<td>855</td>
</tr>
</tbody>
</table>

3.2.1 Case I: No energy recovery

The energy balance for the furnace, established using (1) and the same input data as Kamfjord et al. [7], is presented in Fig. 3. The numbers refer to a 10 MW furnace. Thermal losses include thermal energy lost to the surroundings from the furnace, by radiation and convection, and from the product during cooling and solidification. The enthalpy in the off-gas is lost as thermal energy to the surroundings. Hot cooling water from this furnace is used for heating purposes [7]. This is not taken into consideration in this work. All energy streams leaving the furnace, except the product stream, represent thermal energy losses to the surroundings.

![Energy balance diagram](image)

Fig. 3. Energy balance for one submerged arc furnace operated at a Norwegian silicon plant. The energy balance is established using the same input data as Kamfjord et al. [7]. The numbers are given on a basis of one hour production in a 10 MW furnace.
3.2.2 Case II: Energy recovery

To investigate the potential for energy recovery of thermal energy in the off-gas for this furnace, Kamfjord et al. [7] used data from [9] to recalculate new energy flows for the case of energy recovery. Using the energy balance given in Fig. 3, and data from [9] we recalculate new energy flows for the case when energy recovery equipment is installed in the off-gas system, see Fig. 4. All energy streams leaving the process, except the product and the power produced, represent thermal energy losses to the surroundings.

Fig. 4. Energy balance for one submerged arc furnace operated at a silicon plant in Norway with energy recovery equipment installed in the furnace off-gas system. The energy balance is established using the same input data as [7] and numbers in [9]. The numbers are given on a basis of one hour production in a 10 MW furnace.

3.3 Differences between the theoretical and the industrial process

The industrial process has thermal energy losses from the furnace, losses in the electric supply system, loss of carbon to the off-gas system and use of non-pure raw materials in addition to other minor deviations from the theoretical process [4]. The main differences between the theoretical and the industrial silicon process are summarized in Table 3.

Table 3. Main differences between the theoretical silicon production process and the industrial silicon production process [4].

<table>
<thead>
<tr>
<th></th>
<th>Theoretical process</th>
<th>Industrial process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw materials:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>pure 100%</td>
<td>Non-pure &lt; 100%</td>
</tr>
<tr>
<td>reductants</td>
<td>100% carbon</td>
<td>fixed carbon, volatile matter, moisture, trace elements</td>
</tr>
<tr>
<td>Product</td>
<td>100% Si</td>
<td>&lt; 100% Si</td>
</tr>
<tr>
<td>Silicon yield</td>
<td>Can be 100%</td>
<td>Less than 100%</td>
</tr>
<tr>
<td>Thermal energy loss to surroundings:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radiation and convection from furnace</td>
<td>NO</td>
<td>YES</td>
</tr>
<tr>
<td>Thermal energy cooling water</td>
<td>NO</td>
<td>YES</td>
</tr>
</tbody>
</table>
4. Calculation details

4.1 Theoretical silicon production process

We calculated the material streams for several silicon yields (9) for a furnace load of 10 MW. We take the off-gas temperatures to be 300 °C and 800 °C and determine the amount of air flow into the gas treatment section from the energy balance (1) by assuming the gas treatment section to be adiabatic. This calculation is performed using the thermochemical software HSC Chemistry® 6.1 from Outotec [10]. This software is chosen because it is commonly used by the ferroalloy producers and researchers within this field. The air consists of 20 % O₂ and 80 % N₂. All gas streams are assumed to behave ideally.

4.2 A submerged arc furnace operated at a Norwegian silicon plant

Operating data were supplied for the furnace operating at an Elkem silicon plant in Norway [8]. In calculating the exergy input to the furnace, we considered the amount of fixed carbon and volatile matter supplied to the process, cf. Table 2. When calculating the exergy in the product, we assumed the product to be pure silicon. The environmental temperature and pressure were taken to be \( T_0 = 25 \) °C and \( p_0 = 1 \) atm.

4.3 Thermodynamic data

We used standard chemical exergies given by Kotas [2] for all components except SiO(g) and the volatile matter in the carbon materials. Kotas gives the standard chemical exergies for a standard state of \( T_0 = 25 \) °C and \( p_0 = 1 \) atm for a reference environment originally developed by Szargut and co-workers.

The chemical exergy of SiO(g) was calculated by (5), using O₂ as the reactant component and SiO₂ as the product. Value for the Gibbs energy \( \Delta G_0 \) together with values for the enthalpy and entropy differences needed in the calculation of the physical exergies (4) were found from HSC Chemistry® [10]. HSC uses 1 bar as reference pressure for thermodynamic data which is slightly different from the environmental pressure of 1 atm. This difference is neglected in the calculations. As a crude first estimate for the exergy of the volatile matter in the reduction materials, we use the enthalpy for the exergy of the volatile matter. These are estimated values given in [11].

5. Results and discussion

5.1 Theoretical silicon production process

The exergy flow for the theoretical process will naturally depend upon the silicon yield as well as the off-gas temperature. The purpose of the simple Grassman diagram given in Fig. 5 is to illustrate the characteristics of the exergy flow for the theoretical silicon production process. The amount of exergy in a stream is represented by the width of the stream in the diagram. We observe that the exergy content in the gas stream and the product stream leaving the furnace are both large. The SiO(g) and CO(g) are burned in excess of air in the gas treatment section, the exergy in the off-gas leaving this section is mainly thermal exergy and depends upon the temperature which is controlled by the excess of air inlet. The off-gas exergy represents the potential for power production by installation of energy recovery equipment in the off-gas system. The difference between the exergy in the product stream in and out of the product treatment section is due to the thermal exergy loss from the product during cooling and solidification.
The overall exergy input, exergy in the product and the total exergy losses for the theoretical process are given in Table 4 for several silicon yields. The total exergy losses in the process amounts to 52.5 % of the total exergy input to the process for a silicon yield of 1.0 and increases to 63.6 % for a silicon yield of 0.7.

Table 4. The total exergy in and out and the total exergy losses of the theoretical silicon production process. The numbers refer to one hour of production in a furnace with 10 MW electric load.

<table>
<thead>
<tr>
<th>Silicon yield</th>
<th>1.0</th>
<th>0.9</th>
<th>0.8</th>
<th>0.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exergy into process (MWh)</td>
<td>19.45</td>
<td>19.06</td>
<td>18.67</td>
<td>18.26</td>
</tr>
<tr>
<td>Exergy in product (MWh)</td>
<td>9.23</td>
<td>8.38</td>
<td>7.52</td>
<td>6.64</td>
</tr>
<tr>
<td>Exergy losses (MWh)</td>
<td>10.22</td>
<td>10.68</td>
<td>11.15</td>
<td>11.62</td>
</tr>
<tr>
<td>Exergy losses as % of exergy into the process</td>
<td>52.5</td>
<td>56.0</td>
<td>59.7</td>
<td>63.6</td>
</tr>
</tbody>
</table>

Table 5 shows the distribution of the total exergy losses over the three subsystems and the exergy lost with the furnace off-gas for a silicon yield of 0.8 and for off-gas temperatures of 300 °C and 800 °C for the theoretical process. Table 5 shows that the furnace accounts for about 20 % of total losses and the product treatment for around 6 % while exergy loss in the gas treatment section and the non-utilized exergy in the off-gas accounts for about 70 % in total. The gas treatment section has the largest contribution to the exergy losses for an off-gas temperature of 300 °C; almost half of the total exergy loss is located here while the exergy lost with the off-gas amounts to around one quarter of the total losses. The exergy content of the gas stream entering the gas treatment section is large and is almost exclusively chemical exergy. Combustion reactions are associated with large exergy losses [12], and a big fraction of the exergy entering the gas treatment section is destroyed due to this. The large exergy loss associated with burning of CO(g) is well known, and there have been attempts in designing closed silicon furnaces [13] with no success so far.

Table 5 shows that increasing the off-gas temperature to 800 °C, by reducing the excess of air inlet, reduces the exergy loss in the gas treatment section and increases the exergy in the off-gas; the exergy loss in the gas treatment section then accounts for about 30 % of total exergy losses while exergy lost with the off-gas accounts for about 45 % of total losses. Thermal exergy is the largest contribution to the exergy in the off-gas leaving the gas treatment section and utilization of this will
reduce the total exergy loss in the process. Furthermore, increasing the off-gas temperature enhances the potential for increasing the overall resource utilization. This is a well-known measure [4, 5, 9, 14] and several plants have installed an energy recovery system in the off-gas system today.

Table 5. Distribution of the exergy loss over the sub-systems and exergy lost with the off-gas for a silicon yield $S = 0.8$ for the theoretical silicon production process.

<table>
<thead>
<tr>
<th>Exergy losses</th>
<th>Exergy (MWh)</th>
<th>% of total losses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Off-gas temperature is 300 ºC:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In furnace</td>
<td>2.34</td>
<td>21.0</td>
</tr>
<tr>
<td>In gas treatment section</td>
<td>5.24</td>
<td>47.0</td>
</tr>
<tr>
<td>With off-gas</td>
<td>2.93</td>
<td>26.3</td>
</tr>
<tr>
<td>In product treatment section</td>
<td>0.64</td>
<td>5.7</td>
</tr>
<tr>
<td>SUM</td>
<td>11.15</td>
<td>100</td>
</tr>
<tr>
<td>Off-gas temperature is 800 ºC:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In furnace</td>
<td>2.34</td>
<td>21.0</td>
</tr>
<tr>
<td>In gas treatment section</td>
<td>3.28</td>
<td>29.4</td>
</tr>
<tr>
<td>With off-gas</td>
<td>4.89</td>
<td>43.9</td>
</tr>
<tr>
<td>In product treatment section</td>
<td>0.64</td>
<td>5.7</td>
</tr>
<tr>
<td>SUM</td>
<td>11.15</td>
<td>100</td>
</tr>
</tbody>
</table>

The exergy analysis put numbers on the quality of energy, in contrast to the energy analysis which put numbers on the quantity of energy, cf. Fig. 3 and Fig. 4. Quality is the potential to do work, and is the theoretical amount of work you can achieve from a given quantity of energy. Thus, the exergy analysis put numbers on the potential for process improvements in terms of resource utilization.

5.2 A submerged arc furnace operated at a Norwegian silicon plant

Table 6 shows the exergy input, exergy in product and exergy losses for the two cases of the furnace operating at a silicon plant in Norway. The exergy in the product for the case of no energy recovery system amounts to about 30 % of the exergy input which means that 70 % of the total exergy input is lost. These numbers correspond to the numbers in [5] for a ferrosilicon furnace at an Elkem plant on Iceland. The furnace load for the furnace in [5] is about 40 MW while it is about 45 MW for the furnace in this study. Therefore, we may assume that the distribution of the losses for the furnace studied in this work follow the same trend as the distribution given in [5] which shows that 47.4 % of the total exergy input is lost in the furnace, which includes the furnace and the gas treatment section in the theoretical process, 18.7 % is lost with the off-gas while about 4 % is lost with heat from furnace, in cooling water and as thermal energy from the product. However, as discussed above, the exergy in the off-gas and the exergy loss in the gas treatment section will depend upon the off-gas temperature and there might be a deviation between the furnace studied in this work and the one in [5].

From Table 6, we see that the exergy loss in the process may be reduced to about 60 % of total exergy input, which is a reduction of about 12 %, by installing energy recovery equipment in the off-gas system. Even though numbers have uncertainties they demonstrate that this effort will improve the exergetic efficiency significantly.

Table 6. Estimated exergy input, exergy in the product and the exergy loss for the two cases of no recovery and recovery of thermal exergy from the furnace off-gas for one furnace operating at a silicon plant in Norway. The numbers are given on a basis of one hour production in a 10 MW furnace. For the case of energy recovery system installed; product includes both the silicon and electric power delivered from the energy recovery system.
### Table 7. Comparing the exergetic efficiencies for several cases of the theoretical silicon production process and for the furnace operated at a Norwegian silicon plant denoted the industrial process in the table. Energy recovery means recovery of thermal exergy in the off-gas.

<table>
<thead>
<tr>
<th>Exergetic efficiency, ε (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Theoretical process: No Energy Recovery:</strong></td>
</tr>
<tr>
<td>Silicon yield is 1.0</td>
</tr>
<tr>
<td>Silicon yield is 0.8</td>
</tr>
<tr>
<td><strong>Theoretical process: Energy Recovery (silicon yield 1.0):</strong></td>
</tr>
<tr>
<td>Off-gas temperature is 300 °C</td>
</tr>
<tr>
<td>Off-gas temperature is 800 °C</td>
</tr>
<tr>
<td><strong>Theoretical process: Energy Recovery (silicon yield 0.8):</strong></td>
</tr>
<tr>
<td>Off-gas temperature is 300 °C</td>
</tr>
<tr>
<td>Off-gas temperature is 800 °C</td>
</tr>
<tr>
<td><strong>Industrial process:</strong></td>
</tr>
<tr>
<td>No energy recovery</td>
</tr>
<tr>
<td>Energy recovery</td>
</tr>
</tbody>
</table>

### 5.3 Comparing the exergetic efficiencies for the theoretical and the industrial process

In evaluating industrial processes, it is useful and necessary to know the practical limit for the resource utilization. The theoretical process serves to give this limit for the silicon production process. Table 7 shows the exergetic efficiencies for several cases for the theoretical process and for the furnace operated at a Norwegian silicon plant. The case of energy recovery for the theoretical process means that all thermal exergy in the off-gas is utilized.

From Table 7 we observe that with no utilization of the thermal exergy in the off-gas for the theoretical process, the exergetic efficiency for a silicon yield of 1.0 is nearly 50 % and that it is reduced to about 40 % for a silicon yield of 0.8. In comparison, the exergetic efficiency for the industrial process with no energy recovery is about 30 %. Utilization of the thermal exergy in the off-gas enhances the exergetic efficiency for the theoretical process to roughly 65 % for an off-gas temperature of 800 °C and silicon yield of 0.8. The exergetic efficiency of the industrial process increases to around 40 % with energy recovery.

### 6. Conclusions

The theoretical silicon production process is established as a first reference case for the silicon production process. For the theoretical process, we have calculated exergetic efficiencies of 47.5 % and 40.3 % for a silicon yield of 1.0 and 0.8, respectively. Utilization of thermal exergy in the off-gas increased the exergetic efficiency to 58.6 % and 67.4 % for off-gas temperatures of 300 °C and 800 °C, respectively, for a silicon yield of 1.0.
For the industrial process, the exergetic efficiency was estimated to be 30.8% and 38.9% with no recovery and recovery of thermal exergy in the off-gas, respectively. This shows, as expected, that it is rather beneficial to recover thermal exergy in the off-gas and that it is still a potential for process improvements.

Acknowledgement
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References
Exergy based indicators for cardiopulmonary exercise test evaluation

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Abstract:
The cardiopulmonary exercise test is one of the most used tests to assess the functional capacity of individuals with varying degrees of physical training. One of the indices that are used for these analyses is the maximum oxygen consumption (maximum capacity of the body to transfer and transport oxygen to tissues). Lactate threshold is another metabolic parameter used to identify the state of the aerobic training. During the experimental procedure, the individuals are submitted to increasing levels of velocities, which is suitable for the obtainment of the blood lactate concentration. The aim of this work is the development of performance indicators for individuals under physical activity based on the concepts of exergy destroyed rate and exergy efficiency. To perform the exergy analysis, it was necessary to calculate heat and mass flow rates, associated with radiation, convection, vaporization and respiration, determined from the measurements and some relations found in the literature. The energy balance allowed the determination of the internal temperature over time. Those information were used to obtain the exergy variation of the body along the experiment. Eventually, it was possible to calculate the destroyed exergy and the exergy efficiency from the exergy analysis. During the tests the following measurements were made: the skin temperature of the trunk, legs and arms, the tympanic temperature, the respiratory gas exchanges, the blood lactate concentration, and some anthropometric parameters. The exergy rates and flow rates are dependent of the exercise level and the body metabolism. The results show that the relation between the destroyed exergy and the metabolism is almost constant during the test; furthermore its value has a great dependence of the subject age. Moreover, the exergy efficiency has a different behavior between the low trained subjects and the others.

Keywords:
Exergy Analysis, Exergy Efficiency, Treadmill Running, Aerobic Threshold.

1. Introduction
Exergy analysis is applied to assess the energy conversion processes that take place in the human body during physical exercise, aiming at developing indicators of performance based on the concepts of exergy destroyed rate and exergy efficiency. The Second Law of Thermodynamics was applied to the human body by several authors [1-15].

Initially the Second Law was applied to biological systems to study the Prigogine and Wiame [1] theory, which states that the entropy production tends to decrease over lifespan. Several authors confirmed this principle [1-7,15].

Batato et al. [8] proposed a pioneer model to perform the exergy analysis to the human body. Later, Prek [9,10], Prek and Butala [11] and Simone et al. [12] performed the exergy analysis for the human body to obtain relations of destroyed exergy with thermal comfort and thermal sensation conditions.
A few authors applied the exergy analysis [14], or the Second Law analysis [5-7] to the human body during physical exercise. Results of Rahman [5] indicate that the entropy generation rate increases with the increment of the exercise level. Silva and Annamalai [6,7] compared the entropy generation and lifespan for individuals under basal conditions, for different content of diets and different levels of physical activities; the authors suggested that physical activities should be kept in a "healthy minimum" if the entropy generations is to be minimized.

Albuquerque-Neto et al. [14] suggested a model of the respiratory and of the thermal system to perform the exergy analysis of the human body under physical activities. According to the exergy analysis, the internal respiration is more effective under physical activity than the external respiration.

The majority of energy analyses of the whole human body under physical exercise are based on the evaluation of the performed work and its efficiency. In the most common approach, the work of walking or running is determined from the dynamic of the mass center and limbs [16,17].

Two efficiencies are normally used in exercise physiology. One is the net efficiency, defined as the relation between the work and the net energy expenditure (the difference between the total and basal metabolism). The other is the delta efficiency, defined as the relation between the increase of the work and the increase of the energy expenditure. According to Kaneko[18], the net efficiency of running decreases while the speed increases, from about 60 to 15% between 3.9 to 9.4 m/s. Ito et al. [19] found that the net efficiency remains approximately the same (55 ± 12.7%);Williams and Cavanagh [20] found the net efficiency of 44% for running at 3.6 m/s; and Bijker et al. [21] found the value of 48% for the delta efficiency running at 2.2 m/s over an inclined treadmill. Those controversial results are mainly due to the calculation of the net energy expenditure, which may be inaccurate during the anaerobic exercise [18], and due to the method used to obtain the work – values from 343 to 1650 W for speeds between 3.6 and 3.9 m/s are found in the literature [20].

The lactate threshold (LT) is nowadays one of the most reliable indicators of functional capacity. It indicates the moment when the anaerobic threshold overtakes the aerobic threshold, which is characterized by the abruptly increase in the lactate concentration. A common experimental protocol used for its determination is the treadmill incremental running test. The subject must stay in the same speed for a time long enough to the lactate level in the blood become stabilized. The lactate threshold is obtained directly from blood analysis.

In the present work, exergy analysis is applied to the human body under treadmill incremental running tests. The analyses are based on experimental results and on the energy and exergy balances.

2. Methods

2.1. Energy analysis

The energy and exergy analysis proposed in the present work is based on a previous study by Mady et al [15]. The heat transfer rate and mass flow rates to the environment were obtained from a procedure described by [23] and by [24].

The total internal energy variation of the body was assumed to be as indicated in (1). Accordingly, it is a sum of the metabolic internal energy (∂U/∂t) and the internal energy variation of the body over time due to the transient environment conditions (∂U/∂t)|ₜₙ₅₉. In the following equation, m is the subject mass, c is the body specific heat, and Tₖ is the representative of the internal temperature of the body.

\[
\frac{dU}{dt} = -M + \frac{dU}{dt}|_{ₜₙ₅₉} = -M + mc\frac{dT_k}{dt}, (1)
\]

The First Law of Thermodynamics (2) can be applied to the subject under physical activity to obtain ∂U/∂t|ₜₙ₅₉ and, therefore, the body temperature variation over time:
\[
\frac{dU}{dt} \bigg|_{AT} = M - (Q_c + Q_r + H_e + \Delta H_{res}) - W,
\]

In (2) \( Q_c \) is the convective heat transfer rate, \( Q_r \) is the radiative heat transfer rate, \( H_e \) is the vaporization flow rate through skin; \( \Delta H_{res} \) is the enthalpy flow rate variation due to the respiration and \( W \) is the performed power.

It is important to highlight that the convection heat transfer coefficient was correlated with the leg speed through relations found in [25]. Moreover, the convection and vaporization coefficients were adjusted so that the calculated internal temperature and the water loss are in accordance with the measured data.

The performed work by the subject used in the present analysis is the external performed work defined by [17] as a function of mass and speed. This choice was based on a discussion present in Ward-Smith [26] about the energy exchanges during running. Besides, this definition provides coherent results for the internal temperature and the net efficiency.

The net efficiency is defined as the relation between the work and the net energy expenditure (the difference between the total and the basal metabolism) as proposed by Kaneko [18]:

\[ \eta_{net} = \frac{W}{M - M_0}, \]  

where \( M_0 \) is the metabolism at basal condition. In the present work, it is considered as the mean metabolism of the initial 5 minutes standing in the treadmill.

### 2.2. Exergy analysis

The Exergy analysis is applied to each subject, with a given environment/reference condition, such as temperature \( T_0 = T_a \), pressure \( P_0 = P_a \) and relative humidity \( \varrho_e = \varrho_a \). Thus, (4) indicates a general equation of the exergy balance.

\[
\frac{dB}{dt} = \sum B_{in} - \sum B_{out} + \sum_k Q_k \left( 1 - \frac{T_0}{T_k} \right) - W - B_{dest},
\]

Similar to the internal energy variation over time, the metabolic exergy \( (B_M) \) constitutes a part of \( dB/dt \) indicated in (5), neglecting the body volume variation over time:

\[
\frac{dB}{dt} = -B_M + \left[ \frac{dU}{dt} \bigg|_{AT} - T_0 \frac{dS}{dt} \bigg|_{AT} \right],
\]

where, \( B \) is the body exergy, \( dB/dt \bigg|_{AT} \) is the exergy variation of the body due to a variation in environmental conditions.

Batato et al. [14] achieved that the metabolic internal energy and the metabolic exergy are very close; therefore, the approximation \( B_M \approx M \) might be used. The term \( dU/dt \bigg|_{AT} \) is calculated from the energy balance (2) and \( dS/dt \bigg|_{AT} \) is calculated from (6):

\[
\frac{dS}{dt} \bigg|_{AT} = mc \ln \left( \frac{T_{b_0}^{i+1}}{T_{b_0}^i} \right),
\]

where, \( T_{b_0}^i \) is the body temperature at instant \( i \) and \( m \) is the body mass.

Equation (7) indicates the exergy balance applied to the human body:

\[
B_{dest} = B_M - (B_c + B_r + B_e + \Delta B_{res}) - \frac{dB}{dt} \bigg|_{AT} - W,
\]
where the exergy rate and flow rates $B_c$, $B_r$, $B_e$ and $\Delta B_{res}=(B_{ex} - B_a)$ are the exergy associated with convection, radiation, vaporization and respiration, as considered by [15].

The exergy efficiency is defined in (8):

$$\eta_b = 1 - \frac{B_{dest}}{B_M + \frac{dB}{dt}|_{LT}}$$

where $B_{dest}$ is the exergy associated with radiation and vaporization, $B_M$ is the exergy associated with metabolism, $dB/dt$ is the rate of change of exergy with time, and $LT$ is the lactate threshold.

2.3. Experimental procedure

Eleven male subjects participated in this study. The mean age was $31.4 \pm 10.1$ (mean ± standard deviation); the mean mass was $73.3 \pm 7.8$ kg; the mean height was $1.76 \pm 0.07$ m; and the mean surface area was $1.89 \pm 0.11$ m$^2$. The subjects were all runners with different levels of training; seven of them trained four or more times a week, and four trained less than four times a week.

After the connection of the subject with the measurement system, 5 minutes of data were collected for control, with the subject standing over the treadmill. Then the subject ran for 3 minutes to warm-up with 30% of his long distance training speed. After that the speed was set to 70% of the training speed. The speed was incremented by 1 km/h every 4 minutes until the subject becomes exhausted. During the experiment, the treadmill was set to 1% of inclination, so that the energy expenditure is equivalent to an outdoor running [22]. The experimental procedure was approved by the Ethics Committee for Analysis of Research Projects (CAPPesq).

A calorimetric system (TruMax 2400 Metabolic Measurement System, Consentius Technologies) was used to measure the ventilation and the oxygen and carbon dioxide concentration in the expired gas. Those data were used to calculate the $O_2$ consumption, the $CO_2$ production and the energy expenditure (metabolism).

In order to obtain the lactate concentration, a blood sample was collected from the fingertip after 3.5 minutes at each speed and analyzed with the Accutrend® Lactate (Roche, type 3012522). Three methods were used to obtain the speed in which the lactate threshold happens: when the difference from the last value was larger than 1 mmol/L; when the absolute value was 4 mmol/L; and by graphical analysis with a logarithmic scale. The mean value of these three methods was used in the analysis.

The skin temperatures were measured with an infrared thermometer (MX2, Raytek) in three locations: center of back, posterior right arm, and posterior right leg. Those measurements were made in the last two minutes of each test speed. The tympanic temperature (representative of the body temperature) was measured before and after the exercise with an ear thermometer (G-Tech).

The internal environmental conditions were measured just before the beginning of each experiment. The mean air temperature was $23.6 \pm 1.5$ °C; the mean radiant temperature was $22.8 \pm 1.5$ °C; and the mean relative humidity was $56.6 \pm 8.5$ %. The barometric pressure of the laboratory was 688 mmHg. The tests were carried out in three different days.

3. Results

Figures 1 to 6 show the main measured and calculated results of the present work for all the subjects. They are separated into three groups, based on the speed in which the lactate threshold (LT) was achieved. The first group (low LT) includes four subjects with the LT speed $\leq 3.1$ m/s. The second group (medium LT) includes three subjects with $3.1 < LT$ speed $<3.5$ m/s. The last group (high LT) includes four subjects with the LT speed $\geq 3.5$ m/s. The mean LT speeds for the groups are $2.8 \pm 0.3$, $3.3 \pm 0.1$, and $3.8 \pm 0.4$m/s.

The graphs of Figs. 1 to 5 show relations between a calculated or measured variable as a function of the treadmill speed. The dots are mean values for the last minute of each speed level (the lines between the dots are only for the identification of each subject). This is a period sufficient for stabilization of several physiological variables. In order to improve the clearness of the graphs, the periods that are not used to obtain the performance indicators (control, warm-up and recovery periods) were not included. The most trained subject that participated in the tests is the only one that
reached a speed greater than 5 m/s. The least trained subject is the one that reached a maximum speed lower than 3 m/s.

In Figure 1a it is indicated the increase of the metabolism (by subject mass) with the treadmill speed for each subject (from lowest, 1; to highest LT, 11). Their relation is approximately linear. The subjects have metabolisms very close for the same speed, independent of the lactate threshold. The largest discrepancy is found in the subject 1 for which the metabolism is clearly greater than the others for the same speed. This subject is the one with the lowest lactate threshold, which may indicate that he is not adapted to run in an efficiency way, in other words, he probably uses more nutrients to develop the same speed. The net efficiencies of the subjects are indicated in Fig. 1b. The subject 1 is the one that reaches the smallest net efficiency. However, this result is not observed in the other subjects with low LT. In fact, the other subjects of the low lactate threshold group reached the largest values of efficiency in low speeds, which were not run by the most trained subjects. The results do not show expressive differences between the groups. The net efficiency for each subject decreases with speed. This result is in agreement with [18] for a large range of speeds.

Figure 2a shows the calculated internal body temperature. The curves have similar trends for all the subjects. In the beginning of the running test, the internal temperature starts to increase in a high rate, but with a tendency to stabilize in a maximum value. However, during the last third of the test, the internal temperature returns to increase in a high rate, which is a consequence of the skin saturation by water due to the sweating regulatory mechanism.

Figure 2b shows the measured mean skin temperature, weighted by the limb surface area. The skin temperature depends mostly of the environment conditions. It is observed in the graph a small variation due to the increase in the physical activity (with exception of one subject from the low LT group whom the skin temperature raised from 29 to almost 33 °C). This happens because the effect of the metabolism increase is compensated by the increase of the convection heat transfer and the evaporation. Moreover, the subject 1 reached the highest skin temperatures is the one with the highest relation between metabolism and speed, as discussed above.

Fig. 1. a) Metabolism and b) energetic net efficiency for each subject (1-11).

Fig. 2. a) Internal temperature, and b) mean skin temperature.
In Fig. 3a it is indicated the calculated total energy transfer rate (per surface area) to the environment through the skin (by convection, radiation and evaporation) and the respiratory enthalphy variation through the ventilation. The energy transfer increases fast in the beginning of the exercise due to the increase in the convection, evaporation and ventilation. The main reasons of the increase in the energy transfer by those mechanisms is the increase of the limb movements (which increase the heat transfer coefficient), the wet surface, and the respiratory tract flow. The saturation of the skin by sweat diminishes the increase of the total energy transfer with the environment, which is clearly observed in the graph.

Figure 3b shows the total exergy transfer rate (by surface area) with the environment. The main mechanisms of exergy transfer with the environment are related with mass transfer. For all subjects, the maximum exergy transferred by convection is $2.1 \text{ W/m}^2$, the maximum exergy transferred by radiation is $1.8 \text{ W/m}^2$, and the maximum exergy variation by the pulmonary ventilation is $3.0 \text{ W/m}^2$. The evaporation through the skin is indicated in Fig. 3c. The exergy transfer reaches a maximum value after the skin gets saturated by the sweat. The subject 1 has a distinct exergy transfer value from the others, as a result of its higher relation between the air temperature and the skin temperature. As indicated by [8,15] for basal conditions, the contributions of heat transfer rate and mass flow rates to the environment during exercise are an order of magnitude higher than their exergy contribution.

![Graph](image)

**Fig. 3** a) Total energy transfer rate to the environment through skin, b) total exergy transfer to the environment, c) evaporative exergy transfer to the environment.

Figure 4a shows the increase in the destroyed exergy (per unit of mass) with the speed, which confirms previous results found on literature [5-7]. The increase for each subject is similar to the increase of the metabolism, but with lower values. For all subjects the trend is similar. Figure 4b indicates the ratio of destroyed exergy and metabolism, which ranged from 56 to 70%. The subject 1 was the one with highest ratio, hence it follows that this subject destroy more exergy than the others for the same speed.
In Fig. 5a, the exergy efficiency is indicated as a function of treadmill speed, where the values ranged between 30 to 44%. An unexpected result is that the subjects with low LT have higher exergy efficiency for the same speed, and their maximum is earlier than others. This last result is justified by the exergy transfer to the environment (mostly evaporative). The exercise for this group began in a lower speed, hence their skin get saturated with sweat earlier. A comparison between the other groups does not show a clear trend. Figure 6b indicates the ratio of exergy efficiency and net energy efficiency, where there is a point of inflection for most subjects.

Table 1 indicates the values of the exergy balance (per unity of mass) integrated over time, for each subject. A comparison with results of basal conditions obtained in [8,15] indicates that the exergy efficiency during physical activities may reach values of 45%, whereas in basal conditions the efficiency is lower than 5% [15] or neglegitable [8]. The exergy variation of the body does not correspond to more than 1% of the total metabolic exergy; and the exergy lost to the environment during test does not correspond to more than 5% of the total metabolic exergy.
### Table 1. Values of exergy balance (per unity of mass) integrated over time and calculated exergy efficiency for each subject

<table>
<thead>
<tr>
<th>Subject</th>
<th>Test Duration (min)</th>
<th>(\Delta b) (J/kg)</th>
<th>(\int b_\text{m}dt) (J/kg)</th>
<th>(\int b_\text{a}dt) (J/kg)</th>
<th>(\int b_\text{env}dt) (J/kg)</th>
<th>(\int wdt) (J/kg)</th>
<th>(\eta_b) (%)</th>
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<tr>
<td>1</td>
<td>29.5</td>
<td>57</td>
<td>16890</td>
<td>11194</td>
<td>769</td>
<td>4870</td>
<td>34</td>
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<tr>
<td>2</td>
<td>34</td>
<td>72</td>
<td>17819</td>
<td>10797</td>
<td>588</td>
<td>6363</td>
<td>40</td>
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<tr>
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<td>29</td>
<td>68</td>
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<td>569</td>
<td>5232</td>
<td>38</td>
</tr>
<tr>
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<td>36</td>
<td>117</td>
<td>17220</td>
<td>9674</td>
<td>474</td>
<td>6956</td>
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</tr>
<tr>
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<td>17750</td>
<td>1014</td>
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<tr>
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<td>89</td>
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<td>20286</td>
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<td>9435</td>
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<tr>
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<td>42761</td>
<td>27971</td>
<td>1366</td>
<td>13277</td>
<td>35</td>
</tr>
</tbody>
</table>

The results of Figure 6 indicate the ratio of the destroyed exergy with the metabolic exergy (Fig. 6a) and the exergy efficiency (Fig. 6b) as a function of subject age. The ratio of the destroyed exergy with the exergy metabolism tends to decrease as a function of age, which confirms the results of basal conditions [1-7,15]. Finally, the exergy efficiency increases as a function of age, which differ from the basal conditions result [15], where the exergy efficiency decreases as a function of age (basal conditions).

**Fig 6. (a) Ratio of the destroyed exergy and metabolism (in exergy basis) and (b) exergy efficiency as a function of the subject age**

### 4. Conclusion

The destroyed exergy and exergy efficiency were determined for the human body for the cardiopulmonary exercise test evaluation. From the analyzed range of parameters, it was possible to conclude that:

- metabolism increases with the increment of treadmill speed, while the net efficiency tends to decrease;
- the body temperature tends to increase as a function of treadmill speed while the skin temperature remains almost constant;
- when the subject is under physical exercise, the heat transfer rate and the mass flow rates are order of magnitude larger that the exergy rates and flow rates, similar to basal conditions [8,15];
the exergy efficiency has a different trend between the low LT group and the medium and high LT groups. Moreover, it is higher for the low LT group. Values of exergy efficiency ranged between 30 to 44%, whereas in basal conditions the exergy efficiency was lower than 5%.

- the destroyed exergy rate increases as a function of speed, as previously obtained in the literature, but for entropy production [5-7];
- the ratio of the destroyed exergy and metabolic exergy remains almost constant independently of the level of exercise, but it tends to decrease as a function of the subject age, as occur for basal conditions [1-7,15]. The exergy efficiency tends to increase with age, which differs from the basal conditions results [15].

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Nomenclature

- $B$: exergy rate and flow rate, W
- $B_b$: body exergy, J
- $b$: specific exergy, W/kg
- $b_b$: body specific exergy, J/kg
- $c$: heat capacity, W/(kg.K)
- $H$: enthalpy flow rate, W
- $LT$: lactate threshold, mmol/L
- $M$: metabolism, W
- $m$: body mass, kg
- $Q$: heat transfer rate, W
- $P$: pressure, Pa
- $S$: entropy rate, W/K
- $T$: temperature, °C or K
- $t$: time, s
- $U$: internal energy, J
- $W$: performed work, W
- $w$: specific performed work, W/kg

Greek symbols

- $\eta$: efficiency
- $\varnothing$: relative humidity, %

Subscripts and superscripts

- $0$: reference
- $a$: environment air
- $b$: body
- $b_b$: exergy
- $c$: convective
- $dest$: destroyed
- $e$: evaporative
en  energy
ex  expired
in  inflow
M  metabolic
out outflow
r  radiative
res respiration
ΔT  due to body temperature variation

References


Abstract

Sometimes, under a thermoeconomic analysis point of view, it is necessary to consider a system as a group of subsystems. The disaggregation of the exergy flows may be also required, and it is usually performed by splitting these flows in several components, for example thermal, mechanical or chemical exergy or even including the fictitious flow called negentropy. In order to disaggregate a system we need to define the product and the fuel of each subsystem. Therefore, the introduction of the negentropy in thermoeconomics represented a great advance in the discipline, since this magnitude allows quantifying the condenser product, which was not possible before because the condenser is a dissipative component, whose product cannot be expressed neither in terms of total exergy nor in terms of thermal, mechanical or chemical exergy. Recently, it was shown that the disaggregation of physical exergy into its enthalpic term \((H-H_0)\) and its entropic term \((T_0S-T_0S_0)\) is a consistent alternative to quantify the condenser product. This approach is called H&S Model. However, neither the inclusion of negentropy itself nor the disaggregation of exergy into enthalpic and entropic terms does not allow defining the product of valves. A more recent approach overcame such limitation by proposing the disaggregation of the physical exergy into three terms, namely internal energy \((U-U_0)\), flow work \((pV-p_0V_0)\) and the entropic term \((T_0S-T_0S_0)\). This approach is called UFS Model. This paper shows that exergy disaggregation is a consistent alternative for total disaggregation of systems in thermoeconomic modeling. Both exergy disaggregation level (H&S and UFS Model) can be used in order to quantify irreversibilities as well as the conventional exergy analysis. Furthermore, the results obtained, by applying theses approaches, show that the product-fuel ratios of each isolated components of the productive structure vary from zero (for totally irreversible processes) to one (for totally reversible ones).

Keywords

Exergy Disaggregation, Dissipative Components, System Disaggregation, Thermoeconomics.

1. Introduction

Thermoeconomics can be considered a new science which, by connecting Thermodynamics and Economics, provides tools to solve problems in complex energy systems that can hardly or not be solved using conventional energy analysis techniques based on First Law of Thermodynamics (mass and energy balance), as for instance a rational price assessment to the products of a plant based on physical criteria [1].

Most analysts agree that exergy, instead of enthalpy only, is the most adequate thermodynamic property to associate with cost (originally an economic property) since it contains information from the second law of thermodynamics and accounts for energy quality. An exergy analysis locates and quantifies the irreversibilities [2].

Depending on the type of analysis, different levels of accuracy of the results are required, i.e., each thermoeconomic analysis requires a specific aggregation level of the components, and of the flows of the plant. During the local optimization and diagnosis, for instance, the total disaggregation of the components of the system is generally required.
According to Torres et al. [3], sometimes, under a thermoeconomic analysis point of view, it is necessary to consider a component as a group of subsystems (made up of a group of subsystems) or a mass or an energy flow rate consisting of several components, for example thermal, mechanical or chemical exergy, or even including fictitious flow streams (negentropy) without a physical existence in the flow sheet of the plant.

In order to disaggregate the components of the systems we need to define the product and the fuel of each of them. Thus, the introduction of the negentropy in thermoeconomics represented a great advance in the discipline, since this magnitude allows quantifying the condenser product, which was not possible before because the condenser is a dissipative component, whose product cannot be expressed in terms of exergy only.

Valero et al. [2] stated that, although the magnitudes applied by most thermoeconomic approaches are exergy, negentropy and money, other magnitudes, like enthalpy and entropy, can also be used. According to Valero et al. [4], the fuels and the products (productive structure) of a system must be defined based in the trajectories that the flows describe in the h,s plane when they work for the specific purpose of the plant. Bearing this in mind, recently, Santos et al. [5] showed that the disaggregation of physical exergy into its enthalpic term \((H-H_0)\) and its entropic term \((T_0S-T_0S_0)\) is a consistent alternative to quantify the condenser product in a Rankine cycle. This approach is called H&S Model.

However, neither the disaggregation of exergy into its enthalpic and entropic terms nor the inclusion of negentropy itself allows defining the product of the valves in a refrigeration or heat pump cycles, which is also a dissipative component.

A more recent approach, proposed by Lourenço et al. [6], overcame such limitation by proposing the disaggregation of the physical exergy into three terms, namely internal energy \((U-U_0)\), flow work \((pV-p_0V_0)\) and the entropic term \((T_0S-T_0S_0)\). This approach is called UFS Model.

This paper shows that both exergy disaggregation level (H&S Model and UFS Model) can be used in order to quantify local irreversibility as well as the conventional exergy analysis, and also the product-fuel ratios of each components of the productive structure vary from zero (for totally irreversible processes) to one (for totally reversible ones). Consequently, this paper shows that the UFS Model is an extension of the H&S Model and its application only could be justified if there is a valve in the flow sheet of the plant, because of the increasing complexity and computational efforts.

2. Physical Exergy Disaggregation

According to Torres et al. [3], the disaggregation of physical exergy in thermoeconomics was proposed by Tsatsaronis in 1990. Tsatsaronis and Pisa [7] defined the fuels and the products of the components by using the physical exergy disaggregated into thermal and mechanical components. But, this kind of disaggregation itself does not allow the isolation of dissipative components. In agreement with Lazzaretto and Tsatsaronis [8], although by considering separate exergy forms improve the accuracy of the results, this splitting might not be always meaningful because of the arbitrariness that might be involved in the separate calculation of mechanical and thermal exergies, particularly when working fluids that can change phases are used in the process being considered.

This arbitrariness does not occur when the physical exergy (1) is disaggregated into its enthalpic (2) and entropic (3) terms during the application of the H&S Model proposed by Santos et al. [5].

\[
E_{i0} = m_i \cdot [(h_i - h_{0i}) - T_0 \cdot (s_i - s_{0i})] \tag{1}
\]

\[
S_{i0} = m_i \cdot T_0 \cdot (s_i - s_{0i}) \tag{2}
\]

\[
H_{i0} = m_i \cdot (h_i - h_{0i}) \tag{3}
\]
Once that the enthalpy can be defined in terms of internal energy and flow work, the physical exergy (4) can be defined into three terms: internal energy (5), flow work (6) and entropic term (7).

\[
E_{i,0} = m_i \cdot [(u_i - u_0) + (p_i \cdot v_i - p_0 \cdot v_0) - T_0 \cdot (s_i - s_0)] 
\]

(4)

\[
U_{i,0} = m_i \cdot (u_i - u_0) 
\]

(5)

\[
F_{i,0} = m_i \cdot (p_i \cdot v_i - p_0 \cdot v_0) 
\]

(6)

\[
S_{i,0} = m_i \cdot T_0 \cdot (s_i - s_0) 
\]

(7)

This kind of disaggregation was the basis for the application of UFS Model by Lourenço et al. [6].

3. Definitions: fuel, product, irreversibility and efficiency

In agreement with Torres et al. [3], all thermoeconomic methodologies need to define a function or a productive purpose to each component of the plant. This is a key factor to know the process of cost formation and to know the causes that generate the cost in complex power plants. The causal of productive interaction between components determines the productive structure. According to Valero et al. [2], irreversibility is the physical magnitude generating the cost. Çengel and Boles [9] defines efficiency as the ratio of desired result for an event to the input required to accomplish the event. Moran and Shapiro [10] stated that efficiency gauges how effectively the input is converted to the product. Thus, we conclude that in thermoeconomics the concept of fuel (\( Fu \)), product (\( Pr \)), irreversibility (\( Ir \)) and efficiency (\( \eta \)) are not independents, as shown in (8) and (9).

\[
Fu - Pr = Ir + Lo 
\]

(8)

\[
\eta = \frac{Pr}{Fu} 
\]

(9)

Thus, in agreement with Çengel and Boles [9], we recognize that there is some disagreement on a general definition of the second-law efficiency, and thus a person may encounter different definitions for the same device. But, the thermodynamicists [9,10] agree that the second-law efficiency serves as a measure of approximation to reversible operation, and thus its value should range from zero in the worst case (totally irreversible process) to one in the best case (totally reversible process). According to Moran and Shapiro [10], it is important to recognize that the limit of 100% second-law efficiency should not be regarded as a practical objective. This theoretical limit could be attained only if there were no irreversibility (\( Ir \)) or losses (\( Lo \)).

With this in mind, during the definition of the productive structure for application of the H&S Model and UFS Model, the fuel and the product of the subsystems must be defined by taking into account that the second-law efficiency ranges from zero (for a totally irreversible process) to 100 percent (for a totally reversible process).

In the H&S Model the physical exergy is disaggregated into its enthalpic and entropic terms, thus, efficiency, cost and behaviour of the system are based in the trajectory in the h,s plane any flow performs when it works for the specific purpose of the plant. The products and the fuels of each subsystem, in terms of the enthalpic term, are defined based on the quantity of enthalpy added to and removed from the working fluid, respectively. On the other hand, because the entropic term has
a negative contribution to de physical exergy, as we can see in (1), this term is the products of the subsystems that decrease the working fluid entropy, and the subsystems that increase the working fluid entropy have the entropic term as fuel. This consideration allows one to define the fuels and the products of the productive component and condensers (dissipative component). However, this way, we can not define de product of the valves in which we consider that enthalpy does not vary.

Using the UFS Model, in which the enthalpic term is disaggregated into internal energy term and flow work term allows one solving this limitation of the H&S Models. As shown in (4), these two new terms have positive contribution to the physical exergy. Thus, in UFS Model, products and fuels of each subsystem, in terms of the internal energy term and flow work term, are defined based on the quantity of these magnitudes added to and removed from the working fluid, respectively. In a valve of a refrigeration or heat pump cycle the internal flow and the flow work of the working fluid vary: the internal energy decreases (fuel) and the flow work increases (product).

4. Application Examples

The beauty of a theory is usually shown in the simplicity of its forms and the generality of its message, but its power resides in its capacity to solve practical cases [11]. Thus, two simple examples of thermal systems are used, in this paper, to illustrate the application of the H&S Model and UFS Model, respectively: a Rankine cycle power plant and a heat pump cycle. By using these plants, this paper shows the capacity and the limitation of the H&S Model and UFS Model to treat two different kind of dissipative components in thermoeconomics: condensers and valves. In order to show the consistency these two models, actual, ideals and reversible cycles are used in this paper.

4.1. Rankine Cycle

4.1.1. Actual Cycle

The physical structure of the Rankine cycle power plant represented in Fig. 1 essentially coincides with the one used by [11] and [12]. The plant is considered made up of four components: boiler (B), turbine and generator (T-G), condenser and cooling water pump (C), and boiler feeding pump (P).

---

![Fig. 1. Physical Structure of the Actual Steam Power Cycle](image)

The external exergy consumption ($Q_F$) is 70.000 kW and the net power ($P_{NP}$) is 20.000 kW. The feeding and the cooling pump consume 155 kW ($P_{PM}$) and 75 kW ($P_{CP}$), respectively. Table 1 shows the main physical flow parameters.

The functional diagram is shown in Fig. 2. The enthalpy of the working fluid is increased as much in the pump as in the boiler. The turbine consumes part of this enthalpy. The operation of these
productive units (pump, boiler and turbine) increases the entropy of the working fluid. The condenser consumes the remaining part of enthalpy while it decreases the entropy of the working fluid. In other words, the condenser product is the entropic term and its fuel is the enthalpic term.

Table 1. Main Parameters of the Main Physical Flows of the Actual Steam Power Cycle

<table>
<thead>
<tr>
<th>PHYSICAL FLOW</th>
<th>Description</th>
<th>m [kg/s]</th>
<th>p [kPa]</th>
<th>T [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water</td>
<td>19.5</td>
<td>7</td>
<td>39.04</td>
</tr>
<tr>
<td>2</td>
<td>Water</td>
<td>19.5</td>
<td>6300</td>
<td>39.50</td>
</tr>
<tr>
<td>3</td>
<td>Steam</td>
<td>19.5</td>
<td>6000</td>
<td>500.0</td>
</tr>
<tr>
<td>4</td>
<td>Moisture (x = 0.9)</td>
<td>19.5</td>
<td>7</td>
<td>39.04</td>
</tr>
</tbody>
</table>

The functional diagram represents graphically the cost formation process of the system. The rectangles are the real units (or subsystems) that represent the actual equipments of the system. The rhombus and the circles are fictitious units called junction and bifurcations, respectively.

Each productive units has inlet and outlet arrows, that represent its fuel (or resource) and products, respectively. There are productive units that have small junction to indicate that they have more than one fuel, and/or a small bifurcation to indicate that they have more than one product.

The productive flows that represent power ($P_{PM}$, $P_{NP}$ and $P_{CP}$) and external fuel ($Q$) are the same flows presented in the physical structure. These flows are total exergy. The remaining productive flows are the variation of an exergy term between two different states ($j$ and $k$) of the physical structure. The productive flows representing the enthalpic ($H_{j:k}$) and the entropic ($S_{j:k}$) terms of the physical exergy are calculated using (10) and (11), respectively.
The mathematical model for cost allocation is obtained by formulating the cost equations balance in each actual and fictitious units of the functional diagram, as shown in (12), where \( c \) is the monetary unit cost of each flow of the productive structure (unknown variable) and \( Y \) is a generical way to represent the flows of the functional diagram, which can be power (\( P \)) and external fuel (\( Q \)), or enthalpic (\( H \)) or entropic (\( S \)) terms of physical exergy added to and removed from the working fluid. The monetary unit cost of a flow is the amount of monetary unit required to obtain one unit of this flow. The variable \( Z \) is the hourly cost of each unit due to the capital cost, operation and maintenance. Note that the monetary unit cost of the external fuel is a known variable.

\[
c_{ufd} \cdot \sum Y_{out} - \sum (c_{in} \cdot Y_{in}) = Z
\]  

(12)

As shown in (12), the H&S Model attributes the same monetary unit cost (\( c_{ufd} \)) to all of the flows leaving the same productive unit or leaving the same bifurcation (\( Y_{out} \)). By modifying (12) in order to formulate the cost balances to provide the exergetic unit cost (\( k \)) of each flow of the productive structure, we obtain (13). The exergetic unit cost of a flow is the amount of exergy required to obtain one unit of this flow. This cost is a measure of the thermodynamic efficiency of the production process generating this flow [2]. In this case, the hourly cost of the subsystem due to the capital cost, operation and maintenance must be equals zero (\( Z = 0 \)) and the monetary unit cost of the external fuel is replaced by the exergetic unit cost of an external resource, which is equal 1.00 kW/kW, because there is no exergy destruction before the productive process is performed [2]. The auxiliary equations are the same as used to obtain the monetary unit cost.

\[
k_{ufd} \cdot \sum Y_{out} - \sum (k_{in} \cdot Y_{in}) = 0
\]  

(13)

The solution of the sets of cost equations obtained by applying (12) and (13) in each device of the productive structure allows the attainment of the monetary and exergetic unit cost of each internal flow and final product, respectively. In this paper, only the exergetic unit costs are obtained. Table 2 shows the productive flows, its exergy values and its respective exergetic unit costs.

<table>
<thead>
<tr>
<th>FLOW ( H_{jk} )</th>
<th>VALUE [kW]</th>
<th>EXERGETIC UNIT COST [kW/kW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_{21} )</td>
<td>146.22</td>
<td>4.150</td>
</tr>
<tr>
<td>( H_{32} )</td>
<td>63,406.09</td>
<td>2.820</td>
</tr>
<tr>
<td>( H_{34} )</td>
<td>21,304.58</td>
<td>2.824</td>
</tr>
<tr>
<td>( H_{41} )</td>
<td>42,247.73</td>
<td>2.824</td>
</tr>
<tr>
<td>( S_{21} )</td>
<td>21.70</td>
<td>2.963</td>
</tr>
<tr>
<td>( S_{32} )</td>
<td>36,731.52</td>
<td>2.963</td>
</tr>
<tr>
<td>( S_{43} )</td>
<td>3,594.51</td>
<td>2.963</td>
</tr>
<tr>
<td>( S_{41} )</td>
<td>40,347.73</td>
<td>2.963</td>
</tr>
<tr>
<td>( P_{PM} )</td>
<td>155.00</td>
<td>3.500</td>
</tr>
<tr>
<td>( P_{CP} )</td>
<td>75.00</td>
<td>3.500</td>
</tr>
<tr>
<td>( P_{NP} )</td>
<td>20,000.00</td>
<td>3.500</td>
</tr>
</tbody>
</table>
According to Valero et al. [2], irreversibility is the magnitude generating the costs. Consequently, in any irreversible (actual) cycle plant, the exergetic unit cost should be increased along the productive structure. Bearing this in mind, the exergetic unit costs of the internal flows and final products obtained by the H&S Model are consistent because they are greater than one, once that the exergetic unit cost of the external fuel is equals one.

In H&S Model, the fuels and products used in the functional diagram in order to calculate the costs coincide with the fuels and product which can be used for calculating efficiency (performance) for both productive and dissipative units, as shown in (14). This equation under any condition, for any subsystem, can be interpreted as, or coincide with the classical and well-known product-fuel definition of efficiency, because it value is less than one for any actual (irreversible) cycle.

\[
\eta_{ufd} = \frac{\sum Y_{out}}{\sum Y_{in}}
\]

The formulas and the values of efficiency (product-fuel ratio) for each unit or subsystem of the functional diagram are shown in Table 3. The product-fuel ratio value (the efficiency) of the turbine and generator was calculated as a single unit, but the efficiencies of the turbine and generator, separately, are 85.56% and 94.96%, respectively. We can see that the efficiency of each unit (subsystem or component) is lower than 100%, including that of the dissipative ones.

<table>
<thead>
<tr>
<th>PRODUCTIVE UNIT</th>
<th>EFFICIENCY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump (P)</td>
<td>( \frac{H_{21}}{S_{21} + P_{p}} )</td>
</tr>
<tr>
<td>Boiler (B)</td>
<td>( \frac{H_{32}}{S_{32} + Q_{f}} )</td>
</tr>
<tr>
<td>Turbine and Generator (T-G)</td>
<td>( \frac{P_{N} + P_{p} + P_{C}}{H_{34} + S_{43}} )</td>
</tr>
<tr>
<td>Condenser and pump (C)</td>
<td>( \frac{S_{43}}{H_{43} + P_{c}} )</td>
</tr>
<tr>
<td>Power Plant (ASC)</td>
<td>( \frac{P_{N}}{Q_{f}} )</td>
</tr>
</tbody>
</table>

The efficiency of the condenser and cooling water pump (Table 3) is 95.33%, but the efficiency of the condenser, alone, is 95.50%. By using the H&S Model, the condenser efficiency in an actual steam power cycle will always be less than 100%, and this efficiency would only be 100% in case it were possible to transfer heat in the condenser at the same temperature, i.e., if the condensation temperature and the reference temperature were the same. In other words, by using the H&S Model, the product-fuel ratio of each component (including the dissipative one, such as the condenser) ranges from zero (for a totally irreversible process) to one (for a totally reversible process).

4.1.2. Reversible Cycle

Although reversible steam cycle cannot actually exist, it can be imagined as the limiting case as irreversibilities are reduced further and further. The physical structure of the reversible steam power cycle, in Fig. 3, is defined by imagining the limit of perfection of the steam cycle used above in Fig. 1. The condensation temperature is equal to the reference temperature and there is no pressure drop in the condenser. Thus, the cooling water pump is neglected. The external exergy consumption \( (Q_{f}) \)
is equal to the exergy transferred to the working fluid in the boiler. Both compression and expansion processes are isentropic. All the conversion processes that involve the working fluid of the reversible steam cycle are considered as prefect. Furthermore, there are no power losses in the electric generator nor in the electric motor of the boiler feed water pump. Table 4 shows the stream parameters and Fig. 4 shows the productive diagram of the reversible steam power cycle.

**Fig. 3. Physical Structure of the Reversible Steam Power Cycle**

**Table 4. Main Parameters of the Main Physical Flows of the Reversible Steam Power Cycle**

<table>
<thead>
<tr>
<th>PHYSICAL FLOW</th>
<th>N°</th>
<th>Description</th>
<th>$m$ [kg/s]</th>
<th>$p$ [kPa]</th>
<th>$T$ [$^\circ$C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Moisture ($x = 0, 325$)</td>
<td>1</td>
<td>19.5</td>
<td>3.2</td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>2 Saturated Water</td>
<td>2</td>
<td>19.5</td>
<td>6000</td>
<td>275.6</td>
<td></td>
</tr>
<tr>
<td>3 Saturated Steam</td>
<td>3</td>
<td>19.5</td>
<td>6000</td>
<td>275.6</td>
<td></td>
</tr>
<tr>
<td>4 Moisture ($x = 0, 674$)</td>
<td>4</td>
<td>19.5</td>
<td>3.2</td>
<td>25.0</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 4. Productive Diagram of the Reversible Steam Power Cycle**

Because both the compression process and the expansion process are isentropic, the condenser product is charged to the boiler, which is the only subsystem that increases the working fluid
Table 5 shows the values of the productive flows present in the productive diagram of the reversible steam power cycle and the respective exergetic unit cost by applying the H&S Model.

**Table 5. Exergetic Unit Cost of the Productive Flows of the Reversible Steam Cycle**

<table>
<thead>
<tr>
<th>FLOW</th>
<th>VALUE [kW]</th>
<th>EXERGETIC UNIT COST [kW/kW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{21}$</td>
<td>6,154.82</td>
<td>1.000</td>
</tr>
<tr>
<td>$H_{32}$</td>
<td>30,628.67</td>
<td>1.000</td>
</tr>
<tr>
<td>$H_{34}$</td>
<td>20,142.77</td>
<td>1.000</td>
</tr>
<tr>
<td>$H_{41}$</td>
<td>16,640.72</td>
<td>1.000</td>
</tr>
<tr>
<td>$S_{41}$</td>
<td>16,640.72</td>
<td>1.000</td>
</tr>
<tr>
<td>$P_{PM}$</td>
<td>6,154.82</td>
<td>1.000</td>
</tr>
<tr>
<td>$P_{NP}$</td>
<td>13,987.95</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Table 5 confirms that H&S Model is a consistent approach, because the productive diagram is defined by isolating the four conversion processes of the reversible steam cycle, the fuel value of each equipment is equal to its product, and consequently, the exergetic unit cost of each productive flow is equal to one, and the efficiency is equal to one too, because there are no irreversibilities.

### 4.2. Heat Pump Cycle

#### 4.2.1. Actual Cycle

The physical structure of the Heat Pump cycle represented in Fig. 5 essentially coincides with the one analysed by Lourenço et al. [6]. The plant is considered made up of four components: the compressor (cmp), the condenser (cnd), the expansion valve (vlv) and the evaporator (evp).

![Fig. 5. Physical Structure of the Actual Heat Pump Cycle](image)

The power consumption is 15.65 kW and the heat supplied exergy is 7.93 kW. The temperature difference between the state 3 and the room that receives the heat supplied is 5 K and the temperature difference between the environment (ref) and the state 4 is 5 K. The refrigerant is Freon R-134a, which mass flow is equal to 0.8 kg/s. Table 6 shows the main physical flow parameters.

**Table 6. Main Parameters of the Main Physical Flows of the Actual Heat Pump Cycle**
The functional diagram is shown in Fig. 6. The internal energy of the working fluid is increased in the evaporator and in the compressor (products). The condenser and the valve decrease the internal energy (fuels). The flow work of the working fluid is decreased in the condenser only (fuel). The remaining components increase the flow work (products). The operations of the productive units (compressor and evaporator) and of the valve increase the entropy of the working fluid (fuels). The condenser decrease the working fluid entropy, i.e., the entropic term is a condenser product.

![Fig. 6. Productive Diagram of the Actual Heat Pump Cycle according to the UFS Model](image)

The productive flows representing the variation of the internal energy ($U_{j:k}$), flow work ($F_{j:k}$) and entropic ($S_{j:k}$) terms of the physical exergy are calculated using (14), (15) and (11), respectively. Table 7 shows the productive flows, its exergy values and its respective exergetic unit costs.

$$U_{j:k} = m_j \cdot (u_j - u_k) \tag{14}$$

$$F_{j:k} = m_j \cdot (p_j \cdot v_j - p_k \cdot v_k) \tag{15}$$

Table 7. Exergetic Unit Cost of the Productive Flows of the Actual Heat Pump by UFS Model
The exergetic unit costs of the internal flows and final product obtained by the UFS Model are consistent too because they are greater than one. The formulas and the values of efficiency (product-fuel ratio) for each unit or subsystem of the functional diagram are shown in Table 8.

Table 8. Product-Fuel Ratio (Efficiency) of the Productive Units of the Actual Heat Pump

<table>
<thead>
<tr>
<th>PRODUCTIVE UNIT</th>
<th>EFFICIENCY</th>
<th>FORMULA</th>
<th>VALUE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressor (cmp)</td>
<td>$\frac{U_{21} + F_{21}}{P + S_{21}}$</td>
<td>91.60</td>
<td></td>
</tr>
<tr>
<td>Condenser (cnd)</td>
<td>$\frac{Q + S_{23}}{U_{23} + F_{23}}$</td>
<td>98.39</td>
<td></td>
</tr>
<tr>
<td>Valve (vlv)</td>
<td>$\frac{F_{43}}{U_{34} + S_{43}}$</td>
<td>62.68</td>
<td></td>
</tr>
<tr>
<td>Evaporator (evp)</td>
<td>$\frac{U_{14} + F_{14}}{S_{14}}$</td>
<td>98.21</td>
<td></td>
</tr>
<tr>
<td>Heat Pump (hp)</td>
<td>$\frac{Q}{P}$</td>
<td>50.67</td>
<td></td>
</tr>
</tbody>
</table>

The results in Table 8 show that the efficiency, obtained by the product-fuel ratio of each unit, subsystem or component, is less than 100%, including that of the dissipative ones.

4.2.2. Ideal Cycle

In this case, we cannot imagine a reversible cycle because of the expansion valve where unavoidably irreversibility occurs. But, it is possible to analyze an ideal heat pump in which: (i) the compression process is isentropic; (ii) there is no difference between the constant condensation temperature in the condenser and the room temperature, and (iii) the constant evaporation temperature in the evaporator is equal to the environment temperature. In other words, the processes of heat transfer in the condenser and in the evaporator are totally reversible. The refrigerant is Freon R-134a, which mass flow is equal to 0.8 kg/s. Table 9 shows the main physical flow parameters.

Table 9. Main Parameters of the Main Physical Flows of the Ideal Heat Pump Cycle
Table 10 shows the productive flows, its exergy values and its respective exergetic unit costs. We can see that, in this case, the exergetic unit costs of the internal flows and final product are not equal one. But, they are consistent too because they are not less than one. These values would be equal to one if all processes were totally reversible, including that of the expansion (valve). The formulas and the values of efficiency (product-fuel ratio) for each unit or subsystem are shown in Table 11, in which we can see that, except the expansion valve, all components are totally reversible.

Table 10. Exergetic Unit Cost of the Productive Flows of the Ideal Heat Pump by UFS Model

<table>
<thead>
<tr>
<th>FLOW</th>
<th>VALUE [kW]</th>
<th>EXERGETIC UNIT COST [kW/kW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>U₂₁</td>
<td>13.37</td>
<td>1.000</td>
</tr>
<tr>
<td>U₂₃</td>
<td>125.49</td>
<td>1.112</td>
</tr>
<tr>
<td>U₃₄</td>
<td>2.63</td>
<td>1.112</td>
</tr>
<tr>
<td>U₁₄</td>
<td>114.75</td>
<td>1.125</td>
</tr>
<tr>
<td>F₂₁</td>
<td>0.46</td>
<td>1.000</td>
</tr>
<tr>
<td>F₂₃</td>
<td>15.99</td>
<td>1.228</td>
</tr>
<tr>
<td>F₄₃</td>
<td>2.63</td>
<td>1.770</td>
</tr>
<tr>
<td>F₁₄</td>
<td>12.90</td>
<td>1.125</td>
</tr>
<tr>
<td>S₂₁</td>
<td>0.00</td>
<td>0.000</td>
</tr>
<tr>
<td>S₂₃</td>
<td>129.18</td>
<td>1.125</td>
</tr>
<tr>
<td>S₄₃</td>
<td>1.54</td>
<td>1.125</td>
</tr>
<tr>
<td>S₁₄</td>
<td>127.64</td>
<td>1.125</td>
</tr>
<tr>
<td>P</td>
<td>13.84</td>
<td>1.000</td>
</tr>
<tr>
<td>Q</td>
<td>12.30</td>
<td>1.125</td>
</tr>
</tbody>
</table>

Table 11. Product-Fuel Ratio (Efficiency) of the Productive Units of the Ideal Heat Pump

<table>
<thead>
<tr>
<th>PRODUCTIVE UNIT</th>
<th>EFFICIENCY</th>
<th>Formula</th>
<th>Value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressor (cmp)</td>
<td></td>
<td>( \frac{U_{21} + F_{21}}{P + S_{23}} )</td>
<td>100</td>
</tr>
<tr>
<td>Condenser (cnd)</td>
<td></td>
<td>( \frac{Q + S_{23}}{U_{23} + F_{23}} )</td>
<td>100</td>
</tr>
<tr>
<td>Valve (vlv)</td>
<td></td>
<td>( \frac{F_{43}}{U_{34} + S_{43}} )</td>
<td>63.1</td>
</tr>
<tr>
<td>Evaporator (evp)</td>
<td></td>
<td>( \frac{U_{14} + F_{14}}{S_{14}} )</td>
<td>100</td>
</tr>
<tr>
<td>Heat Pump (hp)</td>
<td></td>
<td>( \frac{Q}{P} )</td>
<td>88.9</td>
</tr>
</tbody>
</table>

5. Conclusions
This paper showed that exergy disaggregation is a consistent alternative for total disaggregation of systems in thermoeconomic modelling, particularly when there are dissipative components in the system being analysed. Two different approaches based on two different levels of physical exergy disaggregation were presented and applied. The first one is the H&S Model based on the disaggregation into enthalpic and entropic terms. The second is the UFS Model, in which the physical exergy is disaggregated into internal energy, flow work and entropic terms. The first one allows defining the product of one kind of dissipative component (condensers) but it does not work for the valves, which are another kind of dissipative component. The UFS Model overcame this limitation because it allows defining the product of both kinds of dissipative component.

Both exergy disaggregation level (H&S Model and UFS Model) can be used in order to quantify irreversibilities as well as the conventional exergy analysis. The results show that the product-fuel ratios of each components of the productive structure vary from zero (for totally irreversible processes) to one (for totally reversible ones). Thus, in these approaches, the product-fuel ratios can be used in order to quantify the performance of both productive and dissipative components, by establishing a general and systematic link between efficiency and cost in thermoeconomics.

This paper shows that the UFS Model is an extension of the H&S Model, keeping the same characteristics. However, the application of the former only could be justified if there is a valve in the structure of the system, due to its increasing modelling complexity and required computational efforts. However, it is very important to say that this is not a competition among all the thermoeconomics approaches, because we recognize that each methodology has specific fields of application for which it provide proven and efficient solutions. This paper aimed at show that the exergy disaggregation is a coherent and consistent alternative in order to solve this difficult problem in thermoeconomics related to the treatment of the so-called dissipative components.

Acknowledgments
The authors would like to tank ANP, Capes and CNPq for the financial supports.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>monetary unit cost, $/kWh</td>
</tr>
<tr>
<td>E</td>
<td>physical exergy flow, kW</td>
</tr>
<tr>
<td>F</td>
<td>flow work term flow, kW</td>
</tr>
<tr>
<td>Fu</td>
<td>component or control volume fuel, kW</td>
</tr>
<tr>
<td>h</td>
<td>specific enthalpy, kJ/kg</td>
</tr>
<tr>
<td>H</td>
<td>enthalpic term flow, kW</td>
</tr>
<tr>
<td>Ir</td>
<td>component or control volume irreversibility, kW</td>
</tr>
<tr>
<td>k</td>
<td>exergetic unit cost, kW/kW</td>
</tr>
<tr>
<td>Lo</td>
<td>component or control volume loss, kW</td>
</tr>
<tr>
<td>m</td>
<td>mass flow, kg/s</td>
</tr>
<tr>
<td>p</td>
<td>pressure, kPa</td>
</tr>
<tr>
<td>Pr</td>
<td>component or control volume product, kW</td>
</tr>
<tr>
<td>s</td>
<td>specific entropy, kJ/(kg.K)</td>
</tr>
<tr>
<td>S</td>
<td>entropic term flow, kW</td>
</tr>
<tr>
<td>T</td>
<td>temperature, K</td>
</tr>
<tr>
<td>u</td>
<td>specific internal energy, kJ/kg</td>
</tr>
<tr>
<td>U</td>
<td>internal energy term flow, kW</td>
</tr>
<tr>
<td>v</td>
<td>specific volume, m³/kg</td>
</tr>
<tr>
<td>Y</td>
<td>generic productive flow, kW</td>
</tr>
</tbody>
</table>
Z  hourly cost of the subsystem, $/h

Greek symbols

$\eta$  efficiency

Subscripts

in  inlet flow

i  physical stream

j:k  from stream k to stream j

o  environment or reference

out  outlet flow

ufd  subsystem or unit of the functional diagram

References


Abstract:
In view of the continuous yet finite exergy supply to Earth, in addition to the inability to complete recycle this exergy, imposed by the Second Law of Thermodynamics, the proper comparison between different fuels as well as the actual exergy costs necessary for environmental evaluation of any produced good is of great importance. The exergy cost of any product lies on the calculation of the exergy intensity of the used fuels. The calculation of the exergy intensity for petroleum derived fuels is performed by solving the set of linear equations used to describe the cost formation process of these fuels. The production process of petroleum derived fuels is a complex series of processes including primary separation, transportation, atmospheric and vacuum distillation, delayed coking, fluidized catalytic cracking, hydrotreating, hydrogen generation, as well as residues treatment, such as sulphur recovery and sour water treatment. Exergoeconomy analysis provides the rational tool for partitioning the exergy consumed in both: production processes and residues treatment processes among the produced fuels. Furthermore, it provides the exergy efficiency of the utilities produced by refinery utilities plant. Exergy and exergoeconomy analysis were performed in a 415,000 bpd refinery which processes a 28 API crude mixture, mainly from Campos basin in Rio de Janeiro Brazil. The unit exergy cost determined for FCC LPG and gasoline is: 1.08 kJ/kJ while for hydrotreated diesel, which requires more processing steps, is 1.11 kJ/kJ. The exergy intensity obtained for these petroleum derived fuel are: 52.89 MJ/kg, 50.71 MJ/kg and 50.19 MJ/kg, respectively, while values reported for typical sugar cane Brazilian ethanol (a well know renewable fuel) are 3.4 kJ/kJ and 92.56 MJ/kg.

Keywords:
Exergy, Exergoeconomy, Fuels unit exergy cost, Fuels exergy intensity, Petroleum refinery.

1. Introduction

The exergy expenditure for petroleum extraction, transportation and refining and its rational partition among the produced substances can be used to evaluate the exergy intensity of an enormous quantity of goods produced from petroleum derived matter. It can also help fuel polices since it informs the work capacity spent to obtain each petroleum derived fuel which is an important information for comparison between petroleum derived fuels and renewable fuels and among the different fuels produced in a refinery as proposed in [1]. In addition to this, exergy analysis pinpoints the processes responsible for main exergy destructions, properly evaluates the waste heat and waste of mechanical exergy (pressure drop in valves), both present in large scale in petroleum industry. The refining processes are complex and highly integrated, thus thermoeconomy theories [2-7] are of great use to indicate the actual efficiency of production of the several fuels and utilities as well as the exergy destroyed for their production. Although the importance of the subject, few works are found in literature: Dinçer [8] applied exergy analysis to a petroleum refinery and an overall availability efficiency of 5.9% was reported. Rivero [9] conducted an exergy analysis to optimize a 150,000 barrels per day (bpd) refinery. In this analysis the main exergy destruction was present in the utilities plant followed by catalytic cracking unit and combined distillation. Several modifications were performed and new systems were implemented: retrofit of heat exchangers network by the Pinch method, pre-heating air systems, CO steam generators1 and water pre-heaters.

1 This steam generator re-burns the hot CO rich gas exhausted by catalytic cracking unit during catalyst regeneration.
A reduction of 26% of total degraded energy was observed. Some works using exergy analysis were performed in single distillation processes such as [10], [11] and [12]. Exergoeconomy analysis were usually applied for utilities plant alone as in [13] and [14], in the latter a critical point of view is presented. Rivero et al. [15] applied exergoeconomy to a combined distillation unit. Other important works were carried out, however without the direct use of the Second Law of Thermodynamics: a reduction of 31% in energy consumption per barrel processed was reported by [16], due to the modernization of a refinery. The reported modernization may include: CO boiler, increase heat exchange between streams and units, hotter feeds between processes units, more efficient equipment, inclusion of combined cycles in utilities plant, among other typical improvements. The increase in energy consumption and CO$_2$ emission due to increase in the production of hydrotreated fuels$^2$ was highlighted by [17]. None of these works however, performed an exergoeconomy analysis of the entire refinery including processes units such as: combined distillation, fluidized catalytic cracking (FCC), delayed coking and hydrotreating, utilities plant and treatment units such as: sulphur recovery and sour water treatment. In this work exergoeconomy analysis is performed for the whole petroleum sector, Fig. 1. It uses the unit exergy cost of natural gas and petroleum from a production plant (offshore platform), adds the exergy spent during transportation, and uses exergoeconomy to distribute the refinery exergy income among its products. Thus, it is possible to quantify the exergy destroyed to produce each one of the petroleum derived fuels in a thermodynamic rational basis. Furthermore the exergy analysis is applied to the refining process, in which the highest exergy destructions take place, in order to highlight the processes more representative for exergy saving in the sector.

![Fig. 1. Petroleum sector composed by production, transportation and refining](image)

The paper is organised as follows: Section 2 presents the refining process analysed, which is the main exergy consumer in petroleum sector; Section 3 describes the methodology used for refinery exergy and exergoeconomy analysis; Section 4 presents the considerations used to take into account the production and transportation in the exergoeconomy analysis as well as its overall results; Section 5 presents the main conclusions.

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$^2$ Fuels with low sulphur content (< 50 ppm).
2. Refinery description

Exergy and exergoeconomy analysis were performed in a 415,000 bpd refinery which processes a 28 API crude mixture, mainly from Campos basin in Rio de Janeiro Brazil. This refinery is composed of the following process units: combined distillation, FCC, delayed coking, hydrogen generation, hydrotreating, sulphur recovery and sour water treatment. A utilities plant is used to provide steam at three different grades, electricity, mechanical power and water at different pressure levels to the process units.

2.1. Refining scheme

A mixture of crude oils from primary separation units enters in the combined distillation unit. In combined distillation the oil is desalted using rectified water and then it goes to atmospheric distillation. The residue of atmospheric distillation is sent to vacuum distillation in which it distillates at moderate temperatures. The residue of vacuum distillation is sent to delayed coking unit in which lighter products and coke are produced. The feed of FCC unit is a mixture of naphtha and gasoil produced in delayed coking and combined distillation. Products such as gasoline, liquefied petroleum gas (LPG), light cycle oil (LCO) and decanted oil (DECO) are produced in FCC. The hydrogen generation unit receives natural gas in order to provide the hydrogen necessary for hydrotreating process. In hydrotreating process streams in diesel range are treated to produce hydrotreated diesel. The refining scheme together with utilities and residues streams are depicted in Fig.2.

2.2. Combined distillation (CD)

The control volume considered for combined distillation consists of three processes: desalting, atmospheric distillation and vacuum distillation. The desalting process is the first process in combined distillation, it mixtures dilution water in the crude oil in order to dissolve the salts remaining from primary separation, then the salty water is separated by electrostatic separators. After desalting and pre-heating by the products leaving the unit the petroleum is sent to a pre-flash column, where the light fractions are removed so that the main column and furnace can be designed for the heavier fractions only. After leaving the pre-flash column the heavier fractions are sent to the furnace and are heated to temperatures close to 400ºC. Steam is also injected in the tower to strip the residue and to reduce the components partial pressure. The residue of atmospheric distillation is then sent to a vacuum distillation tower in which it is evaporated at temperatures close to 415ºC and sub atmospheric pressures between 30 and 100 (mbar), provided by steam ejectors.

2.3. Fluidized catalytic cracking (FCC)

The fluidized catalytic cracking is a chemical conversion process that uses a zeolite type catalyst. The feed of this process is a mixture of gasoil and naphtha produced by combined distillation and delayed coking processes while the products are high value streams such as: gasoline (GLN) and liquefied petroleum gas (LPG). The catalyst regeneration process is the main energy source for the endothermic reactions present in the process. The catalyst is regenerated by burning the coke that adhere to catalyst surface, thus the hot regenerated catalyst, at temperatures close to 700ºC, and the feed are mixed at the bottom of the riser. The exhausting gas from the catalyst regeneration process is a hot gas rich in carbon monoxide, usually called CO gas, used in a recovery boiler to generate steam. This CO gas represents an important fraction of the energy consumed in the refinery.

3 BSW - Basic Sediments and Water is usually below 1%.
2.4. Delayed coking (DC)

The delayed coking is a thermal cracking process. The vacuum residue is pre-heated at temperatures around 350ºC so that the lighter fraction can bypass the main furnace. The heavier fraction passes through the main furnace and leaves at temperatures close to 500ºC. The not evaporated feed is then sent to the coking drums where it stays for a certain period necessary for coking. The quantity of coke produced is function of the Conradson Carbon Residue (CCR) of the feed. Since it is an intermittent process, several drums are used in parallel so that while one is coking the others can be filled. As the coke has a very low H/C ratio the other streams leaving the delayed coking have a higher H/C ratio, thus the main function of the delayed coking unit is to increase the yield of light fractions by removing coke.

2.5. Hydrogen generation (HG)

Hydrogen is generated by natural gas steam reforming process. This is a catalytic process usually represented by two chemical reactions: (R1) and (R2). The former is an endothermic reaction that forms syngas (CO and H$_2$), and the later is an exothermic reaction known as shift reaction and used to convert the remaining CO in more H$_2$ and CO$_2$.

\[
C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2 \quad (R1)
\]

\[
CO + H_2O \rightarrow CO_2 + H_2 \quad (R2)
\]

After the reactions take place the hydrogen purification is performed by a pressure swing adsorption system (PSA) that allows a 99.9% purity.

2.6. Diesel hydrotreating (HDT)

This process is a catalytic process using a Co-Mo in alumina base catalyst. It aims to remove contaminants, mainly sulphur, (R3), from diesel range streams. It also increases the cetane number of diesel since double bonds are broken to form single bonds.

\[
RSH + H_2 \rightarrow RH + H_2S \quad (R3)
\]

The diesel feed and the hydrogen are mixed and heated in a furnace. The mixture is sent to a reactor where the reactions occur. The products go to a separator where the gaseous fraction is separated. The gaseous stream is directed to an amine scrubber where the sour gas is separated and sent to a sulphur recovery unit while the remaining H$_2$ is recycled.

2.7. Utilities plant

For the sake of simplicity similar components of the utilities plant were aggregated. The synthesis plant is then composed of a gas turbine, a heat recovery steam generator (HRSG) that also burns fuel gas (FG), a CO and fuel gas boiler, a fuel gas and fuel oil (FO) boiler, an extraction and condensation steam turbine for electric power generation, four steam turbines for mechanical power generation, an air compressor, a deaerator, three pumps, a pre-heater, a cooling tower and a water treatment process. The utilities synthesis plant can be seen in Fig.3.

---

4 The cetane number indicates the explosion resistance to pressure of a fuel.
Fig. 2. Refinery configuration
2.8. Sulphur recovery (SR)

All sour gas produced in the refinery is treated in the sulphur recovery unit. The process consists of a series of chemical reactions and it is usually called Claus process. The first step: (R4) and (R5) is a thermal and very exothermic step, occurring at temperatures above 850ºC. This thermal step is responsible for 60% to 70% of conversion of H₂S into elementary sulphur. In the catalytic converter chemical step, (R6) is conducted. The steps can be continually repeated, always with the entrance temperature decreased. The remaining H₂S, after last chemical step, is incinerated. As the reactions present in this process are exothermic, their heat of reaction are used for steam generation.

\[
\begin{align*}
2H_2S + O_2 & \rightarrow 2S + 2H_2O \quad (R4) \\
2H_2S + 3O_2 & \rightarrow 2SO_2 + 2H_2O \quad (R5) \\
2H_2S + SO_2 & \rightarrow 3S + 2H_2O \quad (R6)
\end{align*}
\]

Fig. 3. Utilities plant configuration
2.9. Sour water treatment (SWT)

Sour water is mainly produced by contact with hydrocarbons since steam is extensively used to decrease the partial pressure of the hydrocarbon components. Water is also used in cleaning and decoking, thus large quantities of sour water are produced. Although called "sour water" this water has a pH around 9 and it is called sour because of its characteristic smell. This sour water is sent to a rectifying tower where it is mixed with steam and the contaminants are removed in sour gas form and finally treated in sulphur recovery process. Further information about refining process units can be found in [18] and [19].

3. Methodology

In the analysed refinery all the processes are duplicated, thus only one half of the refinery was studied. A hybrid method composed of real plant data and simulated data was used. The mass flow, elementary composition and lower heating value of each stream were provided by Petro-SIM software for the given feeds of a given unit process. The feed is characterized by its distillation curve: TBP (ASTM-2892), ASTM-86, ASTM-D2887 or ASTM-D1160, when available the feed API gravity and viscosity are used to provide more accurate data. The temperature of the streams connecting the process units is the average of the values collected from plant information system (PI) during a typical operation day. This average temperature takes into consideration all heat changed before the stream leaves the control volume of the unit. The feeds mass flow and utilities consumption are also collected from PI. The utilities plant as well as both treatment process: sulphur recovery and sour water treatment have their products and feed according to the other units requirements, keeping the real production rates and efficiencies constant.

3.1. Exergy calculation

The total specific exergy is calculated as in Szargut [20], as the sum of physical and chemical exergy, (1).

\[ b_{Total} = b_{Physical} + b_{Chemical} \] (1)

The physical exergy was calculated according to (2), using Petro-SIM [21] software to calculate enthalpy and entropy. The reference temperature considered was 25ºC. The Petro-SIM uses correlations such as those explained in Riazi [22], using a proper equation of state and residual properties or an activity model to calculate enthalpy and entropy.

\[ b_{Physical} = (h-h_0) - T_0 \cdot (s-s_0) \] (2)

The chemical exergy is calculated as in (3), using Rivero et al. [23] correlation (4) that differently from Szargut et al. [20] and Kotas [24] also takes the sulphur concentration into account.

\[ b_{Chemical} = \varphi \cdot LHV \] (3)

\[ \varphi = 1.041 + 0.1728 \cdot \left( \frac{x_{H_2}}{x_C} \right) + 0.0432 \cdot \left( \frac{x_{O_2}}{x_C} \right) + 0.2169 \cdot \left( \frac{x_S}{x_C} \right) \cdot \left( 1 - 2.0628 \cdot \left( \frac{x_{H_2}}{x_C} \right) \right) + 0.0428 \cdot \left( \frac{x_{S_2}}{x_C} \right) \] (4)

The factor \( \varphi \) used for coke, solid fuel, was 1.05 provided by Kotas [24].
3.2. Exergy efficiency

3.2.1. Utilities plant

The energy and exergy efficiency equations used for the components of the utilities plant are shown in Table 1. Note that these equations drive the exergoeconomy equations for the respective components. Also note that in gas turbines the exhausting gas exergy was subtracted from the fuel exergy since it is used in heat recovery boilers. The $x$ coefficient is used in steam turbine to include the energy and exergy expenses due to the use of cooling towers: make up water, electric and mechanic power. The quantity of energy in heat form sent to the cooling water was the weighting factor used. All boilers use two fuels, the function of the heat exchangers is to heat the cold fluid, the air compressors and pumps efficiency are for a group of equipment driven by steam and electricity.

3.2.2. Process units

The function of the units of thermal and chemical separation is to increase the chemical exergy of feed, since a mixture is separated into its components. Thus the most adequate efficiency seems to be (5).

$$\eta_b = \frac{\sum B_{PRODUCTS} - \sum B_{FEED}}{\sum B_{CONSUMED}} \quad (5)$$

However, the substantial difference in the exergy magnitude of the products and feed in relation to the consumed exergy prevents this calculation. In the analysed processes the consumed exergy is no more than 2.2% of the feed exergy while the accuracy of the in LHV calculation is near 1.45% [25], the accuracy in $\varphi$ calculation is around 0.38% [24] and considerable errors are expected in the enthalpy and entropy calculations since they are given by a series of correlations [22]. Therefore the exergy efficiency indicator used was given by (6) for all process units.

$$\eta_b = \frac{\sum B_{OUT}}{\sum B_{IN}} \quad (6)$$

Furthermore, the process units were considered responsible for the use of treatment units: sour water treatment and sulphur recovery as well as for cooling water system (cooling towers). Consequently all exergy fluxes consumed and produced by cooling towers and by these treatment units were allocated to the units that produce residues and dissipate exergy through cooling water circuit.
Table 1. Equations used for energy and exergy performance evaluation of utilities plant components

<table>
<thead>
<tr>
<th>Component</th>
<th>Energy performance parameter</th>
<th>Exergy efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas turbines</td>
<td>( \eta_e = \frac{\dot{W}<em>{Electric}}{m</em>{Fuel} \cdot LHV} )</td>
<td>( \eta_b = \frac{\dot{W}<em>{Electric} \cdot m</em>{Fuel} \cdot b_{Fuel} - \dot{m}<em>{Exhausting} \cdot b</em>{Exhausting}}{\dot{m}_{Fuel} \cdot LHV} )</td>
</tr>
<tr>
<td>Steam turbines</td>
<td>( \eta_e = \frac{\dot{W}<em>{Electric/Mechnic}}{H</em>{Steam} - H_{Extraction} - H_{Condensate} + x \cdot (H_{H_2O} + \dot{W}<em>{Electric} + \dot{W}</em>{Mechanic})} )</td>
<td>( \eta_b = \frac{\dot{B}<em>{Steam} \cdot b</em>{Steam} - \dot{B}<em>{Extraction} \cdot b</em>{Extraction} + \dot{B}<em>{Condensate} \cdot b</em>{Condensate} + \dot{W}<em>{Electric} \cdot b</em>{Electric} + \dot{W}<em>{Mechanic} \cdot b</em>{Mechanic}}{\dot{B}<em>{Steam} - \dot{B}</em>{Water}} )</td>
</tr>
<tr>
<td>Pumps</td>
<td>( \eta_e = \sum \left( \frac{\dot{m}<em>{Water} \cdot \Delta P</em>{Water}}{\rho_{Water}} \right) )</td>
<td>( \eta_b = \frac{\sum (\dot{B}<em>{Water</em>{out}} - \dot{B}<em>{Water</em>{in}})}{\sum (\dot{W}<em>{Electric} + (\dot{B}</em>{Steam_{in}} - \dot{B}<em>{Steam</em>{out}}))} )</td>
</tr>
<tr>
<td>Steam generators</td>
<td>( \eta_e = \frac{\dot{H}<em>{Steam} + \dot{H}</em>{Water}}{m_{Fuel1} \cdot LHV_{Fuel1} + m_{Fuel2} \cdot LHV_{Fuel2}} )</td>
<td>( \eta_b = \frac{\dot{B}<em>{steam} + \dot{B}</em>{water}}{m_{Fuel1} \cdot b_{Fuel1} + m_{Fuel2} \cdot b_{Fuel2}} )</td>
</tr>
<tr>
<td>Heat exchangers</td>
<td>( \varepsilon = \frac{C_{Cold}(T_{Cold_{in}} - T_{Cold_{out}})}{C_{Cold}(T_{Cold_{in}} - T_{Cold_{in}})} )</td>
<td>( \eta_b = \frac{B_{cold_{out}} - B_{cold_{in}}}{B_{Hot_{in}} - B_{Hot_{out}}} )</td>
</tr>
<tr>
<td>Valves</td>
<td>( \eta_e = \frac{\dot{H}<em>{Out}}{\dot{H}</em>{In}} )</td>
<td>( \eta_b = \frac{\dot{B}<em>{Out}}{\dot{B}</em>{In}} )</td>
</tr>
<tr>
<td>Deaerators</td>
<td>( \eta_e = \frac{\sum \dot{H}<em>{Out}}{\sum \dot{H}</em>{In}} )</td>
<td>( \eta_b = \frac{\sum \dot{B}<em>{Out}}{\sum \dot{B}</em>{In}} )</td>
</tr>
<tr>
<td>Air compressors</td>
<td>( \eta_{IsoTherm} = \frac{\sum (\dot{m} \cdot R \cdot T_0 \cdot \ln \left( \frac{P_{Air_{out}}}{P_0} \right))}{\sum (\dot{W}<em>{Electric} \cdot (\dot{H}</em>{Steam_{in}} - \dot{H}<em>{Steam</em>{out}}))} )</td>
<td>( \eta_b = \frac{\sum (\dot{B}<em>{Air</em>{out}} - \dot{B}<em>{Air</em>{in}})}{\sum (\dot{W}<em>{Electric} + (\dot{B}</em>{Steam_{in}} - \dot{B}<em>{Steam</em>{out}}))} )</td>
</tr>
<tr>
<td>Water treatment</td>
<td>( \eta_e = \frac{\dot{H}<em>{Water</em>{out}} - \dot{H}<em>{Water</em>{in}}}{\dot{W}_{Electric}} )</td>
<td>( \eta_b = \frac{\dot{B}<em>{Water</em>{out}} - \dot{B}<em>{Water</em>{in}}}{\dot{W}_{Electric}} )</td>
</tr>
</tbody>
</table>
### 3.3. Exergoeconomy

The principles used for exergoeconomy formulation are in general the ones proposed by Lazzareto and Tsatsaronis [2]. The set of exergoeconomy equations for utilities plant components were driven by the exergy efficiencies given in Table 1. The exergoeconomy formulation for process units, (7), considers that each process unit has its own unit for sour water treatment (SWT) and sulphur recovery (SR) as well as its own cooling water circuit as shown in Fig.4. The coefficients $x_1$, $x_2$ and $x_3$ are used to weight, using mass flow and heat, the exergy input and output of the given process due to the use of auxiliary process, see (8), (9) and (10). In the following equations $i$ represents the analysed process unit and $m$ the auxiliary units.

\[
\sum_i \left( c_{\text{PRODUCTS}} \cdot \dot{B}_{\text{PRODUCTS}} \right)_i + c_{\text{MP Steam}} \cdot \dot{B}_{\text{MP Steam}} + c_{\text{LP Steam}} \cdot \dot{B}_{\text{LP Steam}} + c_{\text{RW}} \cdot \dot{B}_{\text{RW}} + c_S \cdot \dot{B}_S - c_{\text{Cond}} \cdot \dot{B}_{\text{Cond}} =
\]

\[
x_1 \cdot \sum_m \left( c_{\text{B in SWT}} \cdot \dot{B}_{\text{in SWT}} \right)_m + x_2 \cdot \sum_m \left( c_{\text{B in SR}} \cdot \dot{B}_{\text{in SR}} \right)_m +
\]

\[
x_3 \cdot \sum_m \left( c_{\text{B in Tower}} \cdot \dot{B}_{\text{in Tower}} \right)_m + \sum_i \left( c_{\text{FEED}} \cdot \dot{B}_{\text{FEED}} \right)_i + \sum_i \left( c_{\text{B in unit}} \cdot \dot{B}_{\text{in Unit}} \right)_i
\]

\[
x_1 = \frac{\sum_m \dot{m}_{\text{SW out m}}}{\sum_m \dot{m}_{\text{SW in m}}}
\]

\[
x_2 = \frac{\sum_m \dot{m}_{\text{SR out m}}}{\sum_m \dot{m}_{\text{SR in m}}}
\]

\[
x_3 = \frac{\dot{Q}_i \left( \frac{1}{T_0} - \frac{1}{T_{CI}} \right)}{\left( \frac{1}{T_0} - \frac{1}{T_{CW}} \right) \cdot \sum_m \dot{Q}_{\text{in m}}}
\]

The approximation in (10) is feasible since the temperature in which the heat is sent to cooling water, $T_{CI}$, is close to all processes and it is also close to the temperature in which the heat is dissipated by cooling tower, $T_{CW}$.

All the fluxes that leave the control volume of Fig.4 except for the heat sent to the environment and the condensed steam are considered as products of the process unit and have the same unit exergy cost, as shown in (11).

\[
c_{\text{PRODUCT out i}} = c_{\text{MP Steam}} = c_{\text{LP Steam}} = c_{\text{RW}} = c_S = c_{\text{Cond}}
\]

The cost of the condensed steam is provided by (12) since it comes from medium and low pressure steam used as energy source in the unit.

\[
\frac{\sum_i \left( c_{\text{MP Steam}} \cdot \dot{B}_{\text{MP Steam}} \right)_i + \sum_i \left( c_{\text{LP Steam}} \cdot \dot{B}_{\text{LP Steam}} \right)_i}{\sum_i \dot{B}_{\text{MP Steam out i}} + \sum_i \dot{B}_{\text{LP Steam out i}}} = c_{\text{Cond}}
\]
In order to calculate the unit exergy cost of the refinery streams, the exergoeconomy equations for process units together with the exergoeconomy equations for utilities plant components, derived from the efficiencies presented in Table 1, were solved using Engineering Equation Solver (EES) [26].

4. Results

4.1. Exergy analysis results
The exergy efficiency and exergy destroyed in each process unit were calculated. The exergy spent in residue treatment is allocated to the process units responsible for the residue production using the residue mass flow as the weight factor. This approach is also used to distribute the exergy costs related with cooling water circuit (cooling towers), however the weight factor used was the quantity of heat sent to the cooling water. The products of the treatment processes: rectified water, elementary sulphur and steam were distributed to process units using the same criteria.

4.1.1. Combined Distillation
The Grassmann diagram in Fig.5 shows the direct exergy input and output of combined distillation. The combined distillation is responsible for 43.7% of all heat sent to the cooling water circuit and by 24.9% of total sour water produced. Therefore 12.1 MW were added as exergy input to represent the exergy consumed in auxiliary unit and more 3.6 MW were added to products, in order to represent the auxiliary units products: rectified water, elementary sulphur and steam.
As result an exergy efficiency of 98.18% is observed. Approximately 1 kg of brine is produced for 10 kg of processed crude. Despite of high exergy efficiency, 264 MW of exergy are destroyed.

**4.1.2. Fluidized Catalytic Cracking**

Besides the direct exergy flows rates shown in Fig. 6, more 14.8 MW are added as exergy input in FCC control volume since it is responsible for 43% of sour water production and 38% of the total heat sent to cooling water circuit. Also 13.7 MW are added as products since rectified water, elementary sulphur and steam are additionally produced in the auxiliary units.

The exergy efficiency of FCC unit is 98.93%. This high efficiency results from the use of CO gas in CO boilers, thus it is considered as a product, and from the use of heated catalyst from regeneration process as the main exergy input.

**4.1.3. Delayed coking**

In addition to the direct exergy input and output shown in Fig. 7 more 3.9 MW are added as input and more 4.1 MW are added as product due to sour water and sour gas production and heat sent to cooling water. More exergy is added to the products than to input since the sulphur recovery process makes use of the exergy present in the sour gas to produce the elementary sulphur, thus this process has a positive impact in all process units that produce sour gas.
The total exergy efficiency observed was 98%. 61.8 MW of exergy is destroyed.

4.1.4. Hydrogen generation

The process of hydrogen generation produces neither sour gas nor sour water. It sends a very small quantity of heat to cooling water circuit, been penalised by only 12.6 kW.

The process exergy efficiency for hydrogen generation unit is 73.6%, see Fig.8. The total exergy destroyed is 36.7 MW. Note that the steam generated has a significant role in this process.

4.1.5. Hydrotreating

Since the function of hydrotreating unit is to remove sulphur compounds, a great quantity of sour gas is produced (46% of total). Besides sour gas, sour water is also produced and heat is sent to cooling water circuit. Therefore 5.5 MW of exergy is added to the exergy input and 19.6 MW is added to the products.
The hydrotreating exergy efficiency is 92.88%, 192.1 MW of exergy is destroyed, Fig.9. Note that the hydrogen is responsible for only 2% of exergy input.

4.1.6. Utilities plant

For utilities plant an exergy efficiency of 30% was observed. The energy and exergy efficiency given by the equations described in Table 1, for each plant component, can be seen in Fig. 10. The exergy efficiency is higher than energy efficiency for gas turbine (GT) since the exergy of exhausting gas was subtracted from the exergy of the fuel. The recovery boiler (RB) and the conventional boiler (B1, B2) presented an exergy efficiency of 39%, 49% and 40%, respectively. The steam turbines (T) presented a large variation in exergy efficiency: 38% up to 76% highlighting some possible problems. The water treatment process (WTP) has a very low efficiency since it is not an energy conversion process.

![Fig. 10. Energy and exergy efficiency of utilities components](image)

The main exergy destructions in utilities plant were presented in the components in which combustion occurs: boilers and gas turbines, these components are responsible for 85% of the all exergy destroyed, see Fig.11.

![Fig. 11. Exergy destroyed in each utilities plant component](image)

Taking into account all components of utilities plant, 249 MW of exergy are destroyed.
4.1.7. Exergy analysis summary

Table 2. presents a summary of the exergy analysis. Note that the total exergy destroyed is 749.8 MW. The exergy destroyed in SR and SWT treatment processes is allocated to the processes that make use of these units.

<table>
<thead>
<tr>
<th>Unit</th>
<th>$B_{in}$ [kW]</th>
<th>$B_{out}$ [kW]</th>
<th>$B_{dest}$ [kW]</th>
<th>% destroyed</th>
<th>$\eta_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD</td>
<td>14,313,503</td>
<td>14,049,234</td>
<td>264,269</td>
<td>36%</td>
<td>98.18%</td>
</tr>
<tr>
<td>UT</td>
<td>355,931</td>
<td>107,065</td>
<td>248,866</td>
<td>33%</td>
<td>30.08%</td>
</tr>
<tr>
<td>DC</td>
<td>3,190,335</td>
<td>3,100,598</td>
<td>89,737</td>
<td>12%</td>
<td>98.00%</td>
</tr>
<tr>
<td>HDT</td>
<td>2,757,355</td>
<td>2,689,992</td>
<td>67,364</td>
<td>9%</td>
<td>92.88%</td>
</tr>
<tr>
<td>HG</td>
<td>142,457</td>
<td>104,686</td>
<td>37,770</td>
<td>5%</td>
<td>73.50%</td>
</tr>
<tr>
<td>FCC</td>
<td>3,418,041</td>
<td>3,384,802</td>
<td>33,239</td>
<td>4%</td>
<td>98.93%</td>
</tr>
<tr>
<td>TE</td>
<td>13,562,341</td>
<td>13,553,746</td>
<td>8,594</td>
<td>1%</td>
<td>99.94%</td>
</tr>
<tr>
<td>SR</td>
<td>36,754</td>
<td>28,346</td>
<td>8,408</td>
<td>1%</td>
<td>75.56%</td>
</tr>
<tr>
<td>SWT</td>
<td>15,668</td>
<td>14,058</td>
<td>1,610</td>
<td>0%</td>
<td>61.35%</td>
</tr>
</tbody>
</table>

4.1.8. Overall refinery efficiency

The overall exergy efficiency for the refinery is 94.4%. It is worth noting that more than 14 GW of exergy associated to crude oil, natural gas and water are processed and almost 800 MW of exergy are destroyed.

4.2. Improvements possibilities

Some possibilities to decrease exergy destruction are general, extensively studied and reported: Pinch Method for heat exchange network, pre-heating air systems and pre-heating water systems, both using waste heat, decrease the heat loss in the tanks between process, utilization of high efficiency utilities plants, the use of diagnosis and prognosis systems [27] and others. There are some improvement possibilities specific for refineries such as the development of better catalysts, the use of CO boilers as reported by [9,15] (already implemented in studied refinery) and the use of a turbo-expander to generate electricity during the CO gas pressure reduction before the CO boiler. This possibility is used in a great number of refineries and is reported in [28]. The use of the exergy of exhausting gases is very restricted, since for most of the furnaces and boilers the exhausting temperature is controlled to avoid acid condensation. However, the heat sent to cooling water circuit represents an actual improvement possibility since several streams are cooled prior entering transfer and storage area. From combined distillation unit 4.5 MW of exergy (~140ºC) are sent to cooling water circuit. The use of this exergy for power production using organic Rankine cycles (ORC) could improve the refinery efficiency by increasing the use of waste heat while decreases the cooling tower exergy and make-up water consumption.

4.3. Exergoeconomy results

In order to take into account the whole petroleum sector, the exergy spent during production and transportation were considered for evaluation.

4.3.1. Offshore production consideration

To take the primary separation into account, the work of Oliveira Jr. and Hombeeck [29] and Nakashima et al. [30] were considered. In [29] an exergy analysis of an offshore platform is performed while in [30] an exergoeconomy analysis of a petroleum artificial lift systems is conducted. Using a gas turbine efficiency of 30% and the extraction criterion, the related unit exergy cost of the crude oil is 1.006 (kJ/kJ) while 1.034 (kJ/kJ) is obtained for the natural gas. The higher value obtained for the natural gas is mainly due to post separation compression.
4.3.2. Petroleum and natural gas transportation

The unit exergy cost obtained for natural gas and petroleum from the offshore production facility includes their transportation up to an onshore base (~100km). In order to evaluate the transportation contribution from the onshore base to the refinery the following factors were used:

- **2.60 kJ/(kg.km)** for natural gas. This value takes into consideration that the energy for compression comes from gas turbines with 30% of efficiency (LHV basis) and it is based on a real compression station data. The isentropic efficiency reported for gas compression is 87%.

- **0.18 kJ/(kg.km)** for crude oil. This value takes into account that electricity is used to drive the pumps and it is obtained from local grid. This electricity is produced considering a local electricity matrix based on hydroelectricity with 80% of efficiency. A petroleum viscosity of 0.45 Pa.s (450 cP) was considered as well as a pumping efficiency of 50%.

By using the above mentioned considerations the basis for exergy unit cost calculations are the natural resources only: water in the reservoir and petroleum a natural gas in the well, both are the substances having unit exergy cost equals to one. Table 3 shows how the unit exergy cost varies with the distance between the onshore base and the refinery.

<table>
<thead>
<tr>
<th>Distance (km)</th>
<th>0</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG (kJ/kJ)</td>
<td>1.0340</td>
<td>1.0366</td>
<td>1.0393</td>
<td>1.0419</td>
<td>1.0445</td>
<td>1.0471</td>
<td>1.0498</td>
<td>1.0524</td>
<td>1.0550</td>
<td>1.0576</td>
<td>1.0603</td>
</tr>
<tr>
<td>% accumulated</td>
<td>0.25%</td>
<td>0.51%</td>
<td>0.76%</td>
<td>1.02%</td>
<td>1.27%</td>
<td>1.52%</td>
<td>1.78%</td>
<td>2.03%</td>
<td>2.29%</td>
<td>2.54%</td>
<td></td>
</tr>
<tr>
<td>Crude oil (kJ/kJ)</td>
<td>1.0060</td>
<td>1.0062</td>
<td>1.0064</td>
<td>1.0066</td>
<td>1.0068</td>
<td>1.0070</td>
<td>1.0072</td>
<td>1.0074</td>
<td>1.0076</td>
<td>1.0078</td>
<td>1.0080</td>
</tr>
<tr>
<td>% accumulated</td>
<td>0.02%</td>
<td>0.04%</td>
<td>0.06%</td>
<td>0.08%</td>
<td>0.10%</td>
<td>0.12%</td>
<td>0.14%</td>
<td>0.16%</td>
<td>0.18%</td>
<td>0.20%</td>
<td></td>
</tr>
</tbody>
</table>

4.3.3. Overall results

The increment in the unit exergy costs for the products of refinery process units to a distance, between the onshore base and refinery, of 500 km is shown in Fig. 12. A very small sensibility is observed. The same variations are obtained for the exergy intensity.

Since no relevant increment in unit exergy cost of products is observed due to transportation, even for long distances (500 km), the unit exergy costs for the crude oil and natural gas entering the refinery were considered the ones from offshore facility (0 km between onshore base and refinery). By solving the set of linear equation driven from exergy efficiencies provided in Table 1 and the exergoeconomy equations for each refinery process unit, (7), (8), (9), (10), (11) and (12), the unit exergy cost of all streams present in Fig.2 were calculated. Fig.13 shows the unit exergy cost of the utilities produced. It is worth noting that steam is produced by process units (\(_P\)) at a very low exergy cost, thus a medium cost is calculated (\(_M\)). Since the inverse of unit exergy cost is the exergy efficiency, the exergy efficiencies for electricity (EE), mechanical power (MechPw), high
pressure steam, medium pressure steam and low pressure steam generation are: 32%, 23%, 40%, 46% and 52%, respectively. These results show an inefficient mechanical power production and it is in accordance with the low efficiency obtained of some steam turbines, see Fig.10. These costs take into consideration all interaction present, thus they can be used as a quality indicator for utilities production.

![Utilities Exergy Costs (kJ/kJ)](chart)

**Fig. 13. Unit exergy cost of utilities**

The unit exergy cost of the main refinery streams can be seen in Fig.14. It clearly shows the cost aggregation as a given substance is processed by an increasing number of processes. The streams leaving combined distillation (CD) have a unit exergy cost of 1.03 (kJ/kJ). The streams leaving the delayed coking (DC) unit were processed by CD and by DC since the feed of DC is the vacuum residue, thus a unit exergy cost of 1.07 is observed. For the streams leaving FCC process a unit exergy cost of 1.08 is obtained since the feed of this process is composed of products of CD and DC. The HDT products are the ones with highest unit exergy cost, 1.11 (kJ/kJ), due to hydrogen use and due the high unit exergy cost of its feed.

![Fuels Exergy Cost (kJ/kJ)](chart)

**Fig. 14. Unit exergy cost of produced substances**

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5 In Figs 14-16 the mathematical symbol “>” are used to indicate the stream direction. E.g. CD>HGO means the heavy gasoil from combined distillation.

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The exergy intensity of the streams, Fig.15, is calculated by multiplying the unit exergy cost (kJ/kJ) by the specific exergy (kJ/kg) of the stream. Therefore it provides an indicator that besides the cost aggregation due to processing also takes into account the exergy of the stream. As result the high exergy streams with long process chains are the most intensive in exergy: LPG produced by FCC and DC, naphtha produced by HDT, gasoline from FCC and hydrotreated diesel. As a consequence, the low exergy products have low exergy intensity: brine, elementary sulphur and coke.

Figure 15 shows a comparison between unit exergy cost and exergy intensity. The unit exergy cost is function of process chain thus it is the same for the several products of a given process while exergy intensity is also function of the exergy accumulated in a given stream thus it varies from stream to stream. Table 4 shows the values informed in Figs 14, 15 and 16.

Figure 16 shows a comparison between unit exergy cost and exergy intensity. The unit exergy cost is function of process chain thus it is the same for the several products of a given process while exergy intensity is also function of the exergy accumulated in a given stream thus it varies from stream to stream. Table 4 shows the values informed in Figs 14, 15 and 16.
Table 4. Streams unit exergy cost(c) and exergy intensity(EI)

<table>
<thead>
<tr>
<th>STREAM</th>
<th>c (kJ/kJ)</th>
<th>EI (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD&gt;HGO</td>
<td>1.03</td>
<td>45.49</td>
</tr>
<tr>
<td>CD&gt;LGO</td>
<td>1.03</td>
<td>45.76</td>
</tr>
<tr>
<td>CD&gt;HN</td>
<td>1.03</td>
<td>48.20</td>
</tr>
<tr>
<td>CD&gt;LN</td>
<td>1.03</td>
<td>48.83</td>
</tr>
<tr>
<td>CD&gt;LD</td>
<td>1.03</td>
<td>46.82</td>
</tr>
<tr>
<td>CD&gt;K</td>
<td>1.03</td>
<td>47.59</td>
</tr>
<tr>
<td>CD&gt;TCGO</td>
<td>1.03</td>
<td>46.01</td>
</tr>
<tr>
<td>CD&gt;VR</td>
<td>1.03</td>
<td>44.51</td>
</tr>
<tr>
<td>CD&gt;HD</td>
<td>1.03</td>
<td>46.08</td>
</tr>
<tr>
<td>CD&gt;BRINE</td>
<td>1.03</td>
<td>0.05</td>
</tr>
<tr>
<td>DC&gt;HGO</td>
<td>1.07</td>
<td>46.32</td>
</tr>
<tr>
<td>DC&gt;MGO</td>
<td>1.07</td>
<td>46.97</td>
</tr>
<tr>
<td>DC&gt;LGO</td>
<td>1.07</td>
<td>48.18</td>
</tr>
<tr>
<td>DC&gt;HN</td>
<td>1.07</td>
<td>48.24</td>
</tr>
<tr>
<td>DC&gt;LN</td>
<td>1.07</td>
<td>49.78</td>
</tr>
<tr>
<td>DC&gt;LPG</td>
<td>1.07</td>
<td>51.18</td>
</tr>
<tr>
<td>DC&gt;COKE</td>
<td>1.07</td>
<td>40.46</td>
</tr>
<tr>
<td>FCC&gt;LCO</td>
<td>1.08</td>
<td>47.18</td>
</tr>
<tr>
<td>FCC&gt;DECO</td>
<td>1.08</td>
<td>45.81</td>
</tr>
<tr>
<td>FCC&gt;LPG</td>
<td>1.08</td>
<td>52.89</td>
</tr>
<tr>
<td>FCC&gt;GLN</td>
<td>1.08</td>
<td>50.71</td>
</tr>
<tr>
<td>SR&gt;S</td>
<td>1.09</td>
<td>20.82</td>
</tr>
<tr>
<td>HDT&gt;HDIESEL</td>
<td>1.11</td>
<td>50.19</td>
</tr>
<tr>
<td>HDT&gt;WN</td>
<td>1.11</td>
<td>50.75</td>
</tr>
</tbody>
</table>

5. Conclusion

The exergy analysis was applied to a whole refinery. The processes responsible for the main exergy destruction rates are combined distillation, utilities plant (85% in gas turbines and boilers) followed by delayed coking. The overall exergy efficiency observed is 94.4%. This result demonstrates that only a small percentage of the exergy input (~14 GW) is destroyed (~800MW). Organic Rankine cycles to make use of the exergy sent to cooling tower hence reducing the exergy and make-up water consumption while increasing whole process efficiency is suggested as improvement. The exergoeconomy provided the necessary tool to calculated the exergy efficiency of utilities production in the highly integrated and multiproduct processes. By using the unit exergy cost provided by previous works for oil and natural gas from primary separation the exergy cost and exergy intensity of petroleum derived fuels were calculated. The oil and natural gas transportation to the refinery plays a minor role in comparison with refining and production exergy consumption. The exergy intensity of the petroleum derived fuels allows properly quantification of the exergy expenditures for production of petroleum derived goods and fuels. The exergy intensity observed for FCC gasoline and LPG, and for hydrotreated diesel are 50.71 (MJ/kg), 52.89 (MJ/kg) and 50.19 (MJ/kg), while the unit exergy costs are 1.08 (kJ/kJ), 1.08 (kJ/kJ) and 1.11(kJ/kJ), respectively. It is interesting to note that these values are significantly smaller than the value provided in [1] for a typical sugar cane ethanol, 3.4 (kJ/kJ) and 92.56 (MJ/kg).
**Acknowledgments**

The first and last authors of this paper would like to thank CNPq (grants 143302/2009-4 and 306505/2009-6) and Petrobras for the financial support.

**Nomenclature**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Air Compressor</td>
</tr>
<tr>
<td>B</td>
<td>Boiler</td>
</tr>
<tr>
<td>c</td>
<td>Unit exergy cost, (kJ/kJ)</td>
</tr>
<tr>
<td>CCR</td>
<td>Carbon Conradson Residue</td>
</tr>
<tr>
<td>CD</td>
<td>Combined Distillation</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CT</td>
<td>Cooling Tower</td>
</tr>
<tr>
<td>DC</td>
<td>Delayed Coking</td>
</tr>
<tr>
<td>DEA</td>
<td>Deaerator</td>
</tr>
<tr>
<td>DECO</td>
<td>Decanted Oil</td>
</tr>
<tr>
<td>EE</td>
<td>Electric Energy</td>
</tr>
<tr>
<td>EI</td>
<td>Exergy Intensity, (MJ/kg)</td>
</tr>
<tr>
<td>FCC</td>
<td>Fluidized Catalytic Cracking</td>
</tr>
<tr>
<td>FG</td>
<td>Fuel Gas</td>
</tr>
<tr>
<td>GLN</td>
<td>Gasoline</td>
</tr>
<tr>
<td>GO</td>
<td>Gasoil</td>
</tr>
<tr>
<td>GT</td>
<td>Gas Turbine</td>
</tr>
<tr>
<td>HD</td>
<td>Heavy Diesel</td>
</tr>
<tr>
<td>HDT</td>
<td>Hydrotreating</td>
</tr>
<tr>
<td>HG</td>
<td>Hydrogen Generation</td>
</tr>
<tr>
<td>HGO</td>
<td>Heavy Gasoil</td>
</tr>
<tr>
<td>HN</td>
<td>Heavy Naphtha</td>
</tr>
<tr>
<td>HPW</td>
<td>High Pressure Water</td>
</tr>
<tr>
<td>HRSG</td>
<td>Heat Recovery Steam Generator</td>
</tr>
<tr>
<td>HT</td>
<td>Heat transfer</td>
</tr>
<tr>
<td>IP</td>
<td>Intermediate pressure</td>
</tr>
<tr>
<td>K</td>
<td>Kerosene</td>
</tr>
<tr>
<td>LCO</td>
<td>Light Cycling Oil</td>
</tr>
<tr>
<td>LD</td>
<td>Light Diesel</td>
</tr>
<tr>
<td>LGO</td>
<td>Light Gasoil</td>
</tr>
<tr>
<td>LHV</td>
<td>Low Heating Value</td>
</tr>
<tr>
<td>LN</td>
<td>Light Naphtha</td>
</tr>
<tr>
<td>LP</td>
<td>Low Pressure</td>
</tr>
<tr>
<td>LPG</td>
<td>Liquefied Petroleum Gas</td>
</tr>
<tr>
<td>LPW</td>
<td>Low Pressure Water</td>
</tr>
<tr>
<td>MecPw</td>
<td>Mechanical Power</td>
</tr>
<tr>
<td>MGO</td>
<td>Medium Gasoil</td>
</tr>
<tr>
<td>MP</td>
<td>Medium Pressure</td>
</tr>
</tbody>
</table>
MPW  Medium Pressure Water
N  Naphtha
NG  Natural Gas
ORC  Organic Rankine Cycle
P  Pump
PI  Plant Information
PSA  Pressure Swing Adsorption
Q  Heat
RB  Recovery Boiler
RW  Rectified Water
S  Sulphur
SG  Sour Gas
SR  Sulphur Recovery
SW  Sour Water
SWT  Sour Water Treatment
T  Steam Turbine
TBP  True Boiling Point
TCFO  Top Cycling Fuel Oil
TE  Transport and Storage
V  Valve
VR  Vacuum Residue
WN  Wild Naphtha
WTP  Water Treatment Process

Greek symbols
\( \eta \)  efficiency
\( \varphi \)  Correction factor to transform LHV into chemical exergy

Subscripts and superscripts
b  Exergy
Ci  To cooling water
Cond.  Condensed
CW  From cooling water
e  Energy
i  General process
m  General auxiliary unit
LP  Low Pressure
MP  Medium Pressure
RW  Rectified Water
S  Sulphur
SR  Sulphur Recovery
SWT  Sour Water Treatment
0  Environment
References


Exergy-based sustainability evaluation of a wind power generation system

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Abstract:
Huge greenhouse gas (GHG) emission from fossil fuel combustion and unsatisfied energy requirement have forced China to inquire into and change to environmental friendly alternatives that are renewable to sustain the increasing energy demand. Therefore, renewable energy in China has experienced a prosperous development in the last decade and will continue to be the focus and key issue of future energy development planning. However, some environmentalists have long argued that whether renewable energy sources such as wind are preferable to fossil fuels (oil, natural gas and coal), and which kind of renewable energy are more clean and sustainable. Quantitative evaluation to answer these questions thereby should be conducted. As extended exergy accounting (EEA) is a systematic exergo-economic method that adopts a single quantifier to account for materials, energy, labor and capital and to compute a presumed environmental impact based on remediation costs, it is a powerful tool for handling sustainability issues. Thus, aiming at evaluating the sustainability of renewable energy, we employ EEA to monitor the sustainability level of a wind power plant in China from the aspects of economic and environmental performance, and exergy efficiency. The results may provide some useful suggestions to support the environmentally sound renewable energy development.

Keywords:
Extended Exergy Evaluation, Wind Farm, Sustainability.

1. Introduction

Owing to its economic feasibility and great potential in reducing carbon emission, wind power, which is currently the environmentalists' favourite source of renewable energy, is thought to be the most likely renewable energy source to replace fossil fuels in the generation of electricity in the 21st century. However, controversies on if the wind power is more competitive compared with other renewable alternatives are still going on. For energy sources, it is difficult to measure and is often decided in a qualitative manner. Therefore, a quantitative approach aiming at making trade-offs among renewable energy sources is required.

Sustainability of energy sources is regarded an efficient way to determine which energy source is more appropriate. Clearly, judgements of sustainability include conversion efficiency, economic feasibility, and environmental loading that must be ‘treated and recycled’ by the environment. Ultimately, the comprehensive evaluation of sustainability for different energy sources could be factored into policy discussions of future renewable energy planning.

To make decisions towards sustainable energy generation and use, several methods and models have been developed, and classified into indicator-based analytic hierarchy process (AHP) method [1, 2], systematic energy analysis [3, 4], energy analysis [5], and exergetic method [6, 7]. For AHP method, since there are no intrinsic principles for the selection of indicators, especially the identification of weight which is judged subjectively by experts, the derived indicators may be not
suitable to measure the long-term sustainability of energy systems. Although energy analysis (first law analysis) could overcome the subjectivity of AHP method, the non-additivity of different kinds of energy types which vary in quality poses great barriers for monitoring the energy flow of the energy system.

The concept of exergy was first proposed by Rant in 1956, and defined as the maximum amount of work which can be produced by a system or a flow of matter or energy as it comes to equilibrium with a reference environment [8]. This methodology has evolved since the early 1970's and has been extensively applied in empirical studies since late 1990's [9-17]. Compared with energy analysis, exergy is more appropriate in sustainability evaluation. Dincer (2002) has pointed out the importance of exergy from the following aspects: (1) It is a primary tool in best addressing the impact of energy resource utilization on the environment. (2) It is an effective method using the conservation of mass and conservation of energy principles together with the second law of thermodynamics for the design and analysis of energy systems. (3) It is a suitable technique for furthering the goal of more efficient energy-resource use, for it enables the locations, types, and true magnitudes of wastes and losses to be determined. (4) It is an efficient technique revealing whether or not and by how much it is possible to design more efficient energy systems by reducing the inefficiencies in existing systems. (5) It is a key component in obtaining sustainable development.

In the evolution of exergy method, Szargut et al. [18] extended the conventional exergy analysis to cumulative exergy consumption analysis (CECA), which combines exergy analysis with life cycle analysis (LCA) together, and accounts the sum of the values of primary exergy consumed in all the links of the energy and technological network in connection with the fabrication of the considered product.

However, despite that exergy analysis could detailed trace the efficiency of each conversion process in a thermodynamics perspective, it is not regarded as the optimal approach in sustainable evaluation as it couldn’t reflect the economic property of a process. This inability of standard exergy analysis to evaluate sustainability and determine real design optima was perfected by extended exergy accounting (EEA), which was proposed by Sciubba [19]. The conceptual novelty of EEA is represented by the fact that it also includes externalities (capital, labour and environmental impact) measured in homogeneous units (Joules) by a theory of joint economic- and thermodynamic character, properly named ‘thermoeconomics’, This concept was further developed and illustrated by Sciubba [20-23], and Ptasinski et al. [24]. Now, some researchers began to employ extended exergy to evaluate the sustainability of renewable energy sources. Corrado et al. [25] analysed the performance of an innovative high-efficiency steam power plant by means of two ‘life cycle approach’ methodologies, the life cycle assessment (LCA) and the ‘extended exergy analysis’ (EEA). Talens Peiró et al. [26] assessed and compared the production of 1 ton of biodiesel from used cooking oil (UCOME) and rapeseed crops (RME). The cumulative exergetic method is used by Yang et al. [27] to identify the renewability of the total corn-ethanol production in China when capturing all natural nonrenewable resources consumed in the integrated process including agricultural crop production, corn transportation, industrial conversion and waste treatment. However, in the current stage, a comprehensive sustainable indicator system hasn’t been proposed.

In this paper, the extended exergy evaluation method is applied to a wind power generation system, and some extended exergy based sustainability indicators were proposed to comprehensively monitor its environmental, economic and sustainable performances. The rest of the paper is organized as follow: In section 2, the accounting framework as well sustainable indicators are proposed. Using the EEA method, a case study is performed in Section 3. The results and some discussions are then demonstrated in Section 4. Finally, some conclusions are drawn.
2. Methodology

2.1. Extended exergy accounting

Extended exergy, proposed by Sciubba, is an extension of traditional exergy analysis to highlight the primary production factors, including two of neo-classical economics, i.e., labour and capital, and the other three ones, i.e., the exergy, necessary materials and environmental remediation, thus bridging the gap concerning the ‘production of value’ between the majority of economists and energists [28]. Based on the concept of extended exergy, except for the primary exergy resource equivalent “embodied” in the materials and energy sources, the primary resource equivalent of the so-called “externalities”: Labour-, Capital- and Environmental remediation costs is also included in the accounting framework. The calculation of extended exergy in demonstrated in (1).

\[
EE = CExC + E_c + E_w + E_e,
\]

where \( EE \) is the total extended exergy input of a specific system, \( CExC \) is the cumulative exergy costs, \( E_c \) represents the exergy equivalent of the monetary flow, \( E_w \) represents the exergy equivalent of human labour, and \( E_e \) is specified as the environmental remediation costs.

2.2. Extended exergy indices

Extended exergy is observed to be a thermal-economic concept that adopts a single quantifier (exergy, expressed in Joules) to account for materials, energy, labour and capital and to compute a presumed environmental impact based on remediation costs. In consideration of its resource, economic, and environmental implications, a series of extended exergy-based indicators derived from this concept could thereby be proposed to reflect the conversion efficiency, resource consumption, environmental loading, economic benefits as well as sustainability. The calculations of these indicators are demonstrated in (2)-(5).

The conversion efficiency of \( \varepsilon_p \) can be computed as the ratio of the useful output to the sum of the inputs that concurred to produce it [19]:

\[
\varepsilon_p = \frac{\sum EO_j}{\sum EI_i},
\]

where \( \sum EO_j \) is the sum of useful outputs, \( \sum EI_i \) is the total inputs of a specific process. Renewability is defined as the ratio of renewable exergy inputs and cumulative non-renewable exergy inputs, indicating the percentage of the total energy driving a process that is derived from renewable sources. In the long run, only processes with high R% are sustainable.

\[
R\% = \frac{E_R}{CExC},
\]

where \( E_R \) is the renewable exergy inputs and \( CExC \) is the cumulative exergy input, which is the sum of renewable exergy inputs (\( E_R \)) and non-renewable exergy inputs (\( E_{NR} \)).

The economic yield ratio (EYR) is used to reflect the economic feasibility, and is defined as the ratio of the exergy output and the monetary costs, as demonstrated in Equation (4). The larger the amount of monetary costs in the process, the lower the economic yield ratio, vice versa.

\[
EYR = \frac{E_c}{Y},
\]

where \( E_c \) is the exergy equivalent of the monetary flow, and \( Y \) is the exergy output of a process.

Environmental impact degree (EID) is expressed by the proportion of non-renewable exergy inputs and environmental remediation costs to the total exery input. It is used to quantify the environmental impacts exerted by human activities.

\[
EID = \frac{(E_e + E_{NR})}{EE},
\]
3. Case study

3.1. Study site

The wind farm concerned in this paper is constructed in Horqin Right Front Banner, which is located at 45°42'07"-47°01'36" north latitude and 119°31'51"-122°52'07" east longitude. The altitude there declines gradually from the northwest to the southeast. There is a northern continental climate where annual average temperatures of the south, central and north parts are 4.2 °C, 2.1 °C, -3.2 °C, respectively. The annual precipitation is 1198.9 mm and the annual solar duration is 2800 hours. Horqin Right Front Banner is affluent in wind resources; the annual windy days on average about 23 days, with up to 47 days. Wind velocity varies yearly, representing a trend of heavier winds in the winter and spring while the winds abate in the autumn and summer. In addition, the wind velocity in the daytime is larger than at night.

The total installed capacity of the projected wind farm in Horqin Right Front Banner is 150MW and is expected to be completed in three phases. In this paper, the energy and economic feasibility analysis is conducted on the first phase. Based on the characteristic power curve and hourly wind data for the location of the wind farm, ultimately the optimal scheme the first phase is a goal of a gross electricity output of 183.5 GWh annually and the annual electricity to access grid is 111.7GWh, with the equivalent full load operating hours of 2257 h and capacity factor of 0.258. The construction of the wind farm will take 12 months while the operation period will be 20 years.

3.2. System boundary

The system boundary of the wind power generation system is demonstrated in Fig. 1. Exergy inputs include wind resource, non-renewable energy and material used in the electricity generation process, capital investment on equipment and construction, labour input and environmental remediation costs. Meanwhile, the main output of this wind farm is electricity.

![Fig. 1. Exergy flows of the wind power generation system](image)

3.3. Data sources

For calculating the extended exergy of the concerned wind farm, we need disaggregated data of material and energy inputs, capital and labour and additional information about the remediation costs linked to its environmental impact. Material and energy inputs are quantified based on cumulative exergy content of each input, which was calculated by previous works. Economic data is
provided by China Xiehe Wind Power Investment Co., Ltd, including direct cost purchase of equipment cost and installation, instrumentation and control, building work, electrical equipment and materials and service facilities), indirect costs (construction and contingencies) plus maintenance. The environmental impact of the system is calculated based on the investments on waste gas emission, the waste water and solid waste treatment and vegetation restoration. The labour required in the construction and operation stages is also included.

4. Results and discussions

As illustrated in Table 1, the total extended exergy that flows into the wind power generation system is 8.40E+15 J, in which the proportions of renewable exergy input, non-renewable exergy from energy sources, capital input, labour input and environmental remediation input to the total extended exergy input are 83.30%, 0.07%, 15.20%, 1.32% and 0.11%, respectively (Figure 2). Obviously, renewable exergy input makes up the largest proportion, followed by capital input, indicating that although free wind resources are largely and efficiently used, the wind power generation is propelled by a vast of capital investment. The great investment on the wind power increases the cost and price of wind power. As a result, the higher price of wind power makes it less competitiveness compared with other power generation systems. Obviously, the non-renewable energy inputs and environmental remediation costs only constitute a small fraction, implying that the wind powered electricity generation system is a renewable and environmentally friendly energy utility mode.

Table 1. Exergy inputs of the wind power generation system

<table>
<thead>
<tr>
<th>Items</th>
<th>Quantity</th>
<th>Unit</th>
<th>Exergy coefficients</th>
<th>Units</th>
<th>References</th>
<th>Exergy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>00Renewable energy inputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wind</td>
<td>7.00E+15</td>
<td>J</td>
<td>1</td>
<td>J/J</td>
<td>[18]</td>
<td>7.00E+15</td>
</tr>
<tr>
<td>Water</td>
<td>1.00E+04</td>
<td>t</td>
<td>0.05</td>
<td>MJ/kg</td>
<td>[12]</td>
<td>5.00E+11</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>7.00E+15</strong></td>
</tr>
<tr>
<td><strong>Non-renewable energy inputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasoline</td>
<td>1.21E+02</td>
<td>t</td>
<td>1.07</td>
<td>J/J</td>
<td>[29]</td>
<td>5.60E+12</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>5.60E+12</strong></td>
</tr>
<tr>
<td><strong>Capital inputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equipment</td>
<td>3.18E+08</td>
<td>yuan</td>
<td>2.94</td>
<td>MJ/yuan</td>
<td>[28]</td>
<td>9.34E+14</td>
</tr>
<tr>
<td>Building works</td>
<td>6.10E+07</td>
<td>yuan</td>
<td>2.94</td>
<td>MJ/yuan</td>
<td>[28]</td>
<td>1.79E+14</td>
</tr>
<tr>
<td>Interest of loan</td>
<td>1.14E+07</td>
<td>yuan</td>
<td>2.94</td>
<td>MJ/yuan</td>
<td>[28]</td>
<td>3.37E+13</td>
</tr>
<tr>
<td>Others</td>
<td>4.50E+07</td>
<td>yuan</td>
<td>2.94</td>
<td>MJ/yuan</td>
<td>[28]</td>
<td>1.32E+14</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>1.28E+15</strong></td>
</tr>
<tr>
<td><strong>Labor input</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Construction</td>
<td>9.39E+05</td>
<td>Hour</td>
<td>71.9</td>
<td>MJ/Hour</td>
<td>[28]</td>
<td>6.75E+13</td>
</tr>
<tr>
<td>Operation</td>
<td>6.01E+05</td>
<td>Hour</td>
<td>71.9</td>
<td>MJ/Hour</td>
<td>[28]</td>
<td>4.32E+13</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>1.11E+14</strong></td>
</tr>
<tr>
<td><strong>Environmental remediation costs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOx</td>
<td>6.31E+03</td>
<td>kg</td>
<td>2963.3</td>
<td>kJ/kg</td>
<td>[30]</td>
<td>1.87E+10</td>
</tr>
<tr>
<td>SO2</td>
<td>6.07E+03</td>
<td>kg</td>
<td>4892.3</td>
<td>kJ/kg</td>
<td>[30]</td>
<td>2.97E+10</td>
</tr>
<tr>
<td>CO</td>
<td>1.64E+02</td>
<td>kg</td>
<td>9825</td>
<td>kJ/kg</td>
<td>[30]</td>
<td>1.62E+09</td>
</tr>
<tr>
<td>CO2</td>
<td>1.74E+03</td>
<td>t</td>
<td>0.45</td>
<td>PJ/Mt</td>
<td>[31]</td>
<td>7.84E+11</td>
</tr>
<tr>
<td>Waste treatment</td>
<td>6.15E+05</td>
<td>yuan</td>
<td>2.94</td>
<td>MJ/yuan</td>
<td>[28]</td>
<td>1.81E+12</td>
</tr>
<tr>
<td>Vegetation</td>
<td>2.20E+06</td>
<td>yuan</td>
<td>2.94</td>
<td>MJ/yuan</td>
<td>[28]</td>
<td>6.47E+12</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>9.11E+12</strong></td>
</tr>
<tr>
<td><strong>Total input</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>8.40E+15</strong></td>
</tr>
</tbody>
</table>

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The annual electricity output of the wind farm is 183.5 GWh, and the life span of this research is 20 years. As a result, the total electricity output is 3670 GWh. Based on the analysis above, and the extended exergy-based indicators are calculated and demonstrated in Table 2. Compared with the hydrogen-fed steam power plant [25], the renewability of wind power generation system is higher with the value of 0.99.

**Table 2. The extended exergy-based indicators of the wind power generation system**

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Conversion efficiency</th>
<th>Renewability</th>
<th>Economic yield ratio</th>
<th>Environmental impact degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>2.29E+6 J/kWh</td>
<td>0.99</td>
<td>0.23</td>
<td>1.75E-03</td>
</tr>
</tbody>
</table>

## 5. Conclusions

Extended exergy is a powerful tool that adopts a single quantifier to account for materials, energy, labour and capital and to compute a presumed environmental impact based on remediation costs, and handle the sustainability issues. Thus, it is applied in this paper to evaluate the sustainability of wind powered electricity generation system. Also, some extended exergy-based indicators were proposed and used to reflect the resource, environmental and economic performances of the wind power system.

The wind power generation is propelled by a vast of capital investment. The great investment on the wind power increases the cost and price of wind power. As a result, a higher price of wind power makes it less competitiveness compared with other power generation system. Thus, a rational cost compensation mechanism that aims at cost reduction is expected to be established to make wind power competitive. A market oriented incentive mechanism among provinces could be established to mobilize the exploitation and utility positivity of provinces with affluent wind resources. CDM program and Build-Operate-Transfer (BOT) mode are also effective ways in raising capital for wind farm construction.

In addition, the non-renewable energy inputs and environmental remediation costs only constitute a small fraction, implying that the wind powered electricity generation system is a renewable and...
environmentally friendly energy utility mode. Therefore, the development of wind power should be further accelerated in the 12th Five-Year plan period of China to cope with the energy security issue. Obviously, the extended exergy-based indicators provide a platform to compare the economic and environmental performance, conversion efficiency and sustainability of different renewable energy utility modes, and shed lights on the planning and policies of renewable energy development. However, the indicator system is still incomplete and need revisions in future works.

Acknowledgments

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References


Human body exergy metabolism

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Abstract:
The exergy analysis of the human body is a tool that can provide indicators of health and life quality. To perform the exergy balance it is necessary to calculate the metabolism in an exergy basis, or metabolic exergy, although there is not yet consensus in its calculation procedure. Hence, the aim of this work is to provide a general method to evaluate this physical quantity for human body based on indirect calorimetry data. Similarly to the chemical exergy definition for pure substances, the metabolic exergy may be defined as the maximum amount of work that the body can perform from the oxidation of the energy substrates, which are the carbohydrates, lipids and proteins. To calculate the metabolism in an exergy basis it is necessary to define the reference reactions and obtain their exergy variation. The reference reactions of the energy substrates are represented by the oxidation of the glucose, palmitic acid and a representative amino acid. The products of these reactions are carbon dioxide, liquid water and urea; being this last substance formed only in the reaction of the amino acid. From the Gibbs free energy of the oxidation of these substances it is possible to calculate the chemical exergy and their exergy variation. The indirect calorimetry permits the analysis of expired and inspired air (oxygen consumption and carbon dioxide production). Attaching these data to the stoichiometry of the reactions of oxidation it is possible to obtain the consumption rate of the substrates. Hence, from the exergy variation of the reactions and the rate consumption of the substrates, the metabolic exergy is determined. The method to calculate the metabolism in energy basis is well set; it is obtained from the consumption of nutrients and enthalpy variation of the reactions of oxidation. Results, for basal conditions and during physical activities, indicate that the exergy and energy metabolism have difference lower than 5\% similar values only for basal conditions but the difference is not larger than 10\%.

Keywords:
Human Body, Exergy Analysis, Metabolic Exergy.

1. Introduction

The application of the exergy analysis for the human body may be used to assess the quality of the energy conversion processes that take place in its several systems, organs and even cells. Several authors applied the exergy analysis for the human body [1-8] and some of the methods were revised by [5]. To perform the exergy analysis it is necessary to calculate the metabolic exergy in human body, but there is still not a consensus in its calculation.

Initially, the Second Law of Thermodynamics was applied to living organisms as an attempt to confirm the principle of minimum entropy production or Prigogine and Wiame [9] principle. In this principle it is stated that all living organisms tend to sate of minimum entropy production. Therefore, for different types of species, ranging from fish to humans [8,10-15], the minimum entropy production was confirmed.

Batato et al. [1] were one of the first authors that applied the exergy analysis to the human body. In the analysis the energy and exergy metabolism were calculated from indirect calorimetry results, where it was selected representative reactions of oxidation of three types of substance (carbohydrates, lipids and proteins). A comparison between metabolisms in both basis indicated that the difference is not higher than 5\%.

Prek [2,3], Prek and Butala [4] and Simone et al. [5] performed the exergy analysis for the human body to obtain relations of exergy destruction with thermal comfort and thermal sensation.
conditions. In the analyses the metabolic exergy was considered as a heat source, therefore the metabolism in energy and exergy basis have one order of magnitude of difference.

Finally, [14,15] applied the concept of maximum amount of work to biochemical reaction defining the metabolic efficiency, and [7] performed the exergy analysis for the cellular metabolism of glucose and palmitic acid, but the metabolism was not calculated for the body.

Although there is a consensus in literature to calculate the metabolism in energy basis [16], there is not a consensus in its calculus in exergy basis. In this work it is proposed a method to calculate the metabolic exergy from indirect calorimetry results, based on [1,16]. Moreover, it will be held a discussion of the methods of literature to calculate this physical quantity to establish a procedure and an equation to calculate this physical quantity.

2. Model description

Figure 1 indicates a model with a schematic representation of the human body, where it is indicated the heat transfer rate and mass flow rates associated with radiation (\(Q_r\)), convection (\(Q_c\)), vaporization (\(H_v\)), respiration (\(H_{respiration}\), food intake, food wastes, water intake and urine. The term \(Q_M\) is the heat released to the body caused by the cellular metabolism (from the First Law of Thermodynamics \(M = Q_M\)). In this figure the human body is divided in two control volumes, CV1 and CV2. The first one represents the thermal system and respiratory system and the second the cellular metabolism.

According to Rahman [13] in a period of one day the mass input (food, liquids and inspired gases) is equivalent to the mass output (food wastes, urine, expired gases and vaporization). In shorter periods of time this may not be verified. In this article, for the sake of the simplicity, the variation of body mass due to food and water intake, wastes and accumulation are neglected. During the measurements: \(m_{food\ intake}\), \(m_{water\ intake}\), \(m_{food\ wastes}\) and \(m_{urine}\) are considered as a constant rate with the following considerations:

- \(m_{food\ intake} - m_{food\ wastes} = m_{carb} + m_{lip} + m_{ami};\)
- \(m_{water\ intake} - m_{urine} = m_{w,ex} + m_e - m_{w,a} - m_{H2O} - m_{urea};\)
- \(m_{inspired\ air} - m_{expired\ air} = m_{O2} - m_{CO2}.\)

Where, \(m_{w,ex}\) and \(m_{w,a}\) are the mass of water in expired and inspired air; \(m_e\) is mass of water evaporated through skin; \(m_{carb}, m_{lip}, m_{ami}\) are the mass consumption rate of carbohydrates, lipids and proteins; \(m_{O2}\) is the mass consumption rate of oxygen; and \(m_{CO2}, m_{H2O}\) and \(m_{urea}\) are the mass production of carbon dioxide, water and urea.

![Figure 1. Schematic representation of the human body, with the intake of food, water and inspired air; and output of food, urine, expired air, vaporization trough skin and heat release due to radiation and convection](image-url)
The Exergy Analysis is applied in the control volume shown in Fig. 1, with given environment and reference conditions such as temperature ($T_0 = T_a$), pressure ($P_0 = P_a$) and relative humidity ($\varphi_a = \varphi_a$). Thus, (1) indicates a general equation of the exergy balance.

$$\frac{dB}{dt} = \sum B_{in} - \sum B_{out} + \sum_{k} Q_{k} \left( 1 - \frac{T_a}{T_k} \right) - W - B_{dest}, \quad (1)$$

The exergy metabolism ($B_M$) for the whole body is part of the exergy variation of the body over time as indicated in (2). Where $B$ is the body exergy and $\frac{dB}{dt}|_{\Delta T}$ is the exergy variation of the body due to a variation in environmental conditions. This term is related to internal energy and entropy variation of the body over time. In (2) the variation of the volume of the body is neglected.

$$\frac{dB}{dt} = -B_M + \frac{dB}{dt}|_{\Delta T}, \quad (2)$$

Equation (3) indicates the exergy balance applied to CV1. The exergy intake is $B_{QM}$, indicated by (4), where $Q_M$ is the heat transferred to the body caused by the metabolism, $T_0$ is the environment/reference temperature and $T_b$ the body temperature. The exergy rate and flow rates $B_c$, $B_r$, $B_e$ and $\Delta B_{res}$ ($B_{ex} - B_a$) are the exergy associated with convection, radiation, vaporization and respiration, previously determined in [8].

$$B_{dest}^{CV1} = B_{QM} - (B_c + B_r + B_e + \Delta B_{res}) - \frac{dB}{dt}|^{CV1}_{\Delta T}, \quad (3)$$

$$B_{QM} = Q_M \left( 1 - \frac{T_a}{T_b} \right), \quad (4)$$

The cellular metabolism is a representation of the human cells. In this control volume (CV2) the reactions of oxidation of the energy substrates, also called metabolism, take place. The destroyed exergy is indicated in CV2 by (5), where $B_{reac}$ is the exergy content of the reactants (carbohydrates, lipids, amino acids and oxygen) and $B_{prod}$ is the exergy content of the products (urea, liquid water and carbon dioxide).

$$B_{dest}^{CV2} = B_{reac} - B_{prod} - Q_M \left( 1 - \frac{T_a}{T_b} \right) - \frac{dB}{dt}|^{CV2}_{\Delta T}, \quad (5)$$

The exergy metabolism is defined as (6)

$$B_M = B_{reac} - B_{prod}, \quad (6)$$

When the control volume is the whole body, the exergy balance for steady state conditions becomes a sum of (3) and (5). The result is indicated in (7).

$$B_{dest}^{body} = \left( B_M - \frac{dB}{dt}|_{\Delta T} \right) - (B_c + B_r + B_e + \Delta B_{res}), \quad (7)$$

Note that (3) is similar to the exergy analysis proposed by [2-4] (which takes into account only the thermal part of metabolism) and (7) is similar to the analysis proposed by [1]. The difference between these two approaches is that all the exergy destroyed in CV2 are neglected if (3) is used as the metabolic exergy.
2.1. Energy metabolism

As indicated by [16], the metabolism is defined as a set of chemical reactions that release energy from the oxidation of energy substrates and allow the vital processes in human body. Figure 1 indicates the cellular metabolism with the input of glucose, lipids, amino acids and oxygen; and the output of carbon dioxide, urea and water. Moreover, there is a heat rate released to the body caused by the metabolism \(Q_M\).

Diener [16] described a procedure to calculate the metabolism based on the indirect calorimetry technique. In order to calculate metabolic energy and exergy, it is assumed that the oxidation of carbohydrates, lipids and protein are represented by the reactions of oxidation of glucose \((C_6H_{12}O_6)\), palmitic acid \((C_{16}H_{32}O_2)\) and a representative amino acid with mean thermodynamic properties \((C_{4.98}H_{9.8}N_{1.4}O_{2.5})\).

The oxidations of these three organic compounds are indicated in (8) to (10). Note that the oxidation of glucose and palmitic acid results in the formation of carbon dioxide and liquid water, while the oxidation of amino acid results in the formation of carbon dioxide, liquid water and urea. In humans and most of mammals, the excretion of nitrogen content in the amino acids is mostly through urea.

\[
\begin{align*}
C_6H_{12}O_6 + 6O_2 & \rightarrow 6CO_2 + 6H_2O, \quad (8) \\
C_{16}H_{32}O_2 + 23O_2 & \rightarrow 16CO_2 + 16H_2O, \quad (9) \\
C_{4.98}H_{9.8}N_{1.4}O_{2.5} + 5.13O_2 & \rightarrow 4.28CO_2 + 3.5H_2O + 0, 7CH_4N_2O, \quad (10)
\end{align*}
\]

It is important to define the respiratory quotient \((RQ)\) that is the ratio of the carbon dioxide production and oxygen consumption (in molar basis). This value is 1 for (8), 0.7 for (9) and 0.83 for (10). In basal conditions \(RQ\) is approximately 0.83, during heavy aerobic activities it becomes close to 1 [17]. This quotient gives a clue whether the oxidation which prevails is only one type of substance (physical activities) or a combination (basal conditions).

From the stoichiometry of the reactions, it is possible to obtain the consumption of carbohydrates, lipids and proteins in unity of mass, as indicated by (11) to (13), based on [16]. In this equation, oxygen consumption \((m_{O_2})\) and carbon dioxide production \((m_{CO_2})\) are usually measured with the aid of a respirometer. The nitrogen excreted from the body \((m_N)\) is measured from the urine analysis. In the literature, there is a convention adopted that each gram of nitrogen excreted in the urine represents the oxidation of 6.25g of amino acids [1,16].

\[
\begin{align*}
m_{carb} &= -2.14m_{O_2} + 2.24m_{CO_2} - 3.39m_N, \quad (11) \\
m_{lip} &= 1.14m_{O_2} - 0.83m_{CO_2} - 1.50m_N, \quad (12) \\
m_{am} &= 6.25m_N, \quad (13)
\end{align*}
\]

The energy metabolism can be calculated as indicated in (14), where \(\Delta h\) is the enthalpy variation of the reactions indicated in (8) to (10). Note that this procedure is well established on literature and used to calculate the metabolism from indirect calorimetry results.

\[
M = -\Delta H = -\left(m_{carb}\Delta h_{carb} + m_{lip}\Delta h_{lip} + m_{am}\Delta h_{am}\right), \quad (14)
\]

It is important to mention that in literature exists a discussion that in basal conditions the oxidation of proteins may be neglected, because it represents only 2% of the total metabolism if the person is healthy [16].
2.2. Exergy metabolism

The chemical exergy of a compound \((b_{ch})\) may be calculated according to (15), where \(\Delta g_0\) is the specific Gibbs free energy variation of the reference reaction (that has only substances present in the reference environment as co-reactants and products), and \(b_{ch,i}\) is the chemical exergy of the products, or the co-reactants [17].

\[
b_{ch} = -\Delta g_0 + \left[ \sum_i x_i b_{ch,i} \right]_{\text{products}} - \left[ \sum_i x_i b_{ch,i} \right]_{\text{co-reactants}},
\]

To calculate the metabolic exergy it is necessary to define reference reactions that are indicated in (10) to (12). The exergy variation of the reactions of oxidation \((\Delta B)\) can be calculated as indicated in (16), where \(\Delta b\) is the specific exergy variation of each reaction. For the glucose and palmitic acid, the \(\Delta b\) terms are the chemical exergy of these substances, calculated from (15). For the amino acid, \(\Delta b\) is a linear combination of the chemical exergy of amino acid and urea. The consumption rate of the energy substrate is determined from (11) to (13).

\[
\Delta B = m_{carb} \Delta b_{carb} + m_{lip} \Delta b_{lip} + m_{ami} \Delta b_{ami},
\]

The definition of the metabolism in exergy basis is not as simple as in energy basis. Some authors [2-4] calculated the metabolic exergy as \(B_{QM}\), similarly to (3). Herein the metabolic exergy will be considered as the exergy variation of the reactions of the oxidation (17).

\[
B_M = -\Delta B,
\]

3. Experimental data and thermodynamic properties

3.1 Thermodynamic properties

To calculate the metabolism in energy and exergy basis, it is necessary to obtain thermodynamic properties of the energy substrates such as enthalpy variation \((\Delta h)\) and Gibbs free energy variation \((\Delta g)\) of the reactions of oxidation. The references which these data were obtained are Diener [16], Hayne [19] and Cortassa et al. [20]. Table 1 indicates the values of these thermodynamic properties for the complete oxidation of glucose and palmitic acid, and partial oxidation to the formation of liquid water, carbon dioxide and urea for the amino acids. The \(\Delta h\) of the reaction of oxidation of urea (\(\text{CH}_2\text{N}_2\text{O}\)) is obtained from Doran [21] (10527 kJ/kg) and the chemical exergy is obtained from Szargut et al. [17] (11483 kJ/kg).

<table>
<thead>
<tr>
<th></th>
<th>(\Delta h) (kJ/kg)</th>
<th>(\Delta g) (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diener [16]</td>
<td>-15648</td>
<td>-39581</td>
</tr>
<tr>
<td>Hayne [19]</td>
<td>-15600</td>
<td>-39200</td>
</tr>
<tr>
<td>Cortassa et al. [20]</td>
<td>-15594</td>
<td>-39020</td>
</tr>
</tbody>
</table>

Cortassa et al. [20] provides the value of enthalpy variation and Gibbs free energy variation of the complete oxidation for different amino acids. Table 2 indicates the value of these thermodynamic properties for the several amino acids and from these the calculated chemical exergy.

Nelson and Cox [22] provide the average occurrence of each amino acid in nature, indicated in Table 2 representing approximately 96% of the common amino acids found in proteins (exception...
of methionine and cysteine). These percentages are used to calculate the mean molecular formula (C_{4.98}H_{9.8}N_{1.4}O_{2.5}) and mean thermodynamic properties.

**Table 2. Thermodynamic properties of the oxidation of each amino acid until the formation of carbon dioxide, nitrogen and liquid water [17,20] and the average occurrence of each amino acid in nature [22]**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molecule</th>
<th>% Nature</th>
<th>Δh (kJ/kg)</th>
<th>Δg (kJ/kg)</th>
<th>b_{\text{ch}} (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine</td>
<td>C_2H_3NO_2</td>
<td>7.2</td>
<td>-12987</td>
<td>-13480</td>
<td>14150</td>
</tr>
<tr>
<td>Alanine</td>
<td>C_3H_7NO_2</td>
<td>7.8</td>
<td>-19180</td>
<td>-18449</td>
<td>18991</td>
</tr>
<tr>
<td>Serine</td>
<td>C_3H_2NO_3</td>
<td>6.8</td>
<td>-13857</td>
<td>-14305</td>
<td>14783</td>
</tr>
<tr>
<td>Aspartic Acid</td>
<td>C_4H_7NO_4</td>
<td>5.3</td>
<td>-12090</td>
<td>-12677</td>
<td>13189</td>
</tr>
<tr>
<td>Asparagine</td>
<td>C_4H_8N_2O_3</td>
<td>4.3</td>
<td>-14676</td>
<td>-15144</td>
<td>15643</td>
</tr>
<tr>
<td>Threonine</td>
<td>C_4H_9NO_3</td>
<td>5.9</td>
<td>-17681</td>
<td>-17899</td>
<td>18446</td>
</tr>
<tr>
<td>Proline</td>
<td>C_5H_9NO_2</td>
<td>5.2</td>
<td>-23783</td>
<td>-</td>
<td>24856**</td>
</tr>
<tr>
<td>Glutamic Acid</td>
<td>C_5H_9NO_4</td>
<td>6.3</td>
<td>-15306</td>
<td>-15748</td>
<td>16312</td>
</tr>
<tr>
<td>Glutamine</td>
<td>C_5H_{10}N_2O_3</td>
<td>4.2</td>
<td>-17603</td>
<td>-18000</td>
<td>18553</td>
</tr>
<tr>
<td>Valine</td>
<td>C_5H_{11}NO_2</td>
<td>6.6</td>
<td>-24957</td>
<td>-24957</td>
<td>25623</td>
</tr>
<tr>
<td>Histidine</td>
<td>C_6H_{10}N_2O_2</td>
<td>2.3</td>
<td>-22103</td>
<td>-</td>
<td>22629**</td>
</tr>
<tr>
<td>Leucine</td>
<td>C_6H_{13}NO_2</td>
<td>9.1</td>
<td>-27389</td>
<td>-27214</td>
<td>27921</td>
</tr>
<tr>
<td>Isoleucine</td>
<td>C_6H_{13}NO_2</td>
<td>5.3</td>
<td>-27389</td>
<td>-27206</td>
<td>27914</td>
</tr>
<tr>
<td>Lysine</td>
<td>C_6H_{14}N_2O_2</td>
<td>5.9</td>
<td>-25233</td>
<td>-</td>
<td>26541**</td>
</tr>
<tr>
<td>Arginine</td>
<td>C_6H_{14}N_4O_2</td>
<td>5.1</td>
<td>-21517</td>
<td>-21759</td>
<td>22294</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>C_9H_{11}NO_2</td>
<td>3.9</td>
<td>-28200</td>
<td>-28164</td>
<td>29021</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>C_9H_{11}NO_3</td>
<td>3.2</td>
<td>-24514</td>
<td>-24768</td>
<td>25560</td>
</tr>
<tr>
<td>Tryptophan</td>
<td>C_{11}H_{12}N_2O_2</td>
<td>1.4</td>
<td>-27608</td>
<td>-27691</td>
<td>28540</td>
</tr>
<tr>
<td>Average Value</td>
<td>C_{4.98}H_{9.8}N_{1.4}O_{2.5}</td>
<td></td>
<td>-21067</td>
<td>-</td>
<td>21890</td>
</tr>
</tbody>
</table>

*The chemical exergy of these amino acids were calculated for this article

** Chemical exergy calculated using group contribution method, from Szargut et al. [17]

3.2 Experimental data

3.2.1. Basal conditions

To calculate the metabolism in energy and exergy basis, for basal conditions the O\textsubscript{2} consumption, the CO\textsubscript{2} and H\textsubscript{2}O production are considered, respectively: 1.79.10\textsuperscript{-4}, 1.46.10\textsuperscript{-4} and 5.47.10\textsuperscript{-5} mol/s. The RQ is 0.82 (close to basal conditions defined in [17]). These data were obtained from Hardy and Du Bois [18], for basal conditions and were also used by Aoki [12]. Furthermore, it is possible to assume that in one day there is an excretion of 12 g of nitrogen in the urine [16] due to the oxidation of amino acids.

3.2.2 Physical activities

The experimental results for subjects under physical activities were obtained from Sports medicine group and FIFA medical center of excellence of institute of orthopedics and traumatology of the University of São Paulo Medical School. During the experimental procedure, the individuals are submitted to increasing levels of velocities, where it was measured the respiratory gas exchange (O\textsubscript{2} consumption and CO\textsubscript{2} production and the tympanic temperature (representative of the body temperature). Results of treadmill velocities, oxygen consumption rate and carbon dioxide production rate are indicated in Figure 2 for one runner.
4. Results and Discussion

4.1 Thermal properties and metabolism equation

In the present analysis it is important to detach that, carbohydrates and lipids are represented by one substance (glucose and palmitic acid), but amino acids are represented by one amino acid with mean thermodynamic properties. Sorguven and Özilgen [23] obtained the chemical exergy for three types of fatty acids with 18, 20 and 22 carbons in its chain; the difference of the chemical exergy (in mass basis) was not larger than 1%. Table 2 indicates that the difference of the chemical exergy of the amino acids may achieve values as high as 50%. Each amino acid has a different type of chain, with different ramifications.

Table 3 indicates the $\Delta h$, $\Delta g$ and $\Delta b$ of the reactions partial oxidation (carbon dioxide, liquid water and urea) of several amino acids. The mean values are weighted by the occurrence in nature of each amino acid (Table 2). Furthermore, these results indicate a value of $\Delta b/\Delta h$ of 1.047.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molecule</th>
<th>$\Delta h$ (kJ/kg)</th>
<th>$\Delta g$ (kJ/kg)</th>
<th>$\Delta b$ (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine</td>
<td>C$_2$H$_5$NO$_2$</td>
<td>-8776</td>
<td>-8996</td>
<td>-9556</td>
</tr>
<tr>
<td>Alanine</td>
<td>C$_3$H$_7$NO$_2$</td>
<td>-15631</td>
<td>-14671</td>
<td>-15121</td>
</tr>
<tr>
<td>Serine</td>
<td>C$_3$H$_7$NO$_3$</td>
<td>-10850</td>
<td>-11102</td>
<td>-11502</td>
</tr>
<tr>
<td>Aspartic Acid</td>
<td>C$_4$H$_7$NO$_4$</td>
<td>-9716</td>
<td>-10148</td>
<td>-10599</td>
</tr>
<tr>
<td>Asparagine</td>
<td>C$_6$H$_8$N$_2$O$_3$</td>
<td>-9882</td>
<td>-10049</td>
<td>-10424</td>
</tr>
<tr>
<td>Threonine</td>
<td>C$_4$H$_9$NO$_3$</td>
<td>-15027</td>
<td>-15073</td>
<td>-15551</td>
</tr>
<tr>
<td>Proline</td>
<td>C$_5$H$_9$NO$_2$</td>
<td>-21037</td>
<td>-22110</td>
<td></td>
</tr>
<tr>
<td>Glutamic Acid</td>
<td>C$_6$H$_9$NO$_4$</td>
<td>-13158</td>
<td>-13461</td>
<td>-13969</td>
</tr>
<tr>
<td>Glutamine</td>
<td>C$_5$H$_10$N$_2$O$_3$</td>
<td>-13277</td>
<td>-13393</td>
<td>-13834</td>
</tr>
<tr>
<td>Valine</td>
<td>C$_5$H$_11$NO$_2$</td>
<td>-22258</td>
<td>-22083</td>
<td>-22678</td>
</tr>
<tr>
<td>Histidine</td>
<td>C$_6$H$_9$N$_3$O$_2$</td>
<td>-15991</td>
<td>-</td>
<td>-16517</td>
</tr>
</tbody>
</table>
Leucine C_{6}H_{13}NO_{2} -24979 -24647 -25291
Isoleucine C_{6}H_{13}NO_{2} -24979 -24639 -25284
Lysine C_{6}H_{14}N_{2}O_{2} -20907 -24378
Arginine C_{6}H_{14}N_{4}O_{2} -14257 -14375
Phenylalanine C_{9}H_{11}NO_{2} -26286 -26126 -26933
Tyrosine C_{9}H_{11}NO_{3} -22769 -22910 -23657
Tryptophan C_{11}H_{12}N_{2}O_{2} -24512 -24394 -25162
Average Value -17830 -25162

In Table 1 the only value that Hayne [19] does not provide is the Gibbs free energy of the oxidation of amino acids. Applying the result of $\Delta h/\Delta b=1.04$, it is possible to obtain that $\Delta b$ of the oxidation of amino acids is 19760 kJ/kg.

In Table 4, it is indicated the values of $\Delta b$ of the reactions of oxidation as they occur in humans (glucose and palmitic acid the oxidation is complete, amino acids the oxidation is partial). From the values of $\Delta h$ and $\Delta b$ it is possible to formulate an equation of the metabolism in energy basis (which differ from [16] because of the oxygen consumption and carbon dioxide production are per unity of mass) and exergy basis.

Table 4. Exergy variation of the reactions of oxidation of glucose, palmitic acid and proteins.

<table>
<thead>
<tr>
<th></th>
<th>Reference</th>
<th>Glucose</th>
<th>Palmitic Ac.</th>
<th>Amino Ac.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hayne [19]</td>
<td></td>
<td>-16506</td>
<td>-39141</td>
<td>-19760</td>
</tr>
<tr>
<td>Cortassa et al [20]</td>
<td></td>
<td>-16516</td>
<td>-39223</td>
<td>-18359</td>
</tr>
</tbody>
</table>

Finally, (18) and (19) indicate the metabolism in energy basis using the data from Hayne [19]. Equations (20) and (21) indicate the metabolism in energy and exergy basis using the data from Cortassa [20].

\[
M_{\text{Hayne}} = 11371m_{O_{2}} + 2366m_{CO_{2}} + 6891m_{N} \quad (18)
\]
\[
B_{M,\text{Hayne}} = 9363m_{O_{2}} + 4444m_{CO_{2}} + 8764m_{N} \quad (19)
\]
\[
M_{\text{Cortassa}} = 11179m_{O_{2}} + 2502m_{CO_{2}} - 1980m_{N} \quad (20)
\]
\[
B_{M,\text{Cortassa}} = 9435m_{O_{2}} + 4399m_{CO_{2}} - 932.6m_{N} \quad (21)
\]

4.1 Energy and exergy metabolism

4.1.1 Basal conditions

Results in Table 5 indicate the metabolism in energy and exergy basis, considering the oxidation of proteins ($M$ and $B_{M}$) and disregarding the oxidation of proteins ($M_{p}$ and $B_{Mp}$) for the data of Hardy and Du Bois [18]. For this condition, the authors obtained that the metabolism is 79.8W. In all cases the difference between this value and the ones calculated herein is not larger than 4%. Furthermore, the difference of the metabolism using the two different references of thermodynamic properties [19,20] did not differ 3%. The ratio of metabolism in energy and exergy basis (considering and disregarding the oxidation of proteins) does not exceed 1.03. Hence, as in Batato et al. [1], the approximation $B_{M} \approx M$ for basal conditions is valid.

Table 5. Metabolism in energy and exergy basis with the oxidation of amino acids ($M$ and $B_{M}$) and without the oxidation of amino acids ($M_{p}$ and $B_{Mp}$)

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<table>
<thead>
<tr>
<th></th>
<th>Hayne [19] (W)</th>
<th>Cortassa et al. [20] (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$</td>
<td>81.3</td>
<td>79.8</td>
</tr>
<tr>
<td>$M_p$</td>
<td>80.3</td>
<td>80.1</td>
</tr>
<tr>
<td>$B_M$</td>
<td>83.4</td>
<td>82.2</td>
</tr>
<tr>
<td>$B_{Mp}$</td>
<td>82.2</td>
<td>82.3</td>
</tr>
</tbody>
</table>

### 4.1.1 Physical activities

For the experimental results of Figure 2 the metabolism in energy and exergy basis was calculated, using the values of thermodynamic properties of Cortassa et al. [20] indicated in (20) and (21), due to the small difference between results in Table 5.

Figures 3 indicates $M$, $B_M$ and $B_{QM}$ for the experimental data indicated in Fig. 2. The difference of $B_M$ and $B_{QM}$ is one order of magnitude, indicating that when the metabolism is calculated as $B_{QM}$ (taking into account only the thermal exergy), 95% of the exergy content of metabolism is disregarded.

![Figure 3](image_url)

*Figure 3. Result of $M$, $B_M$ and $B_{QM}$ as a function of time during the treadmill test. The first two properties are indicated in the left axis, the last on in the right side axis.*

In Fig. 4 it is demonstrated the ratio of the metabolism in energy and exergy basis as a function of time. In the first five minutes, the ratio $B_M/M$ ranged from 1.04 to 1.08 (time when the subject controlled the respiration and was adapting to the respirometer). Between 5 and 30 minutes, the ratio remained between the same limits. Finally, on the final period of the test the ratio increased to values as close as 1.1. This result indicates that the approximation $B_M\approx M$ may not be always valid, although the ratio was not larger than 1.1.
Figure 4. Ratio of the metabolism in energy and exergy basis during the treadmill test

Figure 5 indicates the ratio of the metabolism considering the oxidation of proteins ($M$) and disregarding the oxidation of this type of substance ($M_p$). The ratio was very close to 1 (5-30min), indicating that during the exercises the body uses more carbohydrates and lipids as energy source. In the beginning of the test the ratio was approximately 99.5%, indicating that the participation of proteins in the total metabolism is larger when the person is resting. Nevertheless, this figure indicates that for a healthy person under physical activities the oxidation of proteins can be disregarded.

Figure 5. Ratio of the metabolism considering and disregarding the oxidation of proteins during the treadmill test
5. Conclusions
In this work analyses of the human metabolism in energy and exergy basis were performed and it was proposed a method and an equation to calculate the metabolic exergy. From the range of tests analyzed it was possible to conclude that:

- For basal conditions results of metabolism in energy and exergy basis did not differ more than 3%, for the different thermodynamic properties. For basal conditions, results obtained from Batato et al. [1] were verified;
- For the treadmill running tests, the results found in Batato et al [1] that the difference of metabolism in energy and exergy basis may not always verified. The ratio exceeds 1.05 in most of the test, but it was not larger than 1.10.
- Finally, the contribution of proteins did not exceed 3% of the total metabolism during physical activities and in basal conditions. The oxidation of proteins may be disregarded in a healthy person in basal conditions and under physical activities.

Acknowledgments
The authors acknowledge FAPESP (São Paulo Research Foundation) for his PhD grant 09/17578-0. The authors acknowledge the Sports medicine group and FIFA medical center of institute of orthopedics and traumatology of the University of São Paulo Medical School.

Nomenclature
b specific exergy, J/kg
B body exergy, J
B exergy flow rate, W
h specific enthalpy, J/kg
H enthalpy flow rate, W
M metabolism, W
m mass flow rate, kg/s
Q heat transfer rate, W
RQ respiratory quotient, -
T temperature, K
t time, min
V velocity, m/s
W work, W

Subscripts and superscripts
0 Reference
ami Amino acids
b Body
c Convective
carb Carbohydrates
dest Destruction
e Evaporative
ex Expired
in Inspired
lip Lipids
M Metabolic
p disregarding proteins
r Radiative
res Respiration

References
Integrating an ORC into a natural gas expansion plant supplied with a co-generation unit

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Abstract:
The paper presents a thermoeconomic analysis of a proposed novel system for natural gas expansion, based on the integration of gas expanders, ICE engine and an organic Rankine cycle (ORC). The objective of a natural gas expansion plant is to generate electric power while reducing the natural gas pressure. In contrast to the throttling process in pressure regulators, gas expanders allow one to utilize the physical exergy of the pressurized gas. However, the necessity of gas pre-heating bound to thy hydrate formation problem decreases the performance of existing expansion plants. Pre-heating systems based on co-generation modules with ICE-engines have better performance that boiler systems, however, as shown in authors’ previous studies, they are burdened with a relatively high irreversibility bound to an excessive temperature difference between the engine exhaust gases and the pre-heated natural gas. The proposed system integrates an ORC between the exhaust gases and natural gas. Pre-heating of natural gas is carried out partially directly by the co-generation module, by means of the engine cooling cycle, and partially indirectly, by means of the engine exhaust gases supplying heat for the ORC, while the ORC condenser is coupled with the first stage of gas pre-heating. It has been demonstrated that the integration of ORC increases the system exergy efficiency to 0.526 compared to the reference case of 0.498. The performance ratio (electric output related to local fuel input) of the system reaches a favourable value of 0.77. The performed detailed thermoeconomic analysis points out the occurrences of irreversibilities and depicts the process of cost formation in particular devices.

Keywords:
Thermoeconomic analysis, Turboexpanders, ORC, Natural gas, Exergy, Hybrid energy systems

1. Introduction

Thanks to the accumulation of organic substances in the Earth’s crust over millions of years, the nature provides us with fossil fuels enclosed in underground fields. Due to the gravity of rocks, the pressure of natural gas in underground reservoirs usually exceeds 100 bar [1] and may reach values as high as 700 bar [2]. However, this pressure may decrease during the extraction period; moreover, as the gas passes the well tubing, the flow control devices in the wellhead and the processing plant, the pressure may eventually decrease to the level of 10–40 bar [1]. Further transportation of the gas to large distances usually requires a higher degree of compression in order to reduce the volumetric flow rate, the resulting pipeline dimensions and the corresponding investment cost. Alternatively, the gas may be liquefied for overseas transportation. In the year 2011, 69.5% of gas traded worldwide was transported in pipelines and the remaining 30.5% was liquefied [3]. In the case of pipeline transportation, the typical pressure range varies between 35 and 100 bars depending on the design optimization result. As the gas reaches its destination (consumption) area, the pressure has to be adjusted to the level suitable for its utilization in gas burners. The latter is determined by the flame speed at a level of only 16–25 milibars above the atmospheric pressure. Hence, a multistage system of pressure reduction stations is required in order to deliver the natural gas to distribution networks and to the final consumers.
The vast majority of the pressure reduction stations (PRS, also called ‘pressure regulating stations’ or ‘city gate stations’) operate with a pressure regulator used to reduce the gas pressure. A pressure regulator is an automatically operated throttling valve, which has the primary purpose to adjust the flow to the current demand of consumers, and the secondary purpose to reduce the gas pressure and maintain it within the desired limits even in the case of unstable demand or supply conditions [4].

From the point of view of energy management, the use of pressure regulators is undesired, since the throttling process destroys the potential of energy generation available in the pressure reduction process. This fact can be detected and quantified by means of exergy analysis [5]. Exergy destruction in a pressure regulator corresponds to the maximum amount of mechanical work that could be generated between given inlet and outlet pressure levels and for the given flow rate. As stated by Szargut [6], accepting the exergy destruction can only be justified by economic reasons, otherwise it should be regarded as an ‘error in the art of engineering’. For this reason, and accounting for huge amounts of natural gas choked worldwide in throttling valves, the possibility of pressurized gas exergy utilization should be thoroughly investigated.

The available physical exergy contained in the pressurized gas may be converted into mechanical work by means of a piston, screw or, most frequently, a turbine expander (turboexpander). The generated work may be converted to electricity, or in particular industrial applications, may be utilized directly [7]. From the technical point of view, the expander technology is well-known and offered by many manufacturers.

The key issue related to the application of expanders is the temperature drop of natural gas. In the conventional throttling process, a moderate temperature drop is observed due to the real-gas Joule-Thompson effect, roughly estimated at 0.5K/bar. The temperature drop may provoke a separation of the solid phase (hydrates) from natural gas or cause external icing of pressure regulators and/or pressure safety valves. These phenomena pose a risk of blocking the devices, leading to excessive outlet pressure, which in turn can result in rare but severe accidents involving losses in human life [8]. Another risk factor is bound to the utilization of polyethylene pipes in distribution networks (downstream of the PRS). Mechanical properties of polyethylene are appropriate for a limited temperature range (lower temperatures decrease the material stress under which rapid crack propagation can occur [9]). In order to exclude any risk of system malfunction, the majority of PRSs are equipped with a gas-fired or electric preheating system. The objective of the preheating system is to maintain the temperature at the regulator outlet above the ‘permissible safe temperature’ [10]; detailed regulations may further specify the value of the limit (e.g. 5–8°C [11]).

If gas expansion is applied instead of throttling, the temperature drop becomes significant due to the conversion of internal energy of gas into mechanical work. It is therefore required to heat the gas upstream of the expander (pre-heating), or design the expander for low temperatures and heat the gas downstream of the expander (post-heating) in order to avoid the supply of cold gas to the downstream network. A review of possible technical solutions is presented in Table 1.

The use of IC engines entails an improvement of efficiency, however, the temperature difference between exhaust gases from the engine and the stream of gas to be heated indicates a potential for further improvement. In this paper, the integration of an ORC between both streams is analyzed by using exergy and thermoeconomic analyses.

The use of ORCs for producing electricity from low and medium temperature heat sources has been analyzed by several authors. In [19], ORC cycles are applied for increasing the power produced by micro-turbines, while in [20] a methodology for process integration of ORC is proposed. In [21] ORC is compared to Stirling and a new concept (the so called inverted Brayton cycle). In [22], the
use of ORC in a polygeneration plant producing power, heat, cold and water is investigated, and a comprehensive list of candidate working fluids is proposed.

Table 1. Natural gas expansion – methods applied for controlling the outlet temperature

<table>
<thead>
<tr>
<th>Heat source</th>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Heating the gas prior to expansion (pre-heating)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electric</td>
<td>Low investment cost / space requirement</td>
<td>In most cases, negative net electricity production excludes this solution</td>
</tr>
<tr>
<td>Gas boilers [5], [12]</td>
<td>Robust design, moderate investment cost</td>
<td>Low performance ratio (power output/fuel consumption), no supporting mechanisms for selling the electricity;</td>
</tr>
<tr>
<td>Gas boilers (expander with low isentropic efficiency) [13]</td>
<td>Preheating cost increases only slightly compared to the throttling process; low investment cost.</td>
<td>Low performance ratio, low output power, the available exergy potential is used only partially;</td>
</tr>
<tr>
<td>CHP with IC engine [14],</td>
<td>High performance ratio, possible support for the generated electricity, high power output, proven successful applications;</td>
<td>Higher investment cost; exergy losses due to a high temperature difference between exhaust gases and natural gas;</td>
</tr>
<tr>
<td>Renewables (solar, geothermal) [16],</td>
<td>Low operational cost, high feasibility, no local CO₂ emissions.</td>
<td>1. Availability 2. Known studies concern pre-heating for the throttling process. Achieving higher gas temperatures can be problematic.</td>
</tr>
<tr>
<td>Waste heat [17]</td>
<td>Low operational cost, high feasibility</td>
<td>Availability</td>
</tr>
<tr>
<td><strong>Heating the gas subsequent to expansion (post-heating)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient air / water</td>
<td>No preheating cost</td>
<td>Risk of destructing the expander by the solid/liquid phase</td>
</tr>
<tr>
<td>Refrigeration system [18]</td>
<td>Optimum use of the exergy potential, two products obtained, possible excellent feasibility indicators</td>
<td>Risk of destructing the expander by the solid/liquid phase; requires integration with external processes; highest demand (summer) corresponds to lowest gas flux.</td>
</tr>
</tbody>
</table>

The use of ORC as a bottoming cycle for internal combustion engines (ICE) has been also investigated as a means for increasing electricity production and thus for improving efficiency. In [23], several types of working fluids (overhanging, nearly isentropic and bell shaped) are compared and Second Law analysis is performed. In [24], the use in automotive applications is analyzed while in [25] ORC and ICE are used in a biomass gasification plant.

In this paper, a hybrid energy generation system comprising turboexpanders, ICE and ORC is simulated and analyzed applying thermoeconomic analysis, and compared with a similar system without ORC. After presenting the fundamentals of thermoeconomic analysis, the thermodynamic and thermoeconomic models are presented. Finally, results of the analysis are shown and discussed.

2. Thermoeconomic analysis – methodology description

In this section, the fundamentals of exergy and thermoeconomic analysis are reviewed in relation to its application to the problem analyzed in this paper.

2.1. Exergy analysis

Exergy is the work potential of a thermodynamic medium with respect to the environment. The concept is particularly useful if pressurized gases are considered, since both the internal energy and enthalpy fail to represent the pressurized medium's ability to perform mechanical work. Methods
for calculating the exergy are given e.g. in [6]. Within this paper, the reference state of $p_0 = 101325$ Pa and $T_0 = 288.15$ K has been chosen for physical exergy calculations, and the chemical exergy of fuel has been assumed at the level of 1.04 LHV, after Szargut's results for high-methane gas [6].

Exergy does not satisfy the conservation law. Therefore, each process is characterized by an internal exergy loss, referred to as irreversibility $I$. For steady-state analyses, it may be written:

$$\sum_i m_i b_i - \sum_e m_e b_e + \sum_j \dot{Q}_j \frac{T_j - T_0}{T_j} - \dot{W} - I = 0,$$

where $i$ denoted all entering flows, $e$ denotes all exiting flows, $j$ denotes all heat sources exchanging heat $\dot{Q}_j$ with the control volume, and $\dot{W}$ denotes work transferred across the control volume.

### 2.2. Thermoeconomic analysis

Thermoeconomic analysis is based on the 2nd law of thermodynamics (exergy) and economics (cost) and provides method for the analysis, diagnosis and optimization of complex energy systems [26]. In particular, the methodology applied in this paper is the thermoeconomic input-output analysis (formerly known as symbolic exergoeconomics) [27].

The thermoeconomic model of a system is represented by its productive structure, where physical flows are substituted by fuel, product and, eventually, waste flows. All system components are numbered starting from 1, and the number 0 corresponds to the environment. $E_{ij}$ is the part of the product of component $i$ that becomes part of the fuel of component $j$. Accordingly, product and fuel of a component are calculated as:

$$P_i = \sum_{j=0}^n E_{ij},$$

$$F_i = \sum_{j=0}^n E_{ji}.\quad (2)$$

A table containing the values of all elements $E_{ij}$ as well as their summations by columns and rows is called the fuel-product table. The unit exergy consumption is defined as the exergy that each component requires from the other components to obtain a unit of its product:

$$\kappa_j = \frac{E_{ij}}{P_j}.\quad (4)$$

The sum of all unit exergy consumptions in a component is the inverse of its exergy efficiency:

$$\frac{1}{\eta_{b,j}} = \sum_{j=0}^n \kappa_{ij} = \frac{F_j}{P_j}.\quad (5)$$

Besides, it is possible to introduce waste flows: $R_{ij}$ is a waste flow produced by component $i$ and charged to component $j$.

The unit exergy cost of a flow is the quotient between the cost of that flow (i.e. the amount of exergy resources needed for producing it) and its exergy:

$$k_{ij} = \frac{E_{ij}}{E_{ij}}.\quad (6)$$

All product flows of a component are considered to have the same formation process and, accordingly, they have the same unit cost. Besides, the cost is formed by two parts, one due to productive flows and the other considering the contribution of waste flows. Thus, the following equation can be written:

$$k_{ij} = k_{P,j}^{\sigma} + k_{P,j}^{\tau}.\quad (7)$$
The previous costs can be calculated by applying the cost balance of all components. In particular, the term corresponding to productive flows can be obtained from the following equation:

$$k_{p,e}^* = (U_D - \langle K_P \rangle)^T k_e^*.$$  

where $\langle K_P \rangle$ is a $(n \times n)$ matrix whose elements are the values of the unit exergy consumption $e_{ij}$ and $k_e^T = (k_{01}, \ldots, k_{on})$ is a $(n \times 1)$ vector whose elements contain the unit consumption of external resources. More details on thermoeconomic input-output analysis can be seen in [26].

3. Gas expansion system description

The gas expansion system analyzed within the present paper is partially based on the nominal data of the Arlesheim gas expansion plant in Switzerland [28]. In particular, the two-stage arrangement, the flux of gas and its parameters, including inlet and outlet pressures and temperatures are based on the plant data. However, the pre-heating system has been re-designed in order to include the ORC between the flux of exhaust gases and natural gas.

<table>
<thead>
<tr>
<th>Device acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1. ICE</td>
<td>Internal Combustion Engine</td>
</tr>
<tr>
<td>D2. HRHE</td>
<td>Heat Recovery Heat Exchanger</td>
</tr>
<tr>
<td>D3. LHP</td>
<td>Low-temperature, High-pressure Pre-heater</td>
</tr>
<tr>
<td>D4. HHP</td>
<td>High-temperature, High-pressure Pre-heater</td>
</tr>
<tr>
<td>D5. GE1</td>
<td>Gas Expander 1st stage</td>
</tr>
<tr>
<td>D6. LMP</td>
<td>Low-temperature, Medium-pressure Pre-heater</td>
</tr>
<tr>
<td>D7. HMP</td>
<td>High-temperature, Medium-pressure Pre-heater</td>
</tr>
<tr>
<td>D8. GE2</td>
<td>Gas Expander 2nd stage</td>
</tr>
<tr>
<td>D9. PM</td>
<td>Power mixer (virtual device)</td>
</tr>
<tr>
<td>D10. EVAP</td>
<td>(ORC) EVAPorator</td>
</tr>
<tr>
<td>D11. ORCT</td>
<td>(ORC) Turbine</td>
</tr>
<tr>
<td>D12. REG</td>
<td>(ORC) heat REGeneration exchanger</td>
</tr>
<tr>
<td>D13. COND</td>
<td>(ORC) CONDenser</td>
</tr>
<tr>
<td>D14. ORCP</td>
<td>ORC Pump</td>
</tr>
<tr>
<td>D15. ST</td>
<td>Stack</td>
</tr>
</tbody>
</table>

The proposed system structure is presented in Fig. 1, and the system devices are listed in Table 2, also explaining the abbreviations used in the following description.

Natural gas (system points 1–9) is pre-heated in LHP and HHP and supplied to the expander GE1. Consecutively, at the medium pressure level is pre-heated in LMP and HMP and supplied to GE2. Low-pressure gas leaves the system, with the exception of a small share extracted as a fuel for the gas engine (ICE).
As can be seen in Fig. 1, heat generated by the ICE is used in two independent subsystems. The high enthalpy of the engine exhaust gases is transferred to the ORC evaporator (D10), and, at a lower temperature level, also to the heat recovery exchanger (D2). Instead of rejecting the ORC waste heat to the environment, it is utilized to supply the low-temperature water cycle (system points 21–27), which in turn serves as the low-temperature section of gas pre-heating (LHP and LMP).

The ICE jacket water is used to supply the high-temperature section of gas-preheating by means of the exchangers HHP and HMP.

The system has four electric outputs: the gas expanders (36 and 37), the ICE output 38, and the net ORC output, determined as the difference of the ORC turbine electric output (39) reduced by the power of the pump (40). The power mixer (D9) has been introduced as a virtual device in order to illustrate the hybrid origin of the total electricity production and to determine the cost of this electricity. The stack has been added because it will be needed as a dissipative device for the thermoeconomic model.
4. Thermodynamic model

A thermodynamic model of the analyzed system comprises a set of mass and energy equations as well as stoichiometry calculations and formulation of the relevant efficiencies. The model has been built in Engineering Equation Solver v8.904. The set of equations describing the system comprises:

- mass balances for flow splits and junctions (steady state); for a given split/or junction it may be written:
  \[ \sum \dot{m}_{\text{in}} = \sum \dot{m}_{\text{out}} \]  
  (9)

- energy balances for system devices (heat losses to the ambient have been neglected); for a given heat exchanger or flow machine the balance is:
  \[ \sum (\dot{m} h)_{\text{in}} = \sum (\dot{m} h)_{\text{out}} + \dot{W} \]  
  (10)

- formulation of ICE electric efficiency:
  \[ \eta_{el} = \frac{\dot{W}_{el,36}}{Q_{n,9} \cdot \text{LHV}} \]  
  (11)

- stoichiometric equations for determination of exhaust gases composition (see e.g. [30]);

- formulation of electromechanical efficiency for the machinery, for \( i \)-th device:
  \[ \eta_{em,i} = \frac{\dot{W}_{el,i}}{\dot{W}_{i}} \]  
  (12)

For heat exchangers and flow machines it is sufficient to analyze changes in the physical enthalpy. The reference state for physical enthalpy of all analyzed fluids has been chosen at 298.15 K and 101 325 Pa. Natural gas has been approximated by pure methane, for which the physical enthalpy has been calculated using real gas properties [29] implemented in the solver (EES). Enthalpy of ICE exhaust gas has been found for the ideal gas model with temperature-dependent specific heat.

All heat exchangers have been assumed isobaric.

Atmospheric air used for combustion has been assumed to have a temperature of 15°C, relative humidity 60% and CO\(_2\) content of 380 ppm. Natural gas supplied to the ICE as a fuel is extracted at the outlet of GE2; the engine pressure regulator (i.e. throttling valve) has been assumed to be part of the engine.

Since the size of ICE is determined by a discrete sequence of available electric powers, the possibility of continuous variation of the power was modelled by choosing a specific engine and applying an engine load factor, defined as:

\[ ELF = \frac{\dot{W}_{el,36}}{\dot{W}_{el,36,\text{nom}}} \]  
(13)

where \( \dot{W}_{el,36} \) is the actual power of the engine in part-load operation and \( \dot{W}_{el,36,\text{nom}} \) is the nominal power. Accordingly, it was also assumed that all flow rates bound to the ICE (fuel, air, exhaust gases, jacket water) are scaled linearly with the same ELF while the temperatures of fluxes remain unchanged. The exhaust gases temperature and oxygen concentration have been assumed according to catalogue data. The chosen engine was Caterpillar G3612 Genset DM5006, 50 Hz with the nominal data given in Table 3.

Within this work, three cases were analyzed in order to evaluate the impact of ORC application on system performance:

A. operation with ORC module;
B. operation without ORC module, this mode is simulated by setting the heat exchange in the evaporator and the ORC working fluid flow rate to 0; heat is transferred from exhaust gases to natural gas only by means of the HRHE. Moreover, the ELF is reduced in order to minimize the exhaust gases stack temperature;

C. operation without ORC module like in case B, however, the ELF is kept at the same level as in case A.

Table 3. Expansion plant data and assumptions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Generic parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural gas inlet flux</td>
<td>$Q_1$</td>
<td>35000 m$^3$/h (at 0°C 101 325 Pa)</td>
</tr>
<tr>
<td>NG inlet parameters</td>
<td>$p_1, T_1$</td>
<td>67 bar abs, 10 °C</td>
</tr>
<tr>
<td>NG parameters at GE1 inlet</td>
<td>$p_3, T_3$</td>
<td>67 bar abs, 82 °C</td>
</tr>
<tr>
<td>NG parameters at GE1 outlet</td>
<td>$p_4, T_4$</td>
<td>17 bar abs, 10 °C</td>
</tr>
<tr>
<td>NG parameters at GE2 inlet</td>
<td>$p_6, T_6$</td>
<td>17 bar abs, 72 °C</td>
</tr>
<tr>
<td>NG parameters at GE2 outlet</td>
<td>$p_7, T_7$</td>
<td>5.5 bar abs, 10 °C</td>
</tr>
<tr>
<td>TE1/TE2 isentropic efficiency (calculated) $a)$</td>
<td>$\eta_{TE1/2}$</td>
<td>68.5%, 76.5%</td>
</tr>
<tr>
<td>ICE Nominal electric power</td>
<td>$W_{el,36,\text{nom}}$</td>
<td>2915 kW</td>
</tr>
<tr>
<td>ICE electric efficiency</td>
<td>$\eta_{el,ICE}$</td>
<td>40.4%</td>
</tr>
<tr>
<td>Exhaust gas temperature</td>
<td>$T_{11}$</td>
<td>405 °C</td>
</tr>
<tr>
<td>Exhaust gas oxygen content (molar dry basis)</td>
<td>$[O_2]$</td>
<td>12.0%</td>
</tr>
<tr>
<td>Heat rejection to jacket water (nominal)</td>
<td>$\dot{Q}_{JW,\text{nom}}$</td>
<td>1234 kW</td>
</tr>
<tr>
<td>Jacket water temperature</td>
<td>$T_{15} / T_{20}$</td>
<td>95 / 70 °C</td>
</tr>
<tr>
<td>Combustion air inlet temperature</td>
<td>$T_{10}$</td>
<td>15° C</td>
</tr>
<tr>
<td>Pinch in LHP</td>
<td>$T_{26} - T_{1}$</td>
<td>10 K</td>
</tr>
<tr>
<td>Pinch in LMP</td>
<td>$T_{25} - T_{4}$</td>
<td>10 K</td>
</tr>
<tr>
<td>Temperature difference in LT water cycle</td>
<td>$T_{22} - T_{27}$</td>
<td>35 K</td>
</tr>
<tr>
<td>Pinch in ORC condenser</td>
<td>$T_{31} - T_{21}$</td>
<td>5K</td>
</tr>
</tbody>
</table>

B. Case-dependent parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORC fluid mass flow rate</td>
<td>$m_{28}$</td>
<td>2.68 kg/s</td>
<td>0 kg/s</td>
</tr>
<tr>
<td>ORC fluid max/min pressure</td>
<td>$p_{28} / p_{29}$</td>
<td>29.9 bar/ 0.44 bar</td>
<td>–</td>
</tr>
<tr>
<td>Electricity production, ICE</td>
<td>$W_{el,36}$</td>
<td>2349 kW</td>
<td>1965 kW</td>
</tr>
<tr>
<td>Pinch in the evaporator (EVAP)</td>
<td>$T_{12} - T_{33}$</td>
<td>10 K</td>
<td>–</td>
</tr>
<tr>
<td>Pinch in the HRHE</td>
<td>$T_{13} - T_{21}$</td>
<td>10 K</td>
<td>20 K</td>
</tr>
<tr>
<td>Exhaust gases stack temperature</td>
<td>$T_{13}$</td>
<td>60.2°C</td>
<td>56°C</td>
</tr>
</tbody>
</table>

In part B of the table, input parameters are set in **bold**.

$^a)$ Values of efficiency are indirectly given by the values of turbine outlet temperature.

Following assumptions have been done for the ORC subsystem:

- the working fluid is benzene;
- the regeneration ratio, defined as:
\[ \varepsilon = \frac{h_{29} - h_{30}}{h_{29} - h_{32}} \]  

has the value of \( \varepsilon = 0.7 \);

- the isentropic efficiency of the ORC expander and pump are 0.80 and 0.75, and the overall mechanic-to-electric conversion efficiency is 0.95 in both cases;
- the maximum temperature of the working fluid in the evaporator is 250°C;
- minimum allowable exhaust gas temperature has been fixed at 56 °C (i.e. 10 degrees above the condensation temperature).

It should be noted that the maximum and minimum pressures of the ORC result from the assumed pinches for the evaporator and condenser. The main technical data and assumptions regarding the system are collected in Table 3. In part B of the table, case-specific parameters are described; in that part certain parameters are input values in one of the cases, and modelling results in the other.

Solving the mass and energy balance equations allows one to determine the values of flow rates and temperatures for all fluxes in the system as well as the energy fluxes exchanged between particular devices. Key results are presented in Table 5.

Exergy efficiency of the whole system can be calculated by considering total plant fuel and total plant product. If this information is taken from Table 9, it yields:

\[ \eta_{\text{b, system}} = \frac{\dot{B}_{29}}{\dot{B}_9 + \dot{B}_{10} + \dot{B}_1 - \dot{B}_7} . \]  

The CO\(_2\) emission factor indicates the emission of carbon dioxide caused by the energy use. The factors can be calculated for primary, secondary or final energy carriers. Utilization of 1 kWh contained in natural gas (determined on the HHV basis) yields an emission of 0.1852 kg CO\(_2\). The CO\(_2\) equivalent of 1 kWh of electricity depends on the sources used and on the efficiency of generation, transmission and distribution. Data for Switzerland ([31], 2009) and Poland ([32], 2007) demonstrate the difference between hydropower and carbon-based generation, the emission factors for these countries are 0.0045 and 0.824 kg CO\(_2\)/kWh respectively. The EU-27 averaged factor was 0.377 in 2010 [33].

Stoichiometric calculations performed as a background for the present study indicate the mole fraction of CO\(_2\) equal 4.513\% while the molar flux of exhaust gases equals 0.1605 kmol/s. This yields a CO\(_2\) mass flow rate of \( \dot{m}_{\text{CO}_2} = 1148 \text{ kg/h} \). The system CO\(_2\) emission factors can be obtained by referring this value to the total electric power generated in the system:

\[ \varepsilon_{\text{CO}_2} = \frac{\dot{m}_{\text{CO}_2}}{\dot{W}_{\text{el},34} + \dot{W}_{\text{el},35} + \dot{W}_{\text{el},36} + \dot{W}_{\text{el},37} - \dot{W}_{\text{el},38}} \]  

Values of the CO\(_2\) emission factors depending on the considered case are presented in Table 5.

### 5. Thermoeconomic model

The first step in the development of the thermoeconomic model is the identification of fuel, product and wastes for each component. This information appears in Table 4. The environment is the complement of the whole plant: receives the electricity produced and provides air, gas for the engine, and difference of exergy of gas before and after expansion. ICE consumes natural gas and air and produces electricity, exergy increment for cooling water, and exhaust gases. HRHE and EVAP use exergy of exhaust gases for increasing the exergy of water for heating gas and ORC, respectively. In gas pre-heaters (LHP, HHP, LMP and HMP), exergy of water decreases for increasing the exergy of gas. Expanders produce electricity from the exergy decrement of gas. The ORC turbine uses exergy drop for producing electricity while the ORC pump uses electricity for
increasing the pressure of the ORC fluid. In the ORC condenser, heat released by the condensing fluid is used for increasing the temperature of water, while in the regenerator, a reduction of temperature of superheated fluid is used for increasing the temperature of liquid fluid. The power mixer collects power of several devices in order to obtain the final product of the system. The stack is a dissipative device (the only one whose output is a waste); it should be noted that the cost of this waste is assigned to the ICE.

Table 4. Fuel-Product-Waste definition. Exergy fluxes are denoted by $B$ instead of $\dot{B}$.

<table>
<thead>
<tr>
<th>Device</th>
<th>Fuel</th>
<th>Product</th>
<th>Waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENVIRONMENT</td>
<td>B39</td>
<td>B9+B16+(B1-B7)</td>
<td></td>
</tr>
<tr>
<td>D1. ICE</td>
<td>B9+B10</td>
<td>B36+(B16-B19)+(B17-B18)+B11</td>
<td></td>
</tr>
<tr>
<td>D2. HRHE</td>
<td>B12-B13</td>
<td>B24+B23-B21</td>
<td></td>
</tr>
<tr>
<td>D3. LHP</td>
<td>B23-B26</td>
<td>B2-B1</td>
<td></td>
</tr>
<tr>
<td>D4. HHP</td>
<td>B16-B19</td>
<td>B3-B2</td>
<td></td>
</tr>
<tr>
<td>D5. GE1</td>
<td>B3-B4</td>
<td>B34</td>
<td></td>
</tr>
<tr>
<td>D6. LMP</td>
<td>B24-B25</td>
<td>B5-B4</td>
<td></td>
</tr>
<tr>
<td>D7. HMP</td>
<td>B17-B18</td>
<td>B6-B5</td>
<td></td>
</tr>
<tr>
<td>D8. GE2</td>
<td>B6-B7</td>
<td>B35</td>
<td></td>
</tr>
<tr>
<td>D9. PM</td>
<td>B34+B35+B36+(B37-B38)</td>
<td>B39</td>
<td></td>
</tr>
<tr>
<td>D10. EVAP</td>
<td>B11-B12</td>
<td>B28-B33</td>
<td></td>
</tr>
<tr>
<td>D11. ORCT</td>
<td>B28-B29</td>
<td>B37</td>
<td></td>
</tr>
<tr>
<td>D12. REG</td>
<td>B29-B30</td>
<td>B33-B32</td>
<td></td>
</tr>
<tr>
<td>D13. COND</td>
<td>B30-B31</td>
<td>B21-B25-B26</td>
<td></td>
</tr>
<tr>
<td>D14. ORCP</td>
<td>B38</td>
<td>B32-B31</td>
<td></td>
</tr>
<tr>
<td>D15. ST</td>
<td>B13</td>
<td></td>
<td>B14</td>
</tr>
</tbody>
</table>

The next step is to create the generic fuel-product table (see annex). In most cases, terms of this table are straightforward from the explanations above, except in two situations: i) the product of condenser and HRHE is fuel for LHP and LMP, and ii) the product of evaporator, ORC pump and regenerator is fuel for the ORC turbine, regenerator and condenser. In these situations, distribution ratio has been introduced for defining the table.

6. Results

Based on the thermodynamic and thermoeconomic models discussed in sections 4 and 5, a set of results describing the plant as a system and its particular components has been obtained. All results are presented for three cases defined in section 4 (Case A – ORC, Case B – without ORC, decreased ICE power, Case C – without ORC, ICE power as in Case A).

Table 5 presents overall system results, showing the system output power, exergy efficiency, performance ratio and CO$_2$ emissions referred to the unit of produced electricity. The table illustrates the hybrid character of the energy generation system. The power generated in natural gas expanders (1790 kW in all cases) constitutes between 40 and 48% of the total system production, depending on the analyzed case. The ORC power (Case A) is only 7.7% of the total production. Therefore, it may be stated that the turboexpanders and the ICE are primary system devices, and the ORC is an auxiliary device, applied in order to improve the overall system performance.

If the operation of expanders were possible without gas pre-heating (i.e. with acceptance of low outlet temperatures), the local performance ratio would approach infinity (since energy would be
generated without on-site fuel input). On the other hand, a performance ratio for a stand-alone ICE corresponds to the engine electric efficiency (0.404 for the analyzed engine). The obtained values of the local performance ratio vary between 0.712 for Case C and roughly 0.77 for Cases A and B. Although the performance ratio should not be referred to as ‘efficiency’, its economic significance for the system operator exactly corresponds to that term, as it represents the ratio of the produced energy flux (intended for sales) to the fuel consumed on-site (determining the cost). From this point of view, the achieved values of the performance ratio should be evaluated as outstanding. Accordingly, also the system CO$_2$ emissions are very low even if compared to average emissions e.g. in Europe. Both advantages are due to the ‘energy-invisible’ part or the input potential, contained in the pressurized gas, and detected by means of exergy analysis.

Table 5. Results summary

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>–</td>
<td>–</td>
<td>4.5% CO$_2$, 10.0% H$_2$O, 10.8% O$_2$, 74.7% N$_2$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ORC Power</td>
<td>kW</td>
<td>343</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total power of NG expanders (GE1+GE2)</td>
<td>kW</td>
<td>906 + 884 = 1790</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total system power</td>
<td>kW</td>
<td>4482</td>
<td>3810</td>
<td>4139</td>
</tr>
<tr>
<td>Performance ratio (local)</td>
<td>–</td>
<td>0.771</td>
<td>0.762</td>
<td>0.712</td>
</tr>
<tr>
<td>Exergy efficiency</td>
<td>–</td>
<td>0.526</td>
<td>0.496</td>
<td>0.485</td>
</tr>
<tr>
<td>Exergy cost of produced electricity</td>
<td>–</td>
<td>1.902</td>
<td>2.015</td>
<td>2.060</td>
</tr>
<tr>
<td>System CO$_2$ emissions</td>
<td>kg/kWh</td>
<td>0.256</td>
<td>0.259</td>
<td>0.277</td>
</tr>
</tbody>
</table>

* – given quantity is a result of calculations, not an input parameter.

Table 6. Irreversibility

<table>
<thead>
<tr>
<th>Device</th>
<th>Irreversibility (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1. ICE</td>
<td>Case A</td>
</tr>
<tr>
<td>D2. HRHE</td>
<td>12.6</td>
</tr>
<tr>
<td>D3. LHP</td>
<td>18.6</td>
</tr>
<tr>
<td>D4. HHP</td>
<td>25.1</td>
</tr>
<tr>
<td>D5. GE1</td>
<td>516.3</td>
</tr>
<tr>
<td>D6. LMP</td>
<td>15.7</td>
</tr>
<tr>
<td>D7. HMP</td>
<td>20.6</td>
</tr>
<tr>
<td>D8. GE2</td>
<td>347.3</td>
</tr>
<tr>
<td>D9. PM</td>
<td>0</td>
</tr>
<tr>
<td>D10. EVAP</td>
<td>79.4</td>
</tr>
<tr>
<td>D11. ORCT</td>
<td>89.7</td>
</tr>
<tr>
<td>D12. REG</td>
<td>9.4</td>
</tr>
<tr>
<td>D13. COND</td>
<td>69.7</td>
</tr>
<tr>
<td>D14. ORCP</td>
<td>3.4</td>
</tr>
<tr>
<td>D15. ST</td>
<td>0</td>
</tr>
</tbody>
</table>
The system exergy efficiency varies between 0.485 for Case C and 0.526 for Case A. Assuming Case B as a reference, it can be seen that the application of ORC increases the system exergy efficiency by 2.8 percent points.

In order to understand better how this efficiency is formed, it is interesting to analyze separately the different components forming the installation. Irreversibility of all components appears in Table 6, for the three situations considered. The most interesting result is the strong reduction of irreversibility in the HRHE (around 500 kW); actually, the interest of using of an ORC is to reduce this irreversibility. Of course, this ORC, as a non-perfect device does not transform all this exergy in electricity but only 347 kW, however, exergy savings are clear. It can be argued that there are other components with higher irreversibility (mainly ICE and expanders). However, this is due because they process more exergy. It should be noted that irreversibility in expanders is the same in all columns, because they are the same components in the three cases. For the ICE, it can be noticed that irreversibility is lower in Case B because the power of the engine is also smaller. Irreversibility levels in gas preheaters (LHP, HHP, LMP and HMP) are by an order of magnitude lower since these devices process less exergy due to low temperature levels.

Table 6 shows the absolute magnitude of irreversibility. In order to eliminate the influence of the component size, a non-dimensional, qualitative parameter has to be used, such as the unit exergy consumption (inverse of the exergy efficiency), which can be seen in Table 7. This table shows clearly that the component with the lowest efficiency is the HRHE in the cases with no ORC. Accordingly, the analysis correctly points out that the matching between the high temperature of exhaust gases and the low temperature of preheated gas has to be improved. One possibility to do that is to introduce a heat engine that takes advantage of this temperature difference, and this is what is analyzed in the paper. Another component with high irreversibility is the ICE, which is bound to the current state of engine technology. It should be noted that most of the values of unit exergy consumption are the same for all cases, because the corresponding devices are either equal or a scaled version (ICE). Neither the power mixer nor the stack have internal irreversibility, accordingly, their unit exergy consumption is equal to one.

Both irreversibility and unit exergy consumption are local parameters characterizing the components individually. In order to have a clear picture, parameters taking into account the different role of the components in the whole system are needed. Unit exergy costs of the products of all components appear in Table 8. It can be seen how the cost increases as the chain of exergy transformation advances. For this reason, the highest values appear in LHP and LMP (they are affected by their own irreversibility, as well as by irreversibility of ICE, HRHE, and components of ORC when present). It can be seen how the use of ORC decreases substantially this value, because irreversibility in the chain decreases.

It may be surprising that, despite the high values commented above, the unit cost of the final product is quite low (around 2). This fact can be explained taking into account that the final electricity production is a result of two or three production chains: expanders, ICE and ORC (when present). As it is shown in Table 6, expanders are very efficient devices; accordingly the percentage of electricity produced by them should be maximized. This fact has to be balanced with the need of low temperature heat for increasing the gas temperature before expansion: if this heat is produced with an efficient system (Case A), efficiency of the whole system improves. However, if the CHP system is oversized (Case C), efficiency decreases. Accordingly, the choice of an optimum size of the ICE is a key point in the efficiency of the system.

Finally, the Fuel-Product table with the values of Case A can be seen in annex.
### Table 7. Unit exergy consumption

<table>
<thead>
<tr>
<th>Device</th>
<th>Case A</th>
<th>Case B</th>
<th>Case C</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1. ICE</td>
<td>1.794</td>
<td>1.794</td>
<td>1.794</td>
</tr>
<tr>
<td>D2. HRHE</td>
<td>1.582</td>
<td>5.680</td>
<td>6.430</td>
</tr>
<tr>
<td>D3. LHP</td>
<td>1.556</td>
<td>1.378</td>
<td>1.556</td>
</tr>
<tr>
<td>D4. HHP</td>
<td>1.278</td>
<td>1.235</td>
<td>1.278</td>
</tr>
<tr>
<td>D5. GE1</td>
<td>1.570</td>
<td>1.570</td>
<td>1.570</td>
</tr>
<tr>
<td>D6. LMP</td>
<td>1.532</td>
<td>1.357</td>
<td>1.532</td>
</tr>
<tr>
<td>D7. HMP</td>
<td>1.394</td>
<td>1.342</td>
<td>1.394</td>
</tr>
<tr>
<td>D8. GE2</td>
<td>1.393</td>
<td>1.393</td>
<td>1.393</td>
</tr>
<tr>
<td>D9. PM</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>D10. EVAP</td>
<td>1.134</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D11. ORCT</td>
<td>1.251</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D12. REG</td>
<td>1.345</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D13. COND</td>
<td>1.924</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D14. ORCP</td>
<td>1.347</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D15. ST</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

### Table 8. Unit exergy cost of the products of devices.

<table>
<thead>
<tr>
<th>Device</th>
<th>Case A</th>
<th>Case B</th>
<th>Case C</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1. ICE</td>
<td>1.875</td>
<td>1.873</td>
<td>1.922</td>
</tr>
<tr>
<td>D2. HRHE</td>
<td>2.966</td>
<td>10.641</td>
<td>12.360</td>
</tr>
<tr>
<td>D4. HHP</td>
<td>2.396</td>
<td>2.314</td>
<td>2.457</td>
</tr>
<tr>
<td>D5. GE1</td>
<td>1.898</td>
<td>2.316</td>
<td>2.388</td>
</tr>
<tr>
<td>D6. LMP</td>
<td>6.019</td>
<td>14.43</td>
<td>18.936</td>
</tr>
<tr>
<td>D7. HMP</td>
<td>2.613</td>
<td>2.515</td>
<td>2.679</td>
</tr>
<tr>
<td>D8. GE2</td>
<td>1.656</td>
<td>2.029</td>
<td>2.091</td>
</tr>
<tr>
<td><strong>D9. PM</strong></td>
<td><strong>1.902</strong></td>
<td><strong>2.015</strong></td>
<td><strong>2.060</strong></td>
</tr>
<tr>
<td>D10. EVAP</td>
<td>2.127</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D11. ORCT</td>
<td>2.736</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D12. REG</td>
<td>2.940</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D13. COND</td>
<td>4.206</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D14. ORCP</td>
<td>3.686</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D15. ST</td>
<td>1.875</td>
<td>1.873</td>
<td>1.922</td>
</tr>
</tbody>
</table>

**a)** Corresponds to the total plant product
7. Conclusions

The main conclusion of the performed analysis is that the objective of integrating the ORC into the system (to decrease exergy losses occurring due to irreversible heat transfer) was accomplished. As a result, efficiency of the system has improved around 3 points compared to the no-ORC case (B).

The fact that the global improvement is not very high compared to the local improvement in the section of heat recovery from exhaust gases can be commented by Jan Szargut’s 16th rule of improving thermodynamic imperfection of processes [6]:

‘Avoid the elongation of the chain of thermodynamic processes’.

In the analyzed case, the introduction of ORC allows one to generate supplementary electricity generation utilizing thus the thermal potential between the hot source (exhaust gases) and the sink (natural gas). However, introducing additional heat exchangers, including evaporators and condensers introduces new sources of exergy losses. Moreover, in order to integrate the ORC several pinch points have to be taken into account in a series of exchangers, and eventually the ICE engine has to be operated at higher load in order to provide sufficient heat as the ORC driving force. The thermoecomonic analysis performed provides rigorous results for assessing this fact.

The integration of the ORC into the gas expansion system does have a significant advantage: the system produces more electric energy with the performance ratio and CO\textsubscript{2} emission factor as high as in a case without ORC. For this reason the interest of the application of an ORC would depend strongly of economic reasons (mainly, the feed-in tariff) that should be analyzed by means of an economic feasibility study while designing a new expansion system for a particular application. Moreover, optimization of the ORC structure, parameters and the working fluid could contribute to the system performance and may be of interest for future research. Another interesting line of development would be the integration of the preheating system with renewable energy sources.

Despite of the case-dependent results of this analysis, the study presented demonstrates the applicability of thermoeconomic analysis as a systemic method for pointing out the possibilities of energy savings.

Acknowledgements

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Nomenclature

\begin{itemize}
  \item \( b \) \hspace{1cm} \text{specific exergy, kJ/kg}
  \item \( \dot{B} \) \hspace{1cm} \text{exergy flux, kW}
  \item \( e_{CO2} \) \hspace{1cm} \text{CO\textsubscript{2} emission factor, kg CO\textsubscript{2}/kWh}
  \item \( E \) \hspace{1cm} \text{exergy flow in a productive structure, kW}
  \item \( E^* \) \hspace{1cm} \text{exergy cost of a flow in a productive structure, kW}
  \item \( F \) \hspace{1cm} \text{fuel flux, kW}
  \item \( h \) \hspace{1cm} \text{specific enthalpy, kJ/kg}
  \item \( I \) \hspace{1cm} \text{irreversibility, kW}
  \item \( k^* \) \hspace{1cm} \text{unit exergy cost, –}
  \item \( LHV \) \hspace{1cm} \text{lower heating value, kJ/m\textsuperscript{3} (at 0°C, 101325 Pa)}
  \item \( \dot{m} \) \hspace{1cm} \text{mass flow rate, kg/s}
\end{itemize}
\( n \)  
number of components of the plant, –

\( \dot{n} \)  
molar flow rate, kmol/s

\( p \)  
pressure, Pa

\( P \)  
product flux, kW

\( Q_n \)  
normalized volumetric flow rate, \( \text{m}^3/\text{h} \) (at \( 0^\circ\text{C}, 101325 \text{ Pa} \))

\( \dot{Q} \)  
heat flux, kW

\( T \)  
temperature, K

\( W \)  
power, kW

\( \mathbf{U}_D \)  
identity matrix \(( n \times n )\)

\( \mathbf{KP} \)  
matrix of unit exergy consumptions \(( n \times n )\)

\( \varepsilon \)  
regeneration ratio

\( \eta_b \)  
exergetic efficiency

\( \kappa \)  
unit exergy consumption

\( \kappa_e \)  
vector of unit exergy consumption of external resources \(( n \times 1 )\)

**Greek symbols**

**Subscripts and superscripts**

\( 0 \)  
exergy reference conditions

\( e_l \)  
electric

\( e_m \)  
electromechanical

\( i,j \)  
generic component in a productive structure

**Abbreviations**

\( \text{abs} \)  
absolute pressure

\( \text{ICE} \)  
Internal Combustion Engine

\( \text{NG} \)  
Natural gas

\( \text{ORC} \)  
Organic Rankine Cycle

**References**


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<table>
<thead>
<tr>
<th></th>
<th>F0</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
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W: B14, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0

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Table 9 (Annex). Generic FP table. Exergy fluxes are denoted by B instead of B. 
Table 10. (Annex) FP table for the system with ORC (Case A). All values are given in kW exergy.

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One-dimensional Model of an Optimal Ejector and Parametric Study of Ejector Efficiency

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Abstract:
Significant numerical and experimental analyses have been devoted to understanding the variety of flow regimes present in steady flow ejectors. Certain regimes are more conducive to achieving high performance (i.e. high entrainment ratios). In particular, the entrainment ratio is seen to be highest when the entrained fluid reaches a choked condition in the mixing region. In addition, the expansion regime of the motive nozzle (under-, perfectly- or over-expanded) appears to influence performance. In this paper, we propose a method to model an ejector of optimal geometry, designed for a favorable flow regime. Then, rather than focusing upon the maximization of efficiency, we seek operational conditions that maximise ejector efficiency, specifically the reversible entrainment ratio efficiency. Ejector efficiency is found to be highest at low compression ratios and at low driving pressure ratios. However, at lower compression ratios, the optimal area of the mixing chamber becomes large relative to the motive nozzle throat area.

Keywords:
Ejector Efficiency, Entrainment Ratio, One-Dimensional Model, Perfect Expansion.

1. Introduction
Ejectors are supersonic flow induction devices employed for the generation of a vacuum for compressing a fluid. Figure 1 shows a straight throat ejector. High pressure motive fluid enters a converging diverging nozzle and is accelerated to a supersonic Mach number. The pressure at section NE is below that of the entrained fluid at its inlet. Consequently, the entrained fluid is drawn into the ejector. The motive and entrained fluids mix between sections NE and U and the uniform mixture is diffused to reach the discharge pressure.

![Fig. 1. Schematic diagram of a straight throat ejector](image-url)
One common ejector application is the withdrawal of non-condensible gases from steam condensers. Other applications employ ejectors to compress a working fluid, such as vapor-compression refrigeration and vapor compression multi-pressure humidification-dehumidification desalination [3]. The operating conditions of an ejector in vacuum generation and compression applications differ significantly. When generating a vacuum, the compression ratio of the ejector, \( P_D/P_E \), is very high whilst the ratio of the mass flow rate of entrained to motive fluid (known as the entrainment ratio) is very high. In compression applications, the compression ratio is low, whilst the entrainment ratio is high. The compression ratios also differ between compression applications. For example, Huang et al. [1] performed experiments on a refrigeration system using R141b. For an evaporator temperature of 8°C and a condenser temperature ranging from 28°C to 42.1°C, the compression ratio of the ejector varied from 2.2 to 3.6. Kamali et al. [2] optimised the design of a seven effect thermal vapour compression multi-effect distillation system with a condenser temperature of 45°C and a first effect temperature of 69°C, corresponding to a compression ratio of 3.1. Narayan et al. [3] optimised an ejector driven humidification dehumidification desalination system and found that the optimal compression ratio lies near 1.2.

For compression applications, the ejector efficiency is of significant importance as it dictates the energy input (or more correctly the exergy input) required to drive the ejector. One means of quantifying ejector performance, suggested by Elrod [4] and analysed in detail by McGovern et al. [5], is the reversible entrainment ratio efficiency, or \( \eta_{RER} \). This efficiency compares the entrainment ratio of a real ejector to a reversible process with the same inlet fluid states and the same discharged pressure:

\[
\eta_{RER} = \frac{ER}{RER}
\]  

When designing an ejector, we could look for more than just a high value of entrainment ratio for fixed inlet conditions and a fixed discharge. Importantly, the entrainment ratio alone is not an indication of the quality of design or the performance of an ejector. We can ask what ejector geometry and what operating conditions are conducive to the highest ejector efficiency. This is the objective of the present work. In Section 2, we identify the flow regimes possible in steady flow ejectors that are most conducive to high efficiency. In Section 3, we discuss how an ejector of optimal geometry may be modelled using 1 dimensional theory. In Section 4, using fluid inlet conditions and ejector discharge pressure as parameters, we identify the operating conditions conducive to the highest values of efficiency. In summary, by focusing upon efficiency rather than solely the entrainment ratio we provide a new insight to optimising ejector design.

2. Regimes of Ejector Operation

One crucial consideration in the analysis and design of ejectors is the variety of flow regimes that are possible, depending on operating conditions and the ejector geometry. In order to design for maximum ejector efficiency one should be able to identify favorable flow regimes. To understand the flow regimes of an ejector we can describe the entrainment ratio in terms of the inlet fluid conditions, the discharged pressure, the motive fluid nozzle throat area and the mixing chamber area.

\[
ER = f(P_M, T_M, P_E, T_E, P_D, A_T, A_C)
\]  

First, we would like to explain the effect of the operating conditions upon an ejector of fixed geometry and second, the effect of the ejector geometry upon the entrainment ratio of an ejector with fixed operating conditions. This is done by considering experimental and numerical analyses present in literature.

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2.1 Flow regimes within an ejector of fixed geometry

The explanation of flow regimes for a fixed ejector geometry is common in literature and revolves around the concept of critical back pressure, \( P_d^* \). A clear description of the critical pressure is provided by Bartosiewicz et al. and Huang et al. [6, 20] using experimental data and by Sriveerakul et al. [7] using a CFD analysis. The motive fluid throat area, the chamber area and the inlet motive and entrained fluid states at the inlet to the ejector are fixed. We may now describe three distinct regimes:

1. Reversed flow region – \( P_d \) is to the right of point A on the x axis of Fig. 2 and the discharged pressure is too high to allow entrainment. Flow through the converging diverging nozzle is overexpanded, resulting in compression shocks (see Bartosiewicz [6]). Motive fluid partially flows back through the entrained fluid inlet.

2. Unchoked entrainment – The discharged pressure drops to point A in Fig. 2, causing the compression shocks at the exit of the motive fluid nozzle to weaken, allowing the pressure at NE to drop and provoke entrainment.

3. Critical operation – The discharged pressure reaches \( P_d^* \), allowing a decrease in pressure upstream and causing the entrained flow to be accelerated to sonic speed within the mixing region.

4. Choked Flow – For values of \( P_d \) below \( P_d^* \) the entrainment ratio remains constant. The motive fluid is choked at the motive fluid nozzle throat and the entrained flow remains choked in the mixing region.

The important message to take from these analyses is that the entrained mass flow rate is constant as the discharge pressure drops below critical. Since the entrained fluid pressure is held constant at the inlet this can only mean that the effective cross-sectional area at which choking occurs in the mixing region must be constant for fixed inlet conditions and ejector geometry, as concluded by Munday and Bagster [8].

![Fig. 2. Evolution of the entrainment ratio with discharge pressure](image)

2.2 Flow regimes within an ejector with fixed operating conditions

Less common in literature is an intuitive explanation of the effect of ejector geometry upon the entrainment ratio. Nahdi et al. [9] and Lu et al. [10] draw important conclusions in this regard. By considering fixed inlet fluid states and a fixed discharged pressure we may identify three regimes which depend upon ejector geometry.

1. Overexpanded Flow – We consider operating conditions such that the motive and entrained fluids are choked at the motive nozzle throat and in the mixing chamber, respectively. The ratio
of chamber to motive nozzle throat area, $\varphi$, is small, such that the motive nozzle is overexpanded.

2. Perfectly Expanded Flow – The value of $\varphi$ is reduced causing a higher value of ER. The pressure at cross section U in Fig. 1 drops, as does the pressure upstream of U. The compression shocks downstream of the motive fluid nozzle weaken until they cease to exist when the nozzle is perfectly expanded. The effective flow area of the entrained fluid increases (since $\varphi$ increases) and the entrainment ratio increases. Nahdi et al. refer to $\varphi$ at this point as the optimal area ratio for a given set of inlet conditions and discharged pressure. The entrainment ratio is maximum, the static pressures of the motive and entrained fluid are equal at section NE in Fig. 1 and the motive nozzle is perfectly expanded.

3. Underexpanded Flow – The value of $\varphi$ is reduced below optimal, causing a decrease in entrainment. The underexpanded motive jet spreads at the exit of the motive nozzle, restricting the flow area of the entrained fluid. The flow structure takes the form of Fig. 3.

Using experimental results, Nahdi et al. [9] recognise that the entrainment ratio of an ejector is maximised when the primary nozzle is perfectly expanded and the entrained fluid reaches a choked condition. They identify, for a working fluid of R11, the area ratio which maximises the ER, as a function of ejector compression ratio, $P_D/P_E$, and driving pressure ratio, $P_M/P_D$.

3. One Dimensional Model of an Optimal Ejector

Using this knowledge we can build a one-dimensional ejector model that captures the performance of an optimal ejector. Coupled with the definition for efficiency (Section 1), this model can be used to identify the ejector operating conditions conducive to high efficiency (Section 4).

Nahdi et al. [9] identified the flow regime that maximised the ER for fixed conditions of operation. Since the reversible entrainment ratio is constant for fixed conditions of operation [4, 5], the flow regime that maximizes the ER must also maximize the reversible entrainment ratio efficiency. Consequently, the purpose of this section is to model an ejector operating in this optimal flow
regime. Using this knowledge we can build a one-dimensional ejector model that captures the performance of an optimal ejector. Coupled with the definition for efficiency (Section 1), this model can be used to identify the ejector operating conditions conducive to high efficiency (Section 4). To simplify the interpretation of results, an ideal gas ejector is modelled, with constant values of specific heats.

3.1 Nozzle Region

We begin by considering flow from the motive and entrained fluid inlets to the cross section NE in Fig. 1. The inlet fluid pressures and temperatures are fixed, \( P_M \), \( P_E \), \( T_M \), \( T_E \). According to Section 3, the motive fluid nozzle is perfectly expanded, meaning that the static pressures of the motive and entrained streams are equal at NE. In addition, the entrained flow is choked at section NE, i.e. the Mach number is unity, such that further decreases in the downstream pressure cannot induce a higher mass flow rate. Considering the motive and entrained flows both to be isentropic and adiabatic, we may solve for the entrained fluid pressure and temperature at the nozzle exit, and then for the motive fluid Mach number and the motive fluid temperature at NE.

\[
\frac{T_E}{T_{NE,E}} = 1 + \frac{\gamma - 1}{2} \tag{3}
\]

\[
\frac{P_E}{P_{NE,E}} = (1 + \frac{\gamma - 1}{2})^\frac{\gamma}{\gamma - 1} \tag{4}
\]

\[
\frac{P_M}{P_{NE,M}} = (1 + \frac{\gamma - 1}{2} M_{NE,M}^2)^\frac{\gamma}{\gamma - 1} \tag{5}
\]

\[
\frac{T_M}{T_{NE,M}} = 1 + \frac{\gamma - 1}{2} M_{NE,M}^2 \tag{6}
\]

In order to fix the capacity of the ejector, we fix the motive fluid throat area, \( A_T \). This allows the mass flow of the motive fluid to be calculated:

\[
\dot{m}_M = \sqrt{\gamma A_T P_M} \frac{RT_M}{(1 + \frac{\gamma - 1}{2})^\frac{\gamma + 1}{2(\gamma - 1)}} \tag{7}
\]

At this point, the mass flow rate (and the flow area at NE) of the entrained fluid is yet to be determined. The modelling until this point is the same as Khoury et al. [11], although their work does not allude to the motive nozzle being perfectly expanded to justify the uniformity of pressure across NE. In the present analysis, the motive nozzle exit is located at the entrance to the mixing region (Fig. 1). In many experimental configurations, the nozzle exit is upstream of the constant area region. Zhu et al. [12] provide a detailed analysis of the influence of the axial position of the nozzle exit upon entrainment ratio.

3.2 Mixing Region

In the constant area mixing region, the mass, momentum, and energy conservation equations are applied between sections NE and U of Fig. 1. The fluid properties and velocity are taken to be uniform over the entrained flow area and motive flow area at NE and over the total flow area at U. Frictional forces on the fluid due to the no slip condition at the wall are assumed to be negligible.

\[
\dot{m}_M + \dot{m}_E = \dot{m}_U \tag{8}
\]
In addition, there is a relationship between the mixing chamber area and the flow areas at the exit of the motive nozzle.

\[ A_{NE} = A_{NE,M} + A_{NE,E} = A_U \quad (11) \]

A number of these assumptions merit further discussion. The mixing process within an ejector is characterised by highly irreversible oblique and sometimes normal shocks coupled with dissipative processes within the shear layer between the motive and entrained fluids. Entropy generation within this region is driven by pressure, velocity and temperature differences, in axial and radial directions. By employing a control volume approach, we are overlooking the details of the mixing process. Instead, by essentially varying the ratio of pressure, velocity and temperature, the motive and entrained fluids at NE and the pressure ratio between sections NE and U, we are essentially altering the scale of the disequilibria responsible for entropy generation. Examples of detailed experimental visualisations of internal flow structures are provided by Desevaux et al. [14] and Dvorak et al. [19], whilst numerical visualisations are provided by Desevaux et al. [13], Hemidi et al. [15], Bartosiewicz et al. [6] and Sriveerakul et al. [7].

By assuming properties and velocity to be uniform at section U in Fig. 1, we intend the ratio of the mixing chamber length to diameter to be sufficiently large for the motive fluid core and the entrained fluid annulus to have mixed very well. The consequence of incomplete mixing is inadequate pressure recovery and compression within the diffuser. The axial length of the mixing section is dependent on the rate of mixing between the two streams. The higher the rate of mixing the greater would be the transverse spread (or growth) of the turbulent shear layer leading to a shorter axial length of the mixing region. Li et al. [16] indicated that the optimum length varies greatly with the operation conditions. In numerical studies, one way to determine the appropriate mixing length is by employing a numerical die tracer, as suggested by Bartosiewicz et al. [6]. Sriveerakul et al. [7] also points out that as the mixing chamber is elongated, total pressure losses due to shear stress at the wall increase, implying that there is an optimal length of the mixing region.

### 3.3 Diffuser

Since the fluid velocity is considered to be uniform at cross section U in Fig. 1, the diffuser is modelled as isentropic.

\[ \frac{T_D}{T_U} = 1 + \frac{\gamma - 1}{2} \frac{M_U^2}{2} \quad (12) \]

\[ \frac{P_D}{P_U} = (1 + \frac{\gamma - 1}{2} M_U^2)^{\frac{\gamma}{\gamma - 1}} \quad (13) \]

In practice, the performance of the diffuser depends largely upon the completeness of mixing in the constant area section. Diffuser efficiency was reported by Varga et al. [17] to be within the range 0.5 to 0.9 depending on both temperature and area ratio. For an ejector of fixed mixing chamber length, the diffuser efficiency is a function of the back pressure. As back pressure increases, normal or oblique shocks will be pushed back into the mixing section, resulting in a more uniform flow at cross section U and consequently improved diffuser performance. This is clearly illustrated by Sriveerakul et al. [7].
3.4 Solution of Equations

Given the following relations for mass flow rate, Mach number and the speed of sound in an ideal gas, the set of equations provided above are closed and may be solved.

\[ \dot{m} = \rho AV \quad (14) \]

\[ M = \frac{V}{c} \quad (15) \]

\[ c = \sqrt{\gamma RT} \quad (16) \]

The equations are solved iteratively using the non-linear equation solver provided by Engineering Equation Solver [18] subject to the restriction that the Mach number obtained at cross section U must be subsonic. For compression applications, the conditions of the fluid obtained at the diffuser exit should be as close as possible to stagnation (zero velocity). Consequently, the flow must be subsonic at the diffuser exit, and preferably within the entire diffuser. For a set of operational conditions (inlet fluid states and discharge pressure), we may calculate the following key variables:

1. The ejector area ratio of \( A_c/A_T \)
2. The entrainment ratio, \( ER \)

4. Results

Given the model of an optimal ejector presented in Section 3, we now seek the conditions of operation that maximize ejector efficiency. We begin by considering the variation in ejector efficiency and area ratio with the compression ratio in Fig. 4. As the compression ratio decreases, the entrainment ratio of the optimal ejector increases at a faster rate than the reversible entrainment ratio, resulting in improved efficiency. Meanwhile, as the compression ratio drops, the optimal area ratio of the mixing chamber to the ejector throat increases to accommodate a greater flow rate of entrained fluid.

![Graph](image)

**Fig. 4. Efficiency and area ratio for a driving pressure ratio of \( P_D/P_E=5 \) and an inlet temperature ratio of \( T_M/T_E=1 \)**

Figure 5 illustrates the effect of the driving pressure ratio upon ejector efficiency and area ratio. Ejector efficiency is less sensitive to the driving pressure ratio of the ejector than the compression ratio.
ratio. As the driving pressure ratio increases, the area ratio of the ejector also increases, resulting in an ejector that is larger in size.

Finally, we consider the effect of the inlet temperature ratio. In Fig. 5, the efficiency of the ejector reaches a maximum at an inlet temperature ratio just above unity. This is the point where the temperature difference between the motive and entrained streams at the nozzle exit are minimum. Also, the ejector area ratio is insensitive to the inlet temperature ratio.

![Graph showing efficiency and area ratio for a compression ratio of $P_D/P_E=2$ and an inlet temperature ratio of $T_M/T_E=1$.]

**Fig. 5.** Efficiency and area ratio for a compression ratio of $P_D/P_E=2$ and an inlet temperature ratio of $T_M/T_E=1$

Finally, we consider the effect of the inlet temperature ratio. In Fig. 5, the efficiency of the ejector reaches a maximum at an inlet temperature ratio just above unity. This is the point where the temperature difference between the motive and entrained streams at the nozzle exit are minimum. Also, the ejector area ratio is insensitive to the inlet temperature ratio.

![Graph showing efficiency and area ratio for a driving pressure ratio of $P_M/P_D=5$ and an inlet temperature ratio of $T_D/T_E=2$.]

**Fig. 6.** Efficiency and area ratio for a driving pressure ratio of $P_M/P_D=5$ and an inlet temperature ratio of $T_D/T_E=2$

### 5. Conclusions

Using a simple model of an optimal ejector, a parametric study has been performed to identify operating conditions conducive to high ejector efficiency. This optimal ejector is designed such that
the motive fluid nozzle is perfectly expanded and the entrained fluid is choked at the entrance to the constant area mixing section. The following is concluded from the parametric study:

- The efficiency of an ideal gas ejector is highest when design for conditions of low compression ratio and low driving pressure ratio.
- At low compression ratios the area ratio of the mixing section to the motive nozzle throat increases, indicating that the required size of the ejector increases.
- As the driving pressure ratio increases, the required size of the ejector increases.
- An optimal inlet temperature ratio of the inlet fluids appears to exist for fixed inlet and discharge pressures, although the ejector area ratio appears insensitive to the inlet temperature ratio.

**Acknowledgments**

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**Nomenclature**

**Letter Symbols**
- $A$ area, m$^2$
- $c$ speed of sound, m/s
- $ER$ entrainment ratio, dimensionless
- $\dot{m}$ mass flow rate, kg/s
- $M$ speed of sound, dimensionless
- $P$ pressure, Pa
- $R$ ideal gas constant, J/kg K
- $RER$ reversible entrainment ratio, dimensionless
- $T$ temperature, K

**Greek symbols**
- $\eta$ reversible entrainment ratio efficiency, dimensionless
- $\gamma$ ratio of specific heats, dimensionless
- $\phi$ Ratio of mixing chamber area to motive nozzle throat area

**Subscripts**
- $C$ mixing chamber area
- $D$ discharge
- $E$ entrained fluid
- $M$ motive fluid
- $NE$ motive nozzle exit
- $T$ motive nozzle throat
- $U$ uniform flow cross section

**Abbreviations**
- ER entrainment ratio
- RER reversible entrainment ratio
References


Optimization and Design of Pin-Fin Heat Sinks Using Minimum Entropy Generation

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Abstract:
This work analyses the entropy generation production for different pin-fin heat sink configurations, optimizing the parameters that must be used in the manufacture of heat sinks. The pin-fin heat sinks are commonly used for cooling in the electronic devices, with the goal of improving the performance, as well as increasing the life span of electronic circuits. In addition to the design parameters, the type of geometrical arrangement is analyzed too (this is because both the in-line and the staggered arrangement could be employed). Once the optimal parameters are determined, the next step is to analyze the type of pin-fin cross-sectional geometry that can be used; for the present work the geometries analyzed are rectangular, circular, elliptical and a constructal theory-based arrangement. The entropy generation and Bejan number are reported for the different geometries, as well as the optimal parameters including fins diameter, the distance between the fins, the air velocity and the number of fins needed.

Keywords:
Entropy Generation, Bejan Number, Pin-Fin Heat Sink.

1. Introduction

Nowadays the electronic industry spends a great deal of capital in the development of faster, smaller and more efficient electronic devices; but this industry has put no interest in an extremely important area for the maintenance and the good operation of the electronic circuits: the thermal design area of the electronic industry. As power dissipation of components increases and component package size decreases, thermal engineers must innovate to ensure that the components will not overheat. Devices that are well cooled increase their period of life utility. Therefore, a heat sink must satisfy thermal design as well as mechanical requirements.

The main techniques for electronic circuits cooling are based on forced convection and using pin-fin heat sinks due to their low cost of manufacturing and easy installing. Different pin-fin heat sink configurations have been used as in-line and staggered arrangement, with different geometries [1]-[3],[23] for the pin-fin cross section: square, circular and elliptical. Aluminium is the material used commonly for its thermal properties, easy manufacturing and cost.

Nowadays the design engineer is faced with integrating coolant passages into an existing piece of equipment, where the space occupied by the coolant passage is at a premium and the available flow rates may be limited by the size of an existing or a retrofit fan or pump, therefore, the following question arises: is there an optimum pin-fin heat sink configuration that minimizes entropy generation and allows for the best performance? To answer that question different experimental and numerical analyses have been performed for the thermal and hydraulic behaviour of the pin-fin heat sinks [4]. Different pin-fins cases have been studied and the optimal parameters have been found. These optimal parameters present a better thermal and hydraulic performance.
2. Background

Several researches [4] have undertaken the characterization of pin-fin heat sinks, the behaviour of the flow within a heat sink is the same as that within a series of tubes of infinite length, except at the end of the walls. Idelchik et al. [21] present correlations for different geometries of tube banks, whereas Zhukauskas et al. [8] present experimental correlations for tubes in cross flow as a function of the Reynolds number, diameter of tubes and space between the tubes. Dugruoz et al. [4] show that the experimental correlations of tubes in cross flow can be used in pin-fin heat sinks analysis for high velocities \( (v>3 \text{ m/s}) \) when the pin-fin geometry is square. On the other hand, Khan et al. [5] reported that the experimental correlations can be used for a wide range of velocities \( (v=1.5 \text{ to } 5 \text{ m/s}) \) when the pin-fin geometry is circular. In the present work a circular pin-fin geometry is employed for obtaining the optimal parameters for the arrangement.

Different studies [4] determine the optimal parameters for the design of a pin-fin heat sink, therefore the optimum number of fins that present the lower thermal resistance, thence finding the greater heat dissipation. However, the optimal configuration is determined by only taking into account the heat transfer performance, but the pressure drop should be also taken into account since it increases as a function of the number of fins.

In the last few years a parameter used for the optimization of thermo-fluidic systems is the entropy. The entropy generation rate has become a useful tool for evaluating the intrinsic irreversibilities associated with a given process or device [18]. The groundbreaking work by Bejan [20] introduced the concept of entropy generation analysis due to fluid flow and heat transfer as a powerful tool to evaluate the effectiveness of different configurations. Since the entropy generation destroys the work availability of a system, it makes good engineering sense to focus on the irreversibility due to heat transfer and fluid flow processes to understand the associated entropy generation mechanisms. References can be found where entropy generation is calculated and minimized in ducts with various cross-sectional shapes for laminar and turbulent flow configurations, with constant heat transfer rate per unit length, with constant heat flux, or with constant wall temperature, and in flows with temperature dependent viscosity [9]-[11].

Numerous studies have shown that in convective heat transfer arrangements the fluid friction and the heat transfer losses are coupled, and that attempts to reduce entropy generation associated with heat transfer will increase the entropy generation associated with fluid friction, and vice versa [12]. This coupling between fluid flow and heat transfer irreversibilities suggests that the geometry and operating conditions can be optimized to minimize the overall entropy generation. Khan et al. [13] employed the entropy generation minimization method as a unique measure to study the thermodynamic losses caused by heat transfer and pressure drop for a fluid in cross flow with tube banks. Analytical and empirical correlations for heat transfer coefficients and friction factors are used, where the characteristic length is used as the diameter of the tubes and reference velocity used in the Reynolds number, and the pressure drop is based on the minimum free area available for the fluid flow. A parametric study is also performed to show the effects of different design variables on the overall performance of tube banks.

On the other hand Culham et al. [14] worked in the specification and design of heat sinks for electronic applications, and presented a procedure that allows the simultaneous optimization of heat sink design parameters based on a minimization of the entropy generation associated with heat transfer and fluid friction. In addition, a novel approach for incorporating forced convection through the specification of a fan curve is integrated into the optimization procedure, providing a link between optimized design parameters and the system operating point.

An important parameter in the design of the pin-fin heat sink is the geometry of the fins. Important investigations in this area have been published like that of Behnia et al. [15]. In their work they compare the heat transfer dissipation capacity of several geometries of fins commonly used. Geometries were optimized to diminish the thermal resistance using moderate air speeds.
New geometries and adjustments are proposed to improve the performance of the pin-fin heat sinks, in this untiring search there is a configuration proposed by Bello et al. [16]; although they propose their configuration for a phenomenon of natural convection, in the present work it will be adapted for forced convection to observe the thermal and hydraulic behavior of such configuration. Bello found that in a space filled with cylinders used to dissipate heat by natural convection, the heat transfer dissipation capacity can be progressively increased by the use of cylinders of several sizes and the optimal place of each cylinder in the adjustment. These authors placed smaller cylinders at the entrance of the adjustment section (the regions of free flow occupied by still air and that is not being used for the heat transfer performance). The optimization of the flow and the development for structures with one and two sizes of cylinders is reported, which correspond to structures with one and two degrees of freedom. In Fig. 1 a) and b) the arrangement adjustments of the cylinders are observed, a) the original adjustment used commonly, and b) the proposed complex adjustment to be used in this work. The proposed arrangement is called honeycomb because it simulates the structure with which the bees construct their honeycomb. The optimal relation between the big and the small cylinders was found by Bello: $D_1/D_0=0.2$.

![Fig. 1. Constructal arrangement.](image)

### 3. Geometric parameters

The present work investigates the impact of the parameters modification on the entropy generation for a pin-fin heat sink. Fig. 2 shows the main parameters of the heat sink that need to be optimized: SL is the pitch longitudinal, ST is the pitch transversal, b is the distance between the fins and a is the magnitude of the fin side. Another parameter to optimize is the flow velocity.

![Fig. 2. Heat sink parameters.](image)

The material used for the pin-fin heat sink manufacturing is aluminium, which has a thermal conductivity of 210 W/(m K). The base of the heat sink has the following dimensions: 6.35 cm of width, 6.35 cm of length and 0.635 cm of height. All fins have a height of 3.175 cm. The heat sink is placed in a channel of rectangular cross-section, air flow pass through this channel at ambient temperature; with this arrangement it is possible to simulate the electronics circuit cooling currently employed in the industry.
Once the optimal parameters of the design for the pin-fin heat sink are found, the different arrangements for the fins are studied; the arrangements studied in this work are shown in Fig. 3 a) and b), which are the in-line and staggered arrangement respectively.

Fig. 3. a) In-line arrangement, b) staggered arrangement.

When the best arrangement for the minimum entropy generation is obtained considering specific geometrical configurations, the manufacturing processes, integration and costs have to be evaluated in order to obtain the best and most reliable heat sink geometrical configuration. 

Fig. 4 shows the different fins geometries analyzed in this work: square, circular, elliptical and constructal arrangement; the dimensions of the fins are obtained using the same hydraulic diameter so they can be compared. In the incessant search to find new geometries and arrangements for a better performance of these heat sink new ideas are proposed, therefore the arrangement proposed by Bello [16] based on the constructal theory for the phenomenon of free convection is analyzed, this arrangement is adapted to forced convection, observing that improvements are observed with this configuration.

Fig. 4. Geometries analysed: square, circular, elliptical and constructal.

4. Entropy Analysis

Following Bejan’s discussions on the subject [12], and applying the mass conservation and energy laws with the entropy balance for a fluid that crosses through a heat sink, an expression for the entropy generation rate can be deduced.

\[ S_{gen} = \left( \frac{Q^2}{T_a T_b} \right) R_{hr} + \frac{m \Delta P}{\rho T_a} \]  

(1)

This is the entropy generation due to heat transfer and pressure drop, therefore it is possible to use it as an objective function for the optimization of the design of the heat sink. The previous relations are based on the previous knowledge of the pressure drop correlations for tube bundles tubes.
[6],[8],[13],[21],[22], which have very good results, as Dugruoz et al. [4] and Khan et al. [5] confirmed.

5. Results
This work finds the optimum variables that lead to the minimum entropy. The effects of certain parameters on the optimum design variables and the corresponding entropy generation rates are studied. Results are shown in Fig. 5; the curves show the entropy generation variation versus the fin diameter. It is observed that the entropy generation depends on the diameter, and the minimum entropy generation is obtained for a diameter between 3 and 3.7 mm. The air velocity and fins number used are 4 m/s and 8 fins.

<table>
<thead>
<tr>
<th>Diameter [m]</th>
<th>S gen [W/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.106</td>
</tr>
<tr>
<td>0.002</td>
<td>0.108</td>
</tr>
<tr>
<td>0.003</td>
<td>0.110</td>
</tr>
<tr>
<td>0.004</td>
<td>0.112</td>
</tr>
<tr>
<td>0.005</td>
<td>0.114</td>
</tr>
</tbody>
</table>

Fig. 5. Entropy generation versus fin diameter.

Another parameter of interest in the present work is the number of fins per row that generates the minimum entropy generation and therefore the optimal number of fins for the heat sinks design. Fig. 6 shows the entropy generations versus the number of fins; from this figure the optimal number of fins for a minimum entropy generation is 8 fins, thus the heat sink arrangement has a total of 64 fins. When the number of fins and the diameter optimal are found, the distance between the fins can be determined for the optimal performance of the heat sink.

<table>
<thead>
<tr>
<th>Fins number</th>
<th>S gen [W/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.110</td>
</tr>
<tr>
<td>5</td>
<td>0.112</td>
</tr>
<tr>
<td>6</td>
<td>0.114</td>
</tr>
<tr>
<td>7</td>
<td>0.116</td>
</tr>
<tr>
<td>8</td>
<td>0.118</td>
</tr>
</tbody>
</table>

Fig. 6. Entropy generation versus number of fins.
The air velocity entering the heat sink is a factor affecting the pressure drop and the amount of heat removed by the heat sink. Therefore in Fig. 7 the entropy generation is plotted versus air velocity. Clearly, an air velocity of 2 m/s leads to obtaining the minimum entropy generation.

![Fig. 7. Entropy generation versus air velocity.](image)

Typically, a heat sink works with an air velocity of 4 m/s, and when the air velocity increases the thermal resistance decreases, although when greater velocities are used the pressure drop increases as well; therefore using the minimum entropy methodology an optimal flow velocity can be obtained. The graph in Fig. 8 shows the entropy generation for different number of fins and for air velocities of 2 and 4 m/s. Clearly a minimum for both velocities occurs: for the 4 m/s case the minimum entropy occurs for 8 fins, and for the 2 m/s case the minimum occurs for an arrangement of 10 fins.

![Fig. 8. Entropy generation versus number of fins for different air velocities.](image)

The results for entropy generation variation versus diameter are observed in Fig. 9 for different inlet velocities; for each velocity a minimum occurs, and the smaller the velocity the lower the entropy generation. The minimum entropy generation is obtained when the air velocity is 1.5 m/s and a fin height of 6 mm is employed.
A comparison of the in-line and staggered arrangement is shown in Fig. 10. Therefore the best arrangement for the heat sink is the in-line arrangement for the studied conditions, since it shows a minimum entropy generation.

The optimal number of fins for both arrangements studied in this work is shown in Fig. 11. For a staggered and in-line arrangement the optimal number of fins for the arrangement is approximately 8 fins. These results depend on the air velocity (as shown in Fig. 9), then the air velocity must be taken into account in any analysis; for the results presented in Fig. 11, an air speed of 4 m/s was used.

In order to select a material to use in the manufacturing of the pin-fin heat sink, Fig. 12 allows to see that the aluminium (k=210 W/(m K)) is a good material for the heat sinks, because its entropy generation is not very different from that generated with materials of higher conductivity; on the
other hand, very interestingly, it is observed that the use of materials with low conductivity leads to an almost exponential increase in the entropy generation.

Fig. 12. Entropy generation variation versus thermal conductivity.

Considering the results shown in Figures 5 to 12, the behavior of the entropy generation by varying the operating and geometrical parameters can be observed. Thus, optimal geometrical configuration of heat sinks can be proposed.

When different fin geometries are analyzed, analytical and empirical correlations cannot be used, because the results will be the same for all geometries, and the best geometry cannot be found for the heat sink. Therefore, the general relation to determine the entropy generation should be written as:

$$S_{gen} = qV\left(\frac{1}{T}\right) - \frac{1}{T}P^\nu \nabla \nabla \cdot v - \frac{1}{T}P : V$$

(2)

where the first term is the entropy related to heat transfer, the second and third terms are due to mechanical dissipation.

A code was developed to solve Equation (2). The input variables for solving Equation (2) are the temperature and pressure drop contours; these are obtained previously with the aid of a commercial code.

In Fig. 13 it is possible to observe the entropy generation by volume unit for each fin geometry and for the constructal arrangement. The geometry that presents the lower entropy generation is the constructal arrangement proposed by Bello [16], although this arrangement is for a phenomenon in free convection but adapted in the present work to forced convection, offering very good results for the thermal and hydraulic performance.

Fig. 13. Entropy generation for the fin geometries analyzed in the present work.
The Bejan number is calculated for each fin geometry and for the constructal arrangement; these results are reported in Fig. 14; the elliptical geometry has the largest Bejan number, indicating that the thermal affects are dominant in the phenomenon analyzed. The constructal arrangement has the smallest Bejan number since the entropy generated by pressure drop effects is considerable due to the large number of pin fins compared with other configurations. A larger hydrodynamic resistance is observed with this increase in the pin fin density.

![Bejan number versus fins geometry](image)

**Fig. 14. Bejan number versus fins geometry.**

6. Conclusions

In the present work an analysis of the entropy generation due to heat transfer and to pressure drop for a pin-fin heat sink arrangement is reported. Using empirical and analytical correlations the optimal diameter, optimal number of fins, the optimal arrangement and the optimal air velocity are found for the manufacturing a pin-fin heat sinks. The material to use for the heat sink manufacturing is analysed as well, this analysis indicated that aluminium is as good a material because it leads to low entropy generation and cost.

Analysing the results for different fin geometries it is concluded that that circular geometry is the best geometry for the performance of the heat sink, although surpassed slightly by the constructal arrangement, which has the minimum entropy generation of all geometries used in this investigation.

It is concluded, thus, that it is possible to obtain the optimal parameters with a new arrangement for pin-fin heat sinks; these results could be used to improve the cooling techniques for the current electronic devices, leading to optimal operating conditions and efficiency.

**Nomenclature**

- $a$: fin side, (m)
- $b$: distance between fins (m)
- $d$: diameter (m)
- $d_1$: diameter major (m)
- $d_2$: diameter minor (m)
- $H$: height of the finned section (m)
- $\dot{m}$: mass flow (kg/s)
- $N$: fins number
- $P$: pressure (Pa)
- $Q$: heat flow rate from heater (W)
- $r_1$: semi major axis length (m)
- $r_2$: semi minor axis length (m)
\( R_{hs} \)  \hspace{1em} \text{thermal resistance (K/W)}

\( S_L \)  \hspace{1em} \text{pitch longitudinal (m)}

\( S_T \)  \hspace{1em} \text{pitch transversal (m)}

\( \xi_{\text{gen}} \)  \hspace{1em} \text{entropy generation rate (W/K)}

\( T_a \)  \hspace{1em} \text{ambient temperature (K)}

\( T_b \)  \hspace{1em} \text{base temperature of the heat sink (K)}

\( U_{\text{int}} \)  \hspace{1em} \text{inlet velocity (m/s)}

\( v \)  \hspace{1em} \text{velocity (m/s)}

\textbf{Greek symbols}

\( \Delta P \)  \hspace{1em} \text{overall pressure drop in the finned section (Pa)}

\( \rho \)  \hspace{1em} \text{density (kg/m}^3\text{)}

\( \mu \)  \hspace{1em} \text{viscosity (N s/m}^2\text{)}

\textbf{References}

- **Journals:**


- Books and other monographs:


- Conference Papers:

Performance analysis of a district heating system

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Abstract:
Lowering the exergy content of heat, required for heating purposes, can decrease the primary energy consumption. District heating systems are often an important link between facilities that generate heat with low exergy content and consumers. Exergetic efficiency of heat distribution is an important factor in heat supply to consumers and can serve as an optimization factor for a more sustainable distribution network operation.

This paper presents a methodology for an exergy-based distribution network analysis of a district heating system. Criteria for performance evaluations are defined. They can be used to evaluate heat supply to different points in the network, or individual system components. A case study is performed on an existing district heating system. Energetic and exergetic efficiencies of supply lines are analysed. Exergy destructions and exergy losses are studied. Exergy destruction rates present less than 1 % of exergy loss rates in their separate consideration. Distribution network operation is discovered as not optimal. An optimal ratio between exergy destruction and exergy losses at fictitious mass flow rate increment is searched. It is found to be in the interval 0.34 to 0.37.

Keywords:

1. Introduction
Exergy of a stream at combustion temperatures of fuels is very close to its energy values. Exergy of a stream at temperatures of heated buildings or domestic hot water is typically in the magnitude of 10 % of its energy value. Direct usage of boilers to supply heat demands therefore results in large thermodynamic irreversibilities. These irreversibilities are in exergy analysis, in dependency of the selected boundaries, known as exergy destruction and exergy losses. With high values of exergy destruction and losses a potential to cause a change is therefore wasted in a great extent. This represents a waste of primary energy resources [1].

Several applications of an exergy analysis to space heating in buildings have been made in the literature. In ref. [2] it is stated that energy and exergy analyses must be conducted from the primary energy transformation until the building envelope including the envelope. It is shown that energy concept alone is not adequate in gaining a full understanding of all the important aspects of energy utilization processes. The building sector has a high potential for reducing the exergy content of energy demand and supply [3]. For this purpose the exergy concept is relevant for design of buildings, heating, ventilation and air-conditioning systems [4, 5]. The low exergy approach is the main object to constitute a sustainable built environment [6]. Low exergy (or LowEx) building systems are studied by many researches and are seen as a possibility for design of high performance buildings [3, 6, 7]. Future exergoeconomic analysis is recommended by some authors when using exergy analysis method for analysis of buildings [2, 8].
A prerequisite for low exergy building systems is low exergy content heat generation with low irreversibilities. This can be achieved by different means. In ref. [9] researchers studied different cases of heat pump systems and compared them to conventional condensation boiler heating system. Approach for energetic analyses, which they used, considers energy chain from primary energy source via building to the sink. The most efficient case in their analyses is a ground source heat pump system which has 25% less primary energy and exergy demand compared to condensation boiler system. In ref. [10] geothermal resources are proposed to be classified as low, medium and high quality resources based on their exergy value. High quality resources can be used for direct generation of electricity. Lower quality resources are more appropriate for heating applications and their utilization results in lower irreversibilities. Solar radiation represents a high quality energy flow. Researchers in ref. [11] proposed a different boundary when analyzing solar energy systems from an exergy perspective, on a physical viewpoint. They stated that thermal energy output of a solar collector field at its corresponding temperature level or electricity output of a PV system should be regarded as primary energy sources. In this way inconsistencies from a physical point of view, when regarding direct (e.g. solar thermal, photovoltaic systems or windows in the building envelope) and indirect (e.g. heat pumps, wind turbines, etc.) use of solar radiation, are avoided. For efficiency determination of different direct-solar conversion systems they propose an additional parameter, namely the total required area to be installed. Accordingly an exergy output of a more efficient direct-solar system at a given area would be higher. This consideration adds solar energy to the heat generation systems with low irreversibility.

Cogeneration is a technique for generating multiple energy products simultaneously in a manner of utilizing high exergy flows for processes where they are needed and remaining low exergy flows where they can be used. Thus an important reduction in irreversibility is achieved in comparison with separate generation of these products. It is often related to generation of electricity and heat with low exergy content for heating and industrial purposes. In this field the implementation of exergy-based analyses for efficiency improvement has been made by researches in the highest extent. In recently published papers they are often in a form of thermoeconomic or exergoeconomic analyses, where costs of irreversibilities are also acquired [1, 12]. In ref. [13] a review is made on the exergoeconomic analysis and optimization of combined heat and power production.

Low exergy heat generation is often possible only at a scale which largely exceeds the local heat demands. In some cases the higher scale of heat generation facilities results in better energy and exergy efficiency. In these cases a district heating system can be used to connect consumers to the heat generation facility. There the distribution network of a district heating system becomes an important part in the heat supply chain. On the distribution network heat losses occur and pumping power is needed to transport the fluid, which carries the heat. Accordingly an exergy-based performance analysis of the distribution network in a district heating system is needed to discover the design and operating parameters that can decrease irreversibilities in supplying heat for thermal demands in buildings. Several authors have used exergy concept to analyze district heating systems. Many of them carried out an exergy analysis [14-18]. One study [19] proposed a model which can serve as a basis for differential tariff determination. There different price factors were calculated for heat supplied to different consumers based on the exergy losses of heat distribution. In ref. [20] authors presented strategies for improving the performance of waste-heat based district heating system. They concluded that an exergy analysis has a clear added value for characterizing and improving the performance of district heating systems. Some studies are also dealing with exergoeconomic analyses of district heating systems. In ref. [21] various studies conducted on geothermal district heating systems from the energetic, exergetic and exergoeconomic point of view are reviewed.

Distribution network of a district heating system is often spread out in a large area. Hot-water pipelines constricting it have a variety of diameters and isolative properties. The heat transported through an individual point in the network varies in a great extent. Distance from the heat generation facilities to the individual consumers is also dependent on the point in the distribution
network. Accordingly an energy or exergy efficiency of the whole distribution network in a district heating system is not informative of the efficiency of heat supply to individual consumer connected to the network. In order to improve the performance of a district heating system from an exergetic and economic point of view, several points in the network have to be considered. As a first step for future exergoeconomic analysis an approach for exergy analysis has to be defined which considers different points in the network and separates supply and return lines. We have not found such a model in the literature. Boundaries and definitions are in this paper in accordance with a widely used and accepted theory in exergoeconomics in [1, 22].

2. Methodology

2.1. Network description

Distribution network in a district heating system is described in this paper using graph theory. In graph theory a graph is a set of points and lines connecting some pairs of the points [23]. Points are called vertices and lines are called edges. Edges represent connections between points and can be attributed with individual properties. A connected graph which has no cycles is called a tree. Distribution network in a district heating system without internal loops can be represented by a directed tree. Fig. 1 shows a simple directed tree. In a distribution network this tree structure can be seen as follows. The first vertex in the network is $v_1$. This is the first point which is subject of analyses. The parameters of the supply and return water here determine the thermal inputs into the distribution network. The edge $e_1$ is a pipeline connecting point $v_2$ to $v_1$. From $v_2$ two edges (pipelines) are connecting vertices $v_3$ and $v_4$. Vertices $v_2$ to $v_4$ can represent branching and/or consumers or just an arbitrary point in the network.

![Fig. 1. Tree structure.](image)

If two vertices are connected by an edge, they are called adjacent, otherwise they are called disjoint. To input graphs into computer adjacency matrix can be used. If vertex $x_i$ is adjacent to vertex $x_j$, than $(i,j)$ entry in the adjacency matrix is 1, else it is 0. Adjacency matrix for the directed graph in Fig. 1, denoted by $M$ is:

$$M = \begin{pmatrix}
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 1 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}.$$ (1)

With the adjacency matrix connections between points in the distribution network of a district heating system are defined. To perform an energy and exergy analysis properties of edges and governing equations also need to be defined.

2.2. Energetic analysis

A positive effect (PE) of a district heating system is the heat supplied to the consumers. The resource expended (RE) to do it is the heat supplied to the distribution network and the energy required for the pumps. We can write an energy balance equation for the whole system:

$$E_{RE} = E_{PE} + (\dot{Q}_L - \dot{W}).$$ (2)
The difference between heat losses and pumping power in Eq. (2) is the amount of heat which has to be supplied to the network in addition to the energy of the PE.

In analogy the PE and the RE can be defined for each individual pipeline (edge in Fig. 1). Resources expended can also be considered as resources needed to supply heat to an individual point in the network. E.g., heat which has to be supplied to the vertex \( v_I \) and energy for the pumps to supply the product to \( v_3 \). Accordingly, the definition of RE and PE depends on a chosen control volume. A flow is entering and exiting every pipe with different parameters, as seen in Fig. 2. Heat is being lost to the pipe surroundings with its temperature.

To calculate the energetic efficiency the PE is divided by the RE:

\[
\eta = \frac{E_{PE}}{E_{RE}}.
\]  (3)

### 2.2.1. Heat losses

When we have water flow inside a pipe and its temperature is higher than the one of the surroundings, heat losses cannot be avoided. To calculate heat losses Eq. (4) is used. There are many different methods how to determine the overall heat transfer coefficient of an insulated district heating pipeline and other network components. It can be calculated or experimentally acquired.

\[
\dot{Q}_L = U \cdot A \cdot \Delta T_{lm}
\]  (4)

Log mean temperature difference in Eq. (4) is calculated as:

\[
\Delta T_{lm} = \frac{(T_i - T_{sur}) - (T_o - T_{sur})}{\ln \left( \frac{T_i - T_{sur}}{T_o - T_{sur}} \right)}.
\]  (5)

### 2.2.2. Pumping power

Pumping power needed to supply the hot water to the consumers can be calculated using Eq. (6).

\[
W_{pump} = \frac{\dot{m} \cdot (p_i - p_o)}{\rho_w}
\]  (6)

Pressure drop \((p_i - p_o)\) is dependent on the wall shear stress between the water and pipe surface. The overall pressure drop for the pipe system consists of the pressure loss due to viscous effects in the straight pipes termed the major loss and the pressure drop in various other components, termed the minor loss [24].

In a distribution network of a district heating system static pressure is maintained at a constant value. As mentioned before, pumping power is needed to cover the pressure losses. Pressure losses are a drop in static pressure over a length of pipe. Pumps are located at several locations in the network and increase the static pressure. However, the location of the pumps has little influence when analyzing the energy or exergy performance of a distribution network with given flow.
parameters. Consequently we can, for a more generally applicable analysis, model the network as it would have a large number of pumps. So large, that their effect to the static pressure could be neglected. This way the whole network (or a part of the network which is physically separated) is considered to have the same static pressure on the length of the pipelines.

### 2.2.3. Water flow temperature

Heat losses cause a temperature change of the water on the length of the pipeline. It is a logarithmic function on the length of the pipeline [25]. For short pipelines, with low temperature change (<0.5 °C), it can be considered as linear. Temperature change is not dependent only on the amount of heat losses, because of the friction caused by the fluid flow. Energy needed to transport the water must also be accounted for. Especially in modern district heating systems with low supply and return temperatures and high pressure gradients in pipelines, as in [26]. Because of the temperature change the heat available to consumers is being decreased on the length of the pipeline. It is decreased by:

\[Q_m = \dot{m} \cdot (h_l - h_o).\]  

We can also calculate it by knowing the heat losses and energy needed for the fluid flow:

\[\dot{Q}_a = \dot{Q}_l - \dot{W}.\]  

In a network as displayed in Fig. 1, the data used to analyze the system can include \(T_i\) at \(v1\) or a desired \(T_o\) at any other vertices. All of the unknown \(T_i\) and \(T_o\) for each of the edges can be calculated individually by using Eq. (8). The solution is acquired numerically.

### 2.3. Exergetic analysis

#### 2.3.1. Reference state

In a reference state the system is in equilibrium with the environment. District heating system is a closed system. Consumers and heat generation facilities are physically separated from the distribution network. In an interaction with the environment only thermal energy is being transferred. Thus a restricted reference state exists, where temperature of the water is equal to the temperature of the environment. The pressure and chemical potential remain unchanged. The available exergy in a water flow in the distribution network is therefore defined by calculating the thermal part of the physical exergy [27]:

\[e_j^T = \left[ (\dot{h}_j - \dot{h}_{j0}) - T_0 (\dot{s}_j - \dot{s}_{j0}) \right]_{p=\text{const}}.\]  

#### 2.3.2. Boundaries on supply and return lines

Exergy balance for a component as well as for the overall system can be written in form exergy fuel/exergy product [1]. Exergy of product is the desired result, expressed in exergy terms, achieved by the system (component). Exergy fuel are the exergetic resources expended to generate the exergy of the product.

Exergy fuel for a pipeline in Fig. 3 is defined as:

\[\dot{E}_p = \dot{E}_{\text{sup,v1}} - \dot{E}_{\text{ret,v1}} + \dot{W}_\text{sup} + \dot{W}_\text{ret}.\]  

Exergy of the product is:

\[\dot{E}_p = \dot{E}_{\text{sup,v2}} - \dot{E}_{\text{ret,v2}}.\]  

Selection of boundaries is an important topic to discuss for correct conduction of the exergy analysis. The choice of boundary determines whether the effect of heat transfer is charged as exergy destruction or an exergy loss. In Fig. 3 a supply line (edge) is defined as our control volume. Heat
losses of the supply pipeline are denoted as $Q_{L,\text{sup}}$ and heat losses of the return $Q_{L,\text{ret}}$. Two different boundaries are defined:

- Boundaries I include just the supply and return pipeline, and
- Boundary II is located outside the system where the temperature corresponds to the ambient temperature, taken here as the temperature of the exergy reference environment $T_0$.

With boundary II, heat transfer occurs at the temperature $T_0$, and thus there is no associated exergy transfer: $\dot{E}_Q = 0$. Accordingly, the value of the exergy loss is: $\dot{E}_L = 0$. The exergy destruction term accounts for exergy destruction owing to friction and the irreversibility of heat transfer to the environment:

$$\dot{E}_D = \dot{E}_F - \dot{E}_P.$$  \hspace{1cm} (12)

With Boundaries I the rate of exergy loss $\dot{E}_L$ equals the rate of exergy transfer associated with heat transfer, and is thus given by:

$$\dot{E}_L = \int_{v1}^{v2} \left( 1 - \frac{T_0}{T_w} \right) \cdot \dot{q}_L \cdot dl.$$  \hspace{1cm} (13)

With different boundary considerations the exergies of fuel and product remain the same. The relation between exergy destruction and exergy loss with different boundaries is described by the following term:

$$\dot{E}_D^{\text{Boundary II}} = \dot{E}_D^{\text{Boundary I}} + \dot{E}_L^{\text{Boundary I}}.$$  \hspace{1cm} (14)

![Fig. 3. Supply and return pipeline with heat transfer to the surroundings.](image)

For a heat exchanger fuel is defined as the exergy difference between input and output of the hot stream \[1\]. The product is defined as the exergy difference between input and output of the cold stream.

With the definition of product and fuel in Eq. (10) and (11) the exergetic efficiency for the selected control volume can be calculated:

$$\varepsilon = \frac{\dot{E}_P}{\dot{E}_F}.$$  \hspace{1cm} (15)

Exergy destruction ratio is a ratio of the exergy destruction rate within a system (subsystem) to the exergy rate of the fuel for the overall system:

$$y_D = \frac{\dot{E}_D}{\dot{E}_F}.$$  \hspace{1cm} (16)
2.4. Consideration of return pipelines

Supply pipelines distribute water from one vertex to others in a tree structure. Direction of water flow in return pipelines is opposite. Let us consider that consumers at \( v_3 \) and \( v_4 \) in Fig. 1 are returning water with the same temperature. When the edges \( e_2 \) and \( e_3 \) are not identical, the temperature of both return flows is not the same in \( v_2 \). Mixing will take place. Similar occurs when the consumers are returning water with different temperatures. This affects the exergy fuel and exergy product through heat losses of the return pipeline and return water temperature in \( v_1 \). Accordingly the return temperature of one consumer affects the efficiency of supplying heat to the other. In a district heating system there can be consumers with higher and lower return temperatures. Supplying heat to consumers with higher return temperatures reduces the distribution network efficiency and supplying heat to consumers with low return temperatures increases it. Accordingly it would be appropriate to separate the efficiencies of heat supply to different consumers as much as possible. We can achieve this by individually considering the return of each consumer. To do it first the return in \( v_4 \) (Fig. 1) defines the temperature in \( v_2 \) and \( v_1 \). For the return in vertices \( v_3 \) and \( v_2 \) the calculations are then repeated. Mass flow rates on edges are in all calculations on the same value as in the supply pipelines. With this consideration we can calculate different efficiencies for consumers with different return temperatures. On the other hand the difference to actual conditions is small, because of much lower heat losses of return than supply pipeline. Therefore this consideration is used for the analyses in this paper.

3. Case study

3.1. District heating of Šaleška valley

In Slovenia 9 % of total heat demand in residential, services and other sectors is supplied by district heating. In Šaleška valley, which is positioned in the northern part of the country, Slovenia’s second largest district heating system is in operation. The heat is produced by a coal-fired cogeneration plant and distributed through a branched distribution network. The electrical power of the cogeneration plant is 779 MW. The maximal heating power supplied to the distribution network is 192 MW. Cooling towers are used for the heat, which has to be transferred to the surroundings in the electricity production process and is not supplied to the distribution network. A part of the distribution network of the district heating system is analyzed in this paper. It covers approximately 25 % of the total distribution network. The analyzed part is presented as a tree structure in Fig. 4. The considered vertices and edges are marked there. To this part of the network heat is supplied through vertex \( v_1 \). Following vertices were introduced where needed: change in diameter of the pipe, water mass flow rate, insulation properties of the pipeline or branching of the network.

Several physical parameters can be defined for edges because they represent pipelines. The ones needed for our analyses are: pipeline diameter, length, isolative properties (overall heat transfer coefficient), mass-flow rate of water and pressure in pipes. The temperature of the surroundings around each of the pipes has to be defined because heat is being transferred to it. Stationary conditions on a winter day were considered in our case study. The parameters used were acquired while determining energy efficiency of the distribution network [28]. They are summarized in Table 1. Pressure in supply pipelines is 16 bars and in return pipelines 15 bars. Temperature of the environment is 0.2 °C. Each edge in Fig. 4 represents supply and return pipeline. The same parameters from Table 1 are considered for both. Internal pipe area was considered for heat transfer, when determining overall heat transfer coefficients.

Temperature of the supply water in vertex \( v_1 \) is defined as 126.5 °C. Temperature of the return for each of the vertices is 75 °C. An exergy analysis of heat exchangers is relatively simple on a level needed for distribution network. In addition the main goal of the case study in this paper is to present the tree structure exergy analysis with different boundaries and fuel – product selections. Consequently a part of the distribution network in Šaleška valley was selected which does not contain any heat exchangers.
Fig. 4. Tree structure of considered distribution network in Šaleška valley.

Table 1. Physical parameters of edges in distribution network in Šaleška valley (stationary conditions on a winter day)

<table>
<thead>
<tr>
<th>Edge</th>
<th>d, mm</th>
<th>l, m</th>
<th>U, m/s</th>
<th>m</th>
<th>$\rho$, $\Omega$</th>
<th>$\sigma$, $\Omega^{-1}$</th>
<th>$T_{sur}$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>e1</td>
<td>350</td>
<td>455</td>
<td>0.64</td>
<td>39.3</td>
<td>0.2</td>
<td>1.02</td>
<td>6.4</td>
</tr>
<tr>
<td>e2</td>
<td>350</td>
<td>445</td>
<td>0.64</td>
<td>39.3</td>
<td>0.2</td>
<td>1.12</td>
<td>4.4</td>
</tr>
<tr>
<td>e3</td>
<td>250</td>
<td>626</td>
<td>0.78</td>
<td>20.1</td>
<td>0.2</td>
<td>1.12</td>
<td>4.4</td>
</tr>
<tr>
<td>e4</td>
<td>250</td>
<td>55</td>
<td>0.78</td>
<td>17.7</td>
<td>0.2</td>
<td>1.38</td>
<td>1.8</td>
</tr>
<tr>
<td>e5</td>
<td>200</td>
<td>630</td>
<td>0.88</td>
<td>11.3</td>
<td>0.2</td>
<td>1.42</td>
<td>1.6</td>
</tr>
<tr>
<td>e6</td>
<td>200</td>
<td>259</td>
<td>0.88</td>
<td>11.3</td>
<td>0.2</td>
<td>1.59</td>
<td>1.0</td>
</tr>
<tr>
<td>e7</td>
<td>200</td>
<td>253</td>
<td>0.88</td>
<td>11.3</td>
<td>0.2</td>
<td>1.59</td>
<td>1.0</td>
</tr>
<tr>
<td>e8</td>
<td>200</td>
<td>321</td>
<td>0.88</td>
<td>11.3</td>
<td>0.2</td>
<td>1.59</td>
<td>1.0</td>
</tr>
<tr>
<td>e9</td>
<td>200</td>
<td>510</td>
<td>0.88</td>
<td>11.3</td>
<td>0.2</td>
<td>1.59</td>
<td>1.0</td>
</tr>
<tr>
<td>e10</td>
<td>150</td>
<td>46</td>
<td>1.02</td>
<td>6.4</td>
<td>0.2</td>
<td>1.12</td>
<td>4.4</td>
</tr>
<tr>
<td>e11</td>
<td>150</td>
<td>115</td>
<td>1.02</td>
<td>6.4</td>
<td>0.2</td>
<td>1.53</td>
<td>1.2</td>
</tr>
<tr>
<td>e12</td>
<td>150</td>
<td>216</td>
<td>1.02</td>
<td>6.4</td>
<td>0.2</td>
<td>1.59</td>
<td>1.0</td>
</tr>
<tr>
<td>e13</td>
<td>150</td>
<td>267</td>
<td>1.02</td>
<td>6.4</td>
<td>0.2</td>
<td>1.89</td>
<td>0.5</td>
</tr>
</tbody>
</table>

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3.2. Results and discussion

In Table 2 results of the performance analysis on a part of the distribution network in Šaleška valley are presented. Representative vertices from Fig. 4 are selected. Table 2 is divided into two sections: Stationary conditions on a winter day and optimal mass flow. Fuel is defined for each vertex individually as exergy supplied to \( v_1 \) and pumping energy needed to transport hot water to this vertex. Product is the quantity of exergy at each vertex.

Analysis of the stationary conditions on a winter day is based on the data described in chapter 3.1. A temperature of water which reaches vertices varies in a significant extent. The biggest temperature change, among the analyzed vertices, occurs in heat supply to \( v_{29} \). The supply water here is 15.4 °C cooler than in \( v_1 \). There are substantial variations in temperatures supplied to different points. PE and RE are calculated for heat supplied to individual points. E.g. to supply 1 kg/s of water from \( v_1 \) to \( v_2 \), 217.9 kW of energy are needed. The heat available to consumers from 1 kg/s of water (product) in \( v_2 \) is 216.2 kW. Energetic efficiency of supplying heat to \( v_2 \) is thus 0.99. The vertex with the lowest energetic efficiency is \( v_{29} \). To supply 1 kg/s of water to it, 254.7 kW of energy are needed. The available heat is 151.8 kW and the energetic efficiency is 0.60. Exergy fuels and exergy products are calculated for individual point in the network. Exergetic efficiencies are also calculated. The benefits of exergy analyses can be seen in separation of exergy destruction and exergy losses in accordance with defined boundary I in chapter 2.2.2. Values of exergy destructions are very low, almost negligible, in comparison to exergy losses. This suggests that measures which would increase exergy destruction and decrease exergy losses could improve the exergy efficiency of heat supply. Exergy destruction in accordance with boundary II and exergy destruction ratio is also calculated (the results are in Table 2).

As discussed above the results of exergy analysis has shown that the operation of the network on the winter day may be far from optimal. The selection of optimal operating parameters for a distribution network is a complex process with possible regulations of supply and return temperatures with combination of water mass-flow rates. Parameter limitations are in the design of a distribution network, consumer equipment and heat generation facilities. Performance of heat generation facilities in dependence of output parameters also plays a key role. Thus optimal parameters are not general and differ in different district heating systems. Heat demands of consumers and the environment is changing during a year or a day. These also affect the optimal parameters. The aim of optimization in this paper is not to select optimal operating parameters, but to present a usage of exergetic analysis in an optimization process.

The ratio between exergy destruction and exergy losses in a distribution network can be increased by increasing the mass flow rate of the water and thus increasing the amount of heat distributed through the network. Optimal mass flow was searched for the distribution network in Fig. 4. Calculation is not based on any real possibilities for increased heat demands of consumers in the system. The purpose is to show the ratio between exergy destruction and exergy losses at the highest exergetic efficiency. Optimal mass flow was searched in series, first for heat supply from \( v_1 \) to \( v_2 \), then from \( v_2 \) to \( v_3 \) and so on until \( v_{40} \). In this procedure mass-flow rate is iteratively increased until the exergetic efficiency is increasing. Because exergetic efficiency is a concave function, the maximum is discovered. Doing this all other parameters from chapter 3.1 are left unchanged. The highest calculated exergetic efficiencies for considered points are at the ratio of exergy destruction and exergy loss 0.34 to 0.37. To achieve it mass flow rates from Table 1 were increased on average for around 300 %. Maximal occurring velocities of water in pipes is 2 m/s. The optimal ratio (\( \dot{E}_D / \dot{E}_L \)) is higher for vertices with lower energetic and exergetic efficiencies. This results show the over dimensioned characteristics of the heat supply lines on the considered winter day and not the technical and physical options for improvement.
Table 2. Energy and exergy analyses results

<table>
<thead>
<tr>
<th>Vertex</th>
<th>Stationary conditions on a winter day</th>
<th>Optimal mass flow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_v$, °C</td>
<td>$e_{RE}$, $\text{kJ/kg}$</td>
</tr>
<tr>
<td>v2</td>
<td>126.3</td>
<td>217.9</td>
</tr>
<tr>
<td>v5</td>
<td>125.4</td>
<td>220.1</td>
</tr>
<tr>
<td>v8</td>
<td>123.9</td>
<td>223.8</td>
</tr>
<tr>
<td>v10</td>
<td>122.8</td>
<td>226.4</td>
</tr>
<tr>
<td>v14</td>
<td>121.5</td>
<td>229.6</td>
</tr>
<tr>
<td>v15</td>
<td>121.1</td>
<td>230.4</td>
</tr>
<tr>
<td>v21</td>
<td>111.2</td>
<td>254.5</td>
</tr>
<tr>
<td>v25</td>
<td>120.3</td>
<td>232.4</td>
</tr>
<tr>
<td>v27</td>
<td>114.4</td>
<td>246.7</td>
</tr>
<tr>
<td>v28</td>
<td>114.0</td>
<td>247.6</td>
</tr>
<tr>
<td>v29</td>
<td>111.1</td>
<td>254.7</td>
</tr>
<tr>
<td>v30</td>
<td>121.2</td>
<td>230.2</td>
</tr>
<tr>
<td>v32</td>
<td>114.0</td>
<td>247.7</td>
</tr>
<tr>
<td>v34</td>
<td>119.6</td>
<td>234.2</td>
</tr>
<tr>
<td>v35</td>
<td>120.4</td>
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<td>222.6</td>
</tr>
<tr>
<td>v40</td>
<td>123.0</td>
<td>225.7</td>
</tr>
</tbody>
</table>
4. Conclusions

In this paper a methodology for an exergy-based analysis of a distribution network in a district heating system is presented. The main differences to other published papers on this subject are in the definition of energetic and exergetic efficiency for a single point in the distribution network and in exergy balance in the form fuel/product. Possibilities for efficiency improvements on different parts of the network can be discovered this way.

Separation of the exergy destruction and exergy losses points out guidelines for exergetic efficiency improvements. The choice of boundaries is important when doing the separation. Low exergy destruction in comparison to exergy losses suggests that with the increase of pumping power on behalf of decrease in heat losses will improve the exergetic efficiency of the distribution network.

Analysis of a part of the distribution network in Šaleška valley has shown large differences in energetic and exergetic efficiencies of heat supply to different points in the network. This part of the distribution network does not include heat exchangers.

Calculated exergy destruction rates on a considered winter day are less than 1 % of the exergy losses in the separate consideration. Accordingly we can conclude that the network is operating below its optimal capacity. The conditions that occur on this day present one of the highest annual heat demands by consumers in the district heating of Šaleška valley. Thus the distribution network, operating with this temperatures and mass-flow rates, is over dimensioned.

The increase of energy transported by individual pipelines, through the mass flow rate increase to optimal values, is searched. Maximal exergetic efficiencies determine the optimal mass flow rates. In separate consideration exergy destruction rates are in the interval 34 to 37 % of exergy loss rates at maximal exergetic efficiencies. They are higher for vertices with lower energetic and exergetic efficiencies.

Nomenclature

\( A \) surface, \( m^2 \)

\( d \) internal diameter, \( m \)

\( \dot{E} \) exergy rate, \( W \)

\( \dot{e} \) specific exergy rate, \( W/\text{kg} \)

\( \dot{E} \) energy rate, \( W \)

\( \dot{e} \) specific energy rate, \( W/\text{kg} \)

\( \dot{h} \) specific enthalpy rate, \( W/\text{kg} \)

\( h \) specific enthalpy, \( J/\text{kg} \)

\( l \) length, \( m \)

\( M \) adjacency matrix

\( \dot{m} \) mass flow rate, \( \text{kg/s} \)

\( p \) pressure, \( \text{bar} \)

\( \dot{Q} \) heat rate, \( W \)

\( \dot{q} \) specific heat rate, \( W/\text{m} \)

\( \dot{s} \) specific entropy rate, \( W/(\text{kgK}) \)

\( T \) temperature

\( U \) overall heat transfer coefficient, \( W/(m^2\text{K}) \)

\( \dot{W} \) pumping power, \( W \)
y  exergy destruction ratio

**Greek symbols**

ε  exergetic efficiency
η  energetic efficiency
ρ  density, kg/m³

**Subscripts and superscripts**

0  thermodynamic environment (reference state)
D  destruction
d  decreased
F  fuel
i  in
L  loss
o  out
P  product
PE  positive effect
RE  resource expended
ret  return
sup  supply
sur  surroundings
w  water

**References**

Abstract:
The paper presents a method of the systems analysis of exergy losses, as well as an example of application in the case of an integrated OFC power plant. The considered system consists of five interconnected modules, among which there also exist feedback relations. For the purpose of modelling an integrated OFC power plant “input-output analysis” was applied. Five main products (corresponding to the given modules) and also five by-products, as well as three supplies delivered entirely from outside are to be distinguished. The basis of the exergy system analysis of an integrated OFC plant is its completed energy balance. The algorithm of the systems analysis of exergy losses is also based on “input-output analysis”. The way of expressing the exergy balance adapted to the convention of “input-output analysis” has been applied. The input exergy (exergy of substance, work, increase of exergy of the source of heat) supplied to given module is the sum of the respective items in the column of the input-output table corresponding to the given module. The output exergy is the exergy of the main product concerning the given module and the exergy of by-products. The difference between the input and the output exergy is the whole exergy loss (internal and external exergy losses) of the considered module. The systems analysis of exergy losses based on “input-output analysis” allows to assess the influence of decreasing the exergy losses in one module on changes of exergy losses in other modules of the integrated OFC plant. The paper presents the system analysis of exergy losses of an exemplary integrated OFC power plant operating using tonnage oxygen with a purity of 95%. Among the analysed five modules the highest relative exergy losses are to be observed in ASU (about 80%). The boiler island is charged with relative exergy losses exceeding 50%. The relative exergy losses in a CPU module amount to about 50%. The steam cycle is characterised by relative exergy losses below 20% and the cooling water system about 5%. The net exergy efficiency of electricity production amounts to 30% in comparison with the energy efficiency of about 34%.

Keywords:
Oxy-fuel combustion, systems analysis, exergy losses, mathematical modelling, input-output analysis.

1. Introduction

A power plant operating in compliance with the Oxy-Fuel Combustion (OFC) technology consists of such modules as boiler island, steam cycle, cooling water system, air separation unit (ASU) and CO₂ purification and compression unit (CPU). Between these modules there exist interbranch connections, some part of which are of feedback character. The interbranch connections become still more complex if process integration is being realised [1]. In an OFC power plant it is possible to integrate both on the thermal side (utilizing the heat from interstage cooling of air and CO₂ compressors) [2] and on the electrical side in the case of pressurized OFC power plant (expansion turbine of nitrogen).

Thus, an integrated OFC power plant is a large energy system, the design of which and also its exploitation ought to be optimised by means of system methods [3,4]. Also the analysis of exergy losses in an integrated OFC power plant requires a system approach [5]. Szargut and Sama state: “consider the influence of the proposed changes in energy management on the exergy losses in
other links of the system” [6]. This means that in a system consisting of many elements, not only the improvement of one of them should be considered, because the decrease of exergy losses in one element may involve in other elements of the system both positive and negative effects. This requirement can be satisfied if the exergy losses are assessed by means of system analysis.

System approach requires that all the balance equations resulting both from the I and II Law of Thermodynamics are considered jointly. In the analysis of large energy systems commonly Leontief’s “input-output analysis” is applied.

The model of energy balance of an integrated OFC power plant is composed of linear equations of the “input-output” type, concerning main products (e.g. live steam, electricity, oxygen) and by-products (e.g. process steam, nitrogen), as well as energy carriers and materials from outside. The coefficients in “input-output” matrices result from the energy characteristics of the energy equipment determined in process models which are usually non-linear. The non-linear characteristics are then approximated by means of the segments of straight lines.

The linear mathematical model of the energy balance is the basis of the system model of exergy losses in an integrated OFC power plant. The input part of the exergy balance are vectors of the consumption of the exergy of the main and by-products, as well as the exergy of the supply from outside (mainly fuels and materials). The output part comprises the vectors of the exergy of main and by-production, as well as exergy losses which are the result of system analysis. The system of direct and indirect interconnections is expressed by the inverse matrix in relation to the “input-output” matrix of the energy balance of main products. From the viewpoint of energy analysis this inverse matrix is the matrix of indices of cumulative energy consumption. This inverse matrix applied in the model of the exergy balance permits to determine the system exergy losses. The suggested system model of exergy analysis will be applied in an integrated OFC power plant.

2. Why system analysis of exergy losses?

The utilization of the limited resources of non-renewable energy ought to comply with the principle of sustainable development. This means rational utilization and warranting ecological security, keeping in mind future generations. Rationalization of the use of energy consists, first of all, in the improvement of the thermodynamic imperfection of phenomena occurring in energy processes. This involves consequently an increased protection of the environment.

Thermodynamic imperfections involve a devaluation of energy (exergy losses). Although, in actual processes this cannot be avoided, they ought to be restricted as far as technically possible and economically justified. Exergy losses may be permitted only in the case when they are indispensable for the reduction of investment outlays. If exergy losses are economically not justified, we have to do with an error from the point of view of the Second Law of Thermodynamics [6]. The elimination of these errors favours the financial effects of the project ensuring most often savings both in exploitation and in the investment outlays. Every design which does not contain any Second Law errors may be considered to be an optimal design [6].

The observance of the twenty practical rules set up by Szargut an Sama [7], referring to previous publications by Sama, Quian and Gaggioli [6], leads to a reduction of the Second Law errors and to a rationalized utilization of energy. Two of these practical rules of thermodynamic imperfections stress the interdependence of thermal processes in the respective elements of energy systems. Any change occurring in one element of the system affects the operation of the other elements. The influence of the suggested energy changes on the losses of exergy should always be taken into account not only in the given considered process but also in the other elements of the system. It should also be kept in mind that by decreasing one exergy loss, no other parallelly occurring exergy loss should increase [7]. In other words, the reduction of the degree of thermodynamic imperfection of energy processes should be assessed by means of systems analysis.
System analysis was formally discovered again just before the Second World War by the biologist Ludwig von Bertalanffy [8]. The first attempt to define the system problem is contained in Aristotle’s philosophy [9]. Before the Second World War (1936) also Leontief’s “input-output analysis” was published, which belongs to the methods of system analysis [10]. This method was applied in the algorithm of systems analysis of exergy losses in an integrated OFC power plant. Wassily Leontief has written about “input-output analysis” [10], “In practical terms, the economic system to which it is applied may be as large as a nation or even the entire world economy, or even a single enterprise” (such a single enterprise is the integrated OFC power plant - the author’s comment). “The advantage of the input-output analysis is that it permits the disentanglement and accurate measurement of the indirect effects” stressed the author of “Input-output economics” [10].

In energy systems many interconnections are feedbacks. The paper [11] provides such an example in a CHP plant with an extraction-condensing turbine. This can be presented more simply by choosing the connections between the boiler and the turbogenerator in the power plant (Fig.1).

![Diagram of the power plant cycle and binary input-output submatrix](image)

If, for example, the production of electric energy is increased, the production of high-pressure steam grows. But this increased production of high-pressure steam leads to a further increase of electric energy production due to its consumption in the boiler (first of all in the coal pulverizer). And again, the demand for high-pressure steam will grow, causing a further increase of the demand for electric energy in the boiler house and so on, and so on due to the existence of the feedback relation between the turbogenerator and the boiler. Therefore, the system approach basing on input-output analysis is necessary. The method of exergy analysis based on a set of the balance equations of exergy of the respective modules of a complex system permits to determine the system exergy losses resulting from the interconnections of energy processes.

In mathematical models of energy systems their specific properties must be taken into account, not like as in Leontief’s classical model [10]. In some energy branches the main production ought to be divided into the basic and peak parts. The basic part of heat production in CHP plants, for instance, is produced in the cogeneration part (heating steam from the outlet of the back-pressure turbine or from the bleed of the extraction-condensing turbine), whereas the peak part of heat production is produced in the hot water boiler [12]. Besides the main production there exists also a by-production which can supplement the main production or be a product not belonging to the set of main products [12]. The amount of by-production in the given energy branch depends on its main production.
3. Linear mathematical model of the energy balance of an integrated OFC power plant

A power plant operating in the oxy-fuel combustion technology consists of such modules as boiler island, steam cycle, cooling water system, air separation unit (ASU) and CO₂ processing unit (CPU) (Fig. 2). Between these modules there exist interbranch connections, which may be described by an "input-output matrix". The connections of the oxy-fuel combustion plant with the environment are described by input and output vectors.

Fig. 2. Simplified block scheme of the Oxy-Fuel Combustion power plant.

The integrated OFC power unit is a system consisting of energy branches (technological modules) connected with each other by interbranch (intermodular) relations. Table 1 presents the system of interbranch connections concerning an oxy-fuel combustion power plant [1]. The energy carriers have been divided into two groups:

I – energy carriers being the main products or by-products of the respective modules of the integrated oxy-fuel combustion power plants,

II – energy carriers supplied from outside (mainly fuels).

Table 1. Input-output table of an integrated OFC power unit

<table>
<thead>
<tr>
<th>Group of energy carriers</th>
<th>Input part</th>
<th>Output part</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Main production</td>
<td>By-production</td>
</tr>
<tr>
<td>First group - I</td>
<td>$\Lambda : G_i$ + 0 + 0</td>
<td>= $\sum_{j=1}^{n} a_{ij}^c G_j$ + $K_i$</td>
</tr>
<tr>
<td>Second group - II</td>
<td>0 + 0</td>
<td>$\Lambda : D_p$</td>
</tr>
</tbody>
</table>

where:
$a^G_{ij}$ - coefficient of the direct consumption of energy carriers,
$a^F_{ij}$ - coefficient of the consumption of by-products,
$a^b_{pi}$ - coefficient of the direct consumption of external supplies of energy carriers,
$f_{ij}$ - coefficient of by-production of energy carriers.

In matrix notation the equation from Table 1 can be presented as:

\[ G + A^G G = K^G, \quad (1) \]
\[ F^G G = A^F G + K^F, \quad (2) \]
\[ D^D = A^D G. \quad (3) \]

Hence, from the set of balance equations concerning the main production of energy carriers we get [1]:

\[ G = (I - A^G)^{-1} K^G, \quad (4) \]

where:
- $G$ - vector of the main production of energy carriers,
- $A^G$ - matrix of the coefficients of the direct consumption of energy carriers,
- $K^G$ - vector of the final production of main products,
- $F^G$ - matrix of the coefficients of by-production not supplementing the main production,
- $A^F$ - matrix of the coefficient of the consumption of by-production,
- $K^F$ - vector of the final production of by-products,
- $D^D$ - vector of external supplies of energy carriers,
- $A^D$ - matrix of the coefficients of the direct consumption of external supplies of energy carriers,
- $I$ - unit matrix.

Equations (1), (2) and (3) describe the mathematical simulation model of an integrated OFC power plant. The input data are in this case $A^G$, $K^G$, $F^G$, $A^F$, $A^D$, $D^D$. The coefficients of the inverse matrix $(I - A^G)^{-1}$ comprise direct and indirect connections existing in the integrated power plant. These coefficients may be called coefficients of cumulative energy consumption for the considered integrated power plant.

The main products corresponding to technological modules are live steam, electricity, cooling water, oxygen and the CO$_2$ product. Besides the mentioned main production, the following by-productions can be distinguished: heat from the interstage cooling system of ASU and CPU, nitrogen from ASU, bottom ash in the boiler island, dust and gypsum in CPU. This production depends strictly on the main production. External supplies are fuel (bituminous coal), raw water (supplied from the municipal system) and limestone for wet flue gas desulphurization.

The boiler was designed for pulverized coal as the main fuel. The parameters of live steam are: $p = 28.4$ MPa, $t = 600$ °C / 620 °C. The steam cycle is based on supercritical conditions, concerning the high- (HP), intermediate- (IP) and low-pressure (LP) part. The CO$_2$ processing unit (CPU) is based on the cryogenic distillation system. ASU is based on cryogenic distillation, producing 95% pure oxygen. The heat of compression from air and CO$_2$ compressors is directly transferred to the cooling-water system.
Table 2. Example of an input-output table (input part)

<table>
<thead>
<tr>
<th>No</th>
<th>Energy carrier or material</th>
<th>Main product</th>
<th>By-production</th>
<th>External supply</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Live steam [MJ]</td>
<td>$G_1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Electricity [MJ]</td>
<td>$G_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Cooling water [Mg]</td>
<td>$G_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Oxygen [Mg]</td>
<td>$G_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>CO$_2$ product [Mg]</td>
<td>$G_5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Waste heat [MJ]</td>
<td></td>
<td>$f_{61}G_1$</td>
<td>$f_{62}G_2$</td>
</tr>
<tr>
<td>7</td>
<td>Nitrogen [Mg]</td>
<td></td>
<td></td>
<td>$f_{74}G_4$</td>
</tr>
<tr>
<td>8</td>
<td>Bottom ash [Mg]</td>
<td></td>
<td>$f_{81}G_1$</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Dust [Mg]</td>
<td></td>
<td></td>
<td>$f_{92}G_5$</td>
</tr>
<tr>
<td>10</td>
<td>Gypsum [Mg]</td>
<td></td>
<td></td>
<td>$f_{103}G_5$</td>
</tr>
<tr>
<td>11</td>
<td>Bituminous coal [MJ]</td>
<td></td>
<td></td>
<td>$D_{11}$</td>
</tr>
<tr>
<td>12</td>
<td>Raw water [Mg]</td>
<td></td>
<td></td>
<td>$D_{12}$</td>
</tr>
<tr>
<td>13</td>
<td>Limestone [Mg]</td>
<td></td>
<td></td>
<td>$D_{13}$</td>
</tr>
</tbody>
</table>

Table 3. Example of an input-output table (output part)

<table>
<thead>
<tr>
<th>No</th>
<th>Energy carrier or material</th>
<th>Interbranch flows</th>
<th>Final product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Live steam [MJ]</td>
<td>$a_{12}^G G_2$</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Electricity [MJ]</td>
<td>$a_{22}^G G_2$</td>
<td>$a_{23}^G G_3$</td>
</tr>
<tr>
<td>3</td>
<td>Cooling water [Mg]</td>
<td>$a_{32}^G G_2$</td>
<td>$a_{34}^G G_4$</td>
</tr>
<tr>
<td>4</td>
<td>Oxygen [Mg]</td>
<td>$a_{41}^G G_1$</td>
<td>$a_{45}^G G_5$</td>
</tr>
<tr>
<td>5</td>
<td>CO$_2$ product [Mg]</td>
<td></td>
<td>$K_5$</td>
</tr>
<tr>
<td>6</td>
<td>Waste heat [MJ]</td>
<td></td>
<td>$a_{63}^F G_3$</td>
</tr>
<tr>
<td>7</td>
<td>Nitrogen [Mg]</td>
<td></td>
<td>$K_7$</td>
</tr>
<tr>
<td>8</td>
<td>Bottom ash [Mg]</td>
<td></td>
<td>$K_8$</td>
</tr>
<tr>
<td>9</td>
<td>Dust [Mg]</td>
<td></td>
<td>$K_9$</td>
</tr>
<tr>
<td>10</td>
<td>Gypsum [Mg]</td>
<td></td>
<td>$K_{10}$</td>
</tr>
<tr>
<td>11</td>
<td>Bituminous coal [MJ]</td>
<td>$a_{111}^D G_1$</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Raw water [Mg]</td>
<td>$a_{123}^D G_3$</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Limestone [Mg]</td>
<td></td>
<td>$a_{135}^D G_5$</td>
</tr>
</tbody>
</table>

In Tables 2 and 3 the input part and the output part have been presented concerning the “input-output table” of the considered integrated OFC power plant (Fig 1.). Three groups of energy carriers are to be distinguished. The fundamental part of the “input-output table” comprises energy carriers...
or materials (e.g., CO$_2$ product) corresponding to the main products of basic technological modules of the integrated OFC power plant. As far as the first group of energy carriers and materials is concerned, the row 5 is characteristic for the CO$_2$ product, which is a typical output element with only one-sided connections with other energy carriers. That means that it is the consumer of energy carriers, but it is not consumed in other branches.

As we can see in Table 3, in the main production interbranch flows occur in the case of the first four energy carriers. From among these electricity is consumed in all the five modules (branches). For instance $a_{51}^{G_1}$ denotes the consumption of electricity for the production of live steam and $a_{52}^{G_2}$ the consumption of live steam for the production of electricity. Both these elements, situated on either side of the main diagonal, indicate a connection of feedback character. The main production is accompanied by six by-products, e.g., $f_{65}G_4$ and $f_{66}G_5$ denote waste heat removed from the steam cycle, ASU and CPU, respectively. These streams are passed to the cooling water system - $a_{65}^{G_3}$. Flue gases ($f_{64}G_3$) are also treated as waste heat, although they are passed to the CPU unit - $a_{65}^{G_3}$. The analyzed system is fed by three external supplies, e.g. the supply of coal feeding the boiler - $a_{11}^{G_1}$. The supply of raw water (after its conditioning) supplementing the water cooling system - $a_{12,3}^{G_3}$. Limestone for wet flue gas desulphurization is delivered to CPU - $a_{13,5}^{D_3}$.

### 4. Calculation algorithms of system exergy losses

The calculation algorithms of system exergy losses are based on “input-output analysis”. Figure 3 illustrates the diagram of the exergy balance concerning the module (energy branch) “$j$” formulated in compliance with Table 1 (Section 3).

![Fig. 3. Calculation diagram of exergy losses.](image)

The set of exergy balances concerning all the modules takes the following form:

$$
\sum_{i=1}^{n} a_{ij}^{G_i} b_{G_i} + \sum_{l=n+1}^{m} a_{lj}^{G_j} b_{F_l} + \sum_{p=m+1}^{s} a_{pj}^{D_p} b_{D_p} = G_j b_{G_j} + \sum_{l=n+1}^{m} f_{lj}^G b_{F_l} + \delta B_{in,j} \quad (5)
$$

where:

- $b_{G_i}, b_{G_j}$ - specific exergy of the “$i$-th” or the “$j$-th” main product,
- $b_{F_l}$ - specific exergy of the “$l$-th” by-product,
- $b_{D_p}$ - specific exergy of the “$p$-th” external supply of energy carrier,
- $\delta B_{in,j}$ - exergy losses concerning the “$j$-th”.

In matrix notation of the set of equations (5) looks as follows:

$$
\begin{align*}
\sum_{i=1}^{n} a_{ij}^{G_i} b_{G_i} + \sum_{l=n+1}^{m} a_{lj}^{G_j} b_{F_l} + \sum_{p=m+1}^{s} a_{pj}^{D_p} b_{D_p} &= G_j b_{G_j} + \sum_{l=n+1}^{m} f_{lj}^G b_{F_l} + \delta B_{in,j} \\
\end{align*}
$$

344
\[
\begin{align*}
\left( A_G G^d \right)^T b_G + \left( A_F G^d \right)^T b_F + \left( A_D G^d \right)^T b_D &= G^d b_G + \left( FG^d \right)^T b_F + \delta B \\
\text{Hence:}
\end{align*}
\]
\[
\delta B = \left( \left( A_G G^d \right)^T - G^d \right) b_G + \left( \left( A_F G^d \right)^T - \left( FG^d \right)^T \right) b_F + \left( A_D G^d \right)^T b_D
\]

where:

- \( b_G \) - column-vector of specific exergy of main products,
- \( b_F \) - column-vector of specific exergy of by-products,
- \( b_D \) - column-vector of specific exergy of external supplies of energy carriers.

The column vector \( G \) is calculated from (4) basing on the inverse input-output matrix. The indices \( T \) and \( d \) denote, respectively, the transposed matrix and the formation of the diagonal matrix from the column vector.

The notation of the balance equations of exergy, by means of which the exergy losses can be determined, are of a generalized character. The work and increase or decrease of the exergy of heat sources are not distinguished as separate terms in the balance equations. The symbols:

- \( a_{ij} G_j b_{G_i} \),
- \( a_{ij} G_j b_{F_i} \),
- \( a_{ij} G_j b_{D_p} \)

denote the input exergy delivered to the module “j” (exergy of the substance, decrease of the exergy of the heat source, driving work).

Similarly, the symbols:

- \( G_j b_{G_i} \),
- \( f_{ij} G_j b_{F_i} \)

are to be understood as output exergy (exergy of the main product and by-product, the increase of the exergy of heat sources or output work).

The chemical exergy of the homogenous substance “i” (with a known chemical formula) is determined basing on the tables of the normal chemical exergy [13] (corrections due to small differences between the normal and ambient temperature and the deviation of concentration in the actual environment from normal concentrations have been neglected):

\[
B_{chi} = a_{ij} G_j b_{cha}
\]

where \( b_{cha} \) denotes the specific chemical exergy of homogenous “i-th” substance.

In the case of gases, for which the set of reference substances is the component of the atmospheric air (e.g. tonnage oxygen) the chemical exergy is calculated according to the equation:

\[
B_{chi} = a_{ij} G_j (MR) T_a \sum_i z_k \ln \frac{z_k}{z_{ka}}
\]

where:

- \( (MR) \) - universal gas constant,
- \( T_a \) - ambient temperature,
- \( z_k, z_{ka} \) - molar fraction of the “k-th” component in the considered mixture and in atmospheric air.

As far as solid fuels are concerned, the empirical formula is used [13]:
\[ B_{chi} = a_{ij} G_j \left[ (LHV + r_n w) \left( 1.0437 + 0.1896 \frac{h}{c} + 0.0617 \frac{o}{c} + 0.0428 \frac{n}{c} \right) + (b_{chls} - LHV) s + w b_{chw} + pb_{chp} \right] \] (10)

where:
- \( LHV \) - lower heating value of solid fuel,
- \( r_n \) - specific heat of evaporation,
- \( w \) - mass fracture of moisture,
- \( c, h, o, n, s, p \) - mass fractions of carbon, hydrogen, oxygen, nitrogen, sulphur and ash,
- \( b_{chls}, LHV_s \) - specific exergy and lower heating value of sulphur,
- \( b_{chp} \) - specific exergy of ash.

The presented calculation algorithms of system exergy losses can be used to analyze the influence of process changes in the respective modules of the integrated OFC power plant on the system exergy losses.

If the elements of the matrix \( A_F, F, A_D \) are changed, changes in the system exergy losses may be expressed as follows:

\[
\Delta'(\delta B) = \left( (A_F G^d)^T - (FG^d)^T \right)^T \left( (A_F G^d)^T - (FG^d)^T \right) b_F + \left( (A_D G^d)^T - (A_D G^d)^T \right) b_D
\]

(11)

In such a case the inverse matrix \((I - A_G)^{-1}\), whose elements express both direct and indirect interconnections, remains unchanged.

In the case of a process change affecting changes in the values of the elements of the matrix \( A_G \) a new inverse matrix must be determined and a new vector \( G \) must be calculated. Then the changes of system exergy losses are expressed by the equation:

\[
\Delta''(\delta B) = \left( (A_G G^d)^T - G^d \right)^T \left( (A_G G^d)^T - G^d \right) b_G +
\]

\[
+ \left( (A_F G^d)^T - (FG^d)^T \right)^T \left( (A_F G^d)^T - (FG^d)^T \right) b_F + \left( (A_D G^d)^T - (A_D G^d)^T \right) b_D
\]

(12)

The apostrophes "'" and "'" denote the state after and before the process changes, respectively.

5. Examples of applications of the system analysis of exergy losses

The mathematical model of the integrated OFC power plant described in (1), (2), (3) allows to strike an energy balance. The set of equations described by (5) permits to assess the exergy system losses. Basing on these equations and on the data base concerning the operation of an integrated OFC power plant with a purity of oxygen amounting to 95%, the exergy losses (internal and external ones) concerning the five modules have been investigated. The net exergy efficiency of the integrated OFC unit has been calculated and compared with the net energy efficiency.

The process analyses were carried out basing on the Thermoflex program, by means of which the respective modules of the integrated OFC unit have been modeled. These researches are run within the frame of the strategic project [14]. The results presented in this paper have been achieved in the course of the first tests of applying the Thermoflex program in process investigations. This paper presents possibilities of implementing the system approach in exergy analysis basing on an integrated OFC power plant.

Table 4 presents an example of “input-output” matrices \( A_G \) and \( F_G \) expressing respectively the coefficients of unit consumption of main product, as well as coefficients of the by-production of energy carriers and materials.
Table 4. “Input-output” matrices $A_G$ and $F_G$

$$A_G = \begin{bmatrix} 0 & 1.9582 & 0 & 0 & 0 \\ 0.0226 & 0.0484 & 0.1124 & 603.59 & 519.34 \\ 0 & 0.0233 & 0 & 8.4313 & 30.285 \\ 0.0001 & 0 & 0 & 0 & 0.0083 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$F_G = \begin{bmatrix} 0.000468 & 0.0233 & 0 & 8.7051 & 30.559 \\ 0 & 0 & 0 & 3.1482 & 0 \\ 9.21 \cdot 10^{-07} & 0 & 0 & 0 & 0.0369 \\ 0 & 0 & 0 & 0 & 0.0287 \end{bmatrix}$$

As has already been mentioned before line 5 of the matrix $A_G$ contains merely 0 elements, which proves that the CO$_2$-product is an output element.

An exemplary exergy balance concerning ASU takes the following form:

$$a_{24}^G G_4 b_2 + a_{34}^G G_4 b_3 = G_4 b_4 + f_6 G_3 b_6 + f_7 G_4 b_7 + \delta B_{in}$$ (13)

hence, the sum of internal and external exergy losses is:

$$\delta B_{in} + \delta B_{ex} = a_{24}^{G} G_4 b_2 - G_4 b_4$$ (14)

or the entire relative loss in relation to driving exergy:

$$\frac{\delta B_{in} + \delta B_{ex}}{B_{drive}} = 1 - \frac{b_4}{a_{24}^G b_2}$$ (15)

where:

- $a_{24}^G G_4 b_2$ - electric exergy (energy) - driving exergy,
- $a_{34}^G G_4 b_3$ - exergy of cooling water,
- $G_4 b_4$ - exergy of oxygen,
- $f_6 G_3 b_6$ - exergy of water heated in interstage cooling,
- $f_7 G_4 b_7$ - exergy of nitrogen,
- $\delta B_{in}$ - internal exergy loss,
- $\delta B_{ex}$ - external exergy loss,
- $B_{drive}$ - driving exergy.
Figure 4 presents the relative exergy losses in the particular modules of the integrated OFC power plant. In each considered module the sum of internal and external exergy losses was determined basing on the results of the exergy balance prepared in compliance with the “input-output” model. Thus, both the direct and indirect interconnections between the respective modules constituting the integrated OFC power plant may be taken into account. Quantitatively these properties are expressed by the elements of the inverse matrix \((I - A_G)^{-1}\) (Eq. 4). The sum of internal and external exergy losses corresponds generally to the driving exergy of the respective modules. An exception is the module “cooling water system”, in which, due to the peculiarity of the cooling tower, the relative exergy losses are determined corresponding to the amount of heat given off by the cooling water [15]. The highest relative exergy losses are to be observed in ASU, where they reach almost 80%. This proves a large thermodynamic imperfection of ASU, particularly in the case when nitrogen is not utilized. The second highest relative exergy losses occur in the boiler island (above 50%), then in the CPU (about 50%) and steam cycle (below 20%). In the cooling water system the exergy losses corresponding to the heat are about 5%.

Figure 5. The net energy and exergy efficiencies of an integrated OFC power plant
Figure 5 presents the energy and exergy efficiency of an integrated OFC power plant. The net exergy efficiency is defined as follows:

\[ \eta_{B'} = \frac{K_2 b_2}{a_{11} G_1 b_{11}}, \]  

(16)

where \( K_2 \) denotes the final production of electricity.

Paper [16] determines net exergy efficiency of an oxy-combustion system assuming also CO\(_2\) to be a product, viz. 37.13%. For the seek of comparison also the net exergy efficiency of the analysed system was calculated taking into account CO\(_2\) as a product. The obtained comparative result was 38.4%.

6. Conclusions

The rationalization of utilizing the energy is one of the main factors in the realisation of sustainable development. First of all, it depends on the improvement of the thermodynamic imperfections of phenomena occurring in energy processes. Thermodynamic imperfections involve exergy losses. Although in actual processes they are inevitable, they ought to be restricted as much as technically possible and economically justified.

In large-scale systems, e.g. in an integrated OFC power plant, it should be kept in mind that a decrease of exergy losses in one element of the system may involve exergy losses in other elements of the system due to existing interconnections, some part of which are of feedback character. Therefore the application of system approach is in such an analysis indispensable. A convenient tool is the “input-output analysis”.

For the considered integrated OFC power plant the investigation concerned relative exergy losses. Systems analysis of exergy losses has proved that the highest relative exergy losses (related to driving exergy) occur in ASU, amounting to about 80%. The boiler island is charged with relative exergy losses of more than 50%. The relative exergy losses in a CPU module are about 50%. The steam cycle is also characterised by relative exergy losses below 20%, and the cooling water system by about 5%.

The net exergy efficiency of electricity production amounts to about 30% in comparison with the energy efficiency of about 34%.

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Nomenclature

Main symbols
- \( A \) matrix of the coefficients of the consumption of energy carriers and materials
- \( a_{ij} \) coefficient of consumption of energy carriers and materials
- \( B \) exergy
- \( b \) column-vector of specific exergy
- \( b \) specific exergy
- \( D \) vector of external supplies
- \( D \) external supply
\( \mathbf{F} \) matrix of the coefficients of the by-production

\( f_{ij} \) coefficient of by-production of energy carriers or materials

\( \mathbf{G} \) column vector of the main production

\( G \) main product

\( \mathbf{I} \) unit matrix

\( \mathbf{K} \) column vector of the final production

\( K \) final product

\( p \) pressure, MPa

\( T \) temperature, K

**Greek symbols**

\( \eta \) efficiency

\( \delta \) losses

**Subscripts and superscripts**

\( a \) ambient

\( D, D \) external supply

\( ex \) external

\( ch \) chemical

\( F, F \) by-product

\( G, G \) main product

\( in \) internal

**Abbreviations**

ASU Air Separation Unit

CPU CO\(_2\) Processing Unit (CO\(_2\) purification and compression unit)

OFC Oxy-Fuel Combustion

**References**


What is the cost of losing irreversibly the mineral capital on Earth?

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Abstract:
The exergy replacement cost is presented in this paper as a tool for assessing abiotic resource depletion. Each time we extract minerals from the mines, the deposits become depleted in quantity and grade. As a consequence, more energy is required for the extraction of the next ton of material. The exergy and exergy replacement costs provide a measure for quantifying this degradation, which is systematically being ignored in conventional accounting systems. Hence, this approach allows performing an absolute Life Cycle Analysis, by including a new stage in the accounting: namely the grave to cradle stage. In this methodology, the “cradle” is the state of the mineral deposits at which they are currently found. The “grave” is assumed as being a hypothetical Earth with the absence of concentrated mineral resources and fossil fuels. This degraded planet named as “Thanatia” is the starting point for the assessment of abiotic resource depletion. The exergy measured from Thanatia gives a measure of the quality of the resource. It constitutes a universal, objective and useful tool for classifying resources according to their depletion states.

As the method provides values in energy units, the annual exergy decrease in the mineral endowment of the planet can now take into account the fossil fuel’s exergy plus the nonfuel mineral bonus lost. The results obtained show that the useful energy that man saves thanks to the existence of mineral deposits accounts for about 32% of the whole energy stages. Furthermore, it is in the same order of magnitude as the yearly loss of coal, oil or natural gas.

Keywords:
Exergy, mineral capital, cost, LCA, Thanatia

1. Introduction

Conventional economics only accounts for the energy required in the extraction and refining processes of minerals. Nevertheless a fair accountability of resources should also take into account the use and the decrease of the non-fuel mineral capital endowment. The latter, and as opposed to fossil fuels, do not produce energy, but require huge amounts of energy for their extraction, beneficiation, refining and smelting processes. That energy is only lost when the obtained materials are dispersed. In such a case, more minerals need to be extracted from the Earth and this time with even more energy, as the ore grade decreases with extraction. Furthermore, the environmental and eventually the social impact will increase as well.

Hence, if no serious recycling measures are taken, the Earth will be gradually transformed by man into a depleted state with the absence of concentrated mineral resources. This is a consequence of the Second Law of Thermodynamics. In previous papers, we have described and modeled this end of the planet, which we have called “Thanatia” or the “Crepuscular Earth” [1, 2]. In a hopefully very distant future, there will be no concentrated mineral deposits from which to extract raw-materials. We will either need to obtain them from the bedrock, which is extremely costly, or we will have to recycle every single material used. If we want to avoid this situation, we have to include in the accountability an additional stage: the grave to cradle approach. The latter should
account for the gradual decrease of the concentrated mineral deposits, which will be unavailable for future generations.

It has been argued that the methods for assessing resource depletion in LCA must come from Thermodynamics and must take into account the Second Law of Thermodynamics [3]. We commonly admit that the Second Law plays a central role in the message of Ecological Sciences and Technology.

Energy and Life Cycle Analyses are techniques based on material and energy flow analyses, which in turn are based on Thermodynamics. They do not need rigorous definitions of energy and still they are quite useful and far reaching. On the contrary, i.e., fixing in the Thermodynamic realm a concept well established in Energy and LC Analyses is a matter of precision. For many unrefined analyses we may use both the energy and embodied energy concepts as substitutes of exergy and exergy cost concepts respectively, but in fact, in no way they are synonyms. Both exergy and exergy cost require precise definitions. As is well known, LCA results are relative to the chosen system’s boundary.

Nowadays, no absolute LCA values exist for a given good or service. Notwithstanding that, suppose we start our analysis from a hypothetical cradle in which all the commercial minerals and fossil fuels have been depleted, i.e., Thanatia. This crepuscular planet serves us both as a boundary limit and as a reference environment good enough for calculating the exergy and the exergy costs of any commodity at the industry gate. Theoretically speaking, this could be eventually the only way to get absolute LCA values, by converging LCA with Second Law Analysis using the crepuscular planet as a reference environment.

From now on, Thanatia may become the starting point for the assessment of abiotic resource depletion. The exergy measured from the Crepuscular Earth gives a measure of the quality of the resource and constitutes a universal, objective and useful tool for classifying resources according to their depletion states. Presented over time, exergy can give an indication of the speed at which degradation is occurring. However we must state that even considering a consequent baseline, exergy is still insufficient for realistically quantifying resource depletion and we should additionally resort to the exergy costs.

Hence, from the exergoeological point of view, we propose to introduce a new stage in the LCA’s cradle to grave methodology, namely the grave to cradle approach, as depicted in Fig. 4. It is important to close the whole material’s cycle, as stated by [4] in their book Cradle to Cradle.

2. Methodology

Chapman and Roberts [5] report that in the mining and concentrating stages the fuel is proportional to the quantity of ore processed. In the smelting and refining stages, the fuel is proportional to the quantity of metal produced. Hence, if we start mining from Thanatia, in principle only the fuel required in the mining and concentrating stages will be aected. Bearing in mind this fact, we will now develop the methodology required for assessing the exergy replacement costs of minerals. As explained in [6], the exergy of a mineral resource has at least 2 components (neglecting the cohesion exergy [7]): one associated to its chemical composition and one associated to its concentration.

Hence, the total exergy ($b_t$), representing the minimum exergy required for obtaining the resource from the reference to the initial conditions in the mineral deposit (steps R#0 $\rightarrow$ R#1) in Fig. 4, is calculated as the sum of the chemical $b_{chi}$\(^1\) and concentration $b_{ci}$ exergy components.

\(^1\) The chemical exergy is calculated according to the well known formula proposed by Szargut [8].
where \( R \) is the universal gas constant (8.314 kJ/kmole K), \( T^0 \) is the standard ambient temperature (298.15 K) and \( x \) is the mass concentration of the substance.

The calculation of the concentration exergy implies to know the ore grade which is the average mineral concentration in a mine \( x_m \) as well as the average concentration in the Earth’s crust (in the Crepuscular Earth) \( x_c \). The value of \( x \) in 2 is replaced by \( x_c \) or \( x_m \) to obtain their respective exergies, whilst the difference between them \( \Delta b_c(x_c \rightarrow x_m) \) represents the minimum energy (exergy) required to form the mineral from the concentration in the Earth’s crust to the concentration in the mineral deposits.

\[
\Delta b_c(x_c \rightarrow x_m) = b_c(x = x_c) - b_c(x = x_m)
\]

Hence, even if we use the term \( b_{ci} \) for simplification purposes, it is rather \( \Delta b_c(x_c \rightarrow x_m) \) the correct notation.

On the other hand, the exergy replacement cost is defined as the total exergy required to mine and concentrate the mineral resources from the Crepuscular Earth, with the available technologies. Therefore, these are not absolute and universal values, as opposed to property exergy. The exergy costs are a function of the ore grades, extraction and separation technologies, which in turn vary with time, with the type of mineral analyzed, and with our ability to extract it, i.e. with its learning curve. The exergy costs \( b^*_c \) of the resource commonly have two contributions, its chemical cost \((k_{ch} \cdot b_{ch})\), accounting for the chemical production processes of the substance, and its concentration cost \((k_c \cdot b_{ci})\), accounting for the concentration processes.

\[
b^*_i = k_{ch} \cdot b_{ch} + k_c \cdot b_{ci} = b^*_{ch} + b^*_c
\]

Variable \( k \) (dimensionless) represents the unit exergy cost of a mineral. It is defined as the relationship between the energy invested in the real obtaining process \( (E_{X_m \rightarrow X_r}) \) for mining and concentrating the mineral, and the minimum energy (exergy) required if the process from the ore \( x_m \) to the conditions before the smelting and refining processes take place \( x_r (\Delta b_{X_m \rightarrow X_r}) \).

\[
k = \frac{E(x_m \rightarrow x_r)}{\Delta b_{X_m \rightarrow X_r}}
\]

The chemical exergy cost \( b^*_{ch} \) of the resource comes into play when the reference chosen does not contain the substance under consideration. Since the Crepuscular Earth contains in principle most of the minerals found in the crust, the chemical exergy will not appear. Therefore we will mainly focus on the concentration exergy replacement cost \( b^*_c \) and accordingly the unit concentration costs \( k_c \).

Since the energy required for mining is a function of the ore grade of the mine and of the technology used, so is the unit exergy cost (Eq. 6). As [9] states, both variables have an opposite effect on the energy used. The lower the ore grade, the more energy is required for mining. On the contrary, technological development usually improves the efficiency of mining processes and hence, decreases the energy consumption. The latter will be discussed in more detail in the next section.

\[
k = k(x, t)
\]
The temporal function $k$ is only definable for the past and for each particular mineral. It is therefore difficult to extrapolate it towards the future for the practical impossibility to predict changes in the scientific and technological knowledge that will eventually appear. The second problem with $k$ is that it is not a continuous function. The technology applied can also vary with the concentration ranges of a particular deposit. And in turn, each mining technique (i.e. underground or open-pit mining), has a particular effect on the energy consumption due to different factors such as ore grade, grinding size, nature, depth and processing route. These factors have been analyzed for different commodities like copper and nickel [10], aluminium, iron and copper [11] and nickel laterites through the life cycle assessment methodology [12].

Bearing in mind these limitations and the kind of data available for mining (which is usually very scarce) we will assume that the same technology is applied for the range of concentration between the ore grade $x_m$ in the mine and the pre-smelting and refining grade $x_r$, than between the dispersed state of the crepuscular crust $x_c$ and $x_m$. For that purpose, we will analyze the average energy vs. ore grade trends for different minerals, calculate the corresponding unit exergy cost values, and extrapolate them to ore grades equal to those of the Crepuscular Earth.

**Figure 1. Calculation procedure for obtaining the mineral exergy bonus of a substance**

Summarizing, the first step in obtaining the unit exergy cost for the commodities analyzed is to obtain their real energy consumptions in the mining and concentrating processes (going from $x_m$ to $x_r$) as a function of the ore grade ($x_m$). This information can be obtained from data published in the literature. In a parallel way, the theoretical exergy of the same process is calculated as the difference in concentration exergy (Eq. 2) when $x = x_m$ and $x = x_r$. Finally, the unit exergy costs are calculated...
with Eq. 5 as a function of the ore grade. The latter can be extrapolated to obtain the unit costs at the crepuscular grade $x_c$, which will eventually serve for calculating the exergy replacement costs of the mineral wealth on Earth with Eq. 4. The values used for the crepuscular grade are those $x_c$ obtained in [13]. Average values for $x_m$ have been obtained from the study of [14]. This procedure is depicted in Fig. 1.

Energy consumption values as a function of the ore grade are difficult to find. Very little studies compile these tendencies. Relevant works about this issue are those of [15, 16, 17] or [10]. Chapman and Roberts [5] proposed a general theoretical formula to describe the tendencies of the energy consumptions for metals mining. The latter estimates the energy consumption as a function of two components: 1) the energy used in mining and concentrating the ores, which is inversely proportional to the ore grade and 2) the energy used in smelting and refining.

Following [5], we could make the approximation that the energy required in the mining and concentration processes can be assumed as a constant divided by the ore grade. Note that the corresponding curve derived from this expression is similar to the curve derived from Fig. 2, i.e. as the ore grade tends to zero, the energy required to mining tends to infinity. With this very rough approximation, we could theoretically calculate the energy required in this step for each value of $x_m$. Obviously the results obtained through this approach are very questionable since the energy consumption as a function of the ore grade does not necessarily follow the path of $x_m^{-1}$, nor the technologies for all ranges of $x_m$ must be the same. A more precise evaluation would require more research and compilation efforts of real data sets from companies in the mining industry like those performed by [15] or [10]. Empirical data of energy consumption as a function of the ore grade suggest relationships varying from $x_m^{-0.2}$ to $x_m^{-0.9}$. Hence, for the calculations, it is preferable to work with empirical data of energy vs. ore grade.

Unfortunately it is very uncommon to find data for most of the commodities and we need to resort to approximations.

### 3. The exergy bonus of the minerals on Earth

With the formulas described above and a comprehensive bibliographical search about mineral energy consumption, we can now make an initial assessment of the exergy bonus of the main produced minerals.

Only for five minerals gold, copper, nickel, cobalt and uranium, we could find empirical data of the energy for mining and concentration processes as a function of the ore grade $E(x_m)$ [15, 16, 18, 12]. For the rest of the commodities where no empirical data was found, it has been assumed that the general formula applying for the energy consumption as a function of the ore grade follows the exponential curve given by Eq. 7:

$$E(x_m) = A \cdot x_m^{0.5} \ [x_m, \text{metal concentration \%}]$$  \hspace{1cm} (7)

Coefficient $A$ is determined for each mineral since we know average ore grades $x_m$ and the energy required for concentrating and extracting the mineral at that grade $E(x_m)$. The value of $E(x_m)$ for each commodity is obtained from different bibliographical sources [19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34] It should be noted that $x_m$ values are expressed in Eq. 7 as mass percentage of the element under consideration.

The latter is a very rough approximation and it is derived observing the trends for other commodities where empirical values are available. As stated before, empirical data of energy consumption as a function of the ore grade suggest relationships varying from $x_m^{-0.2}$ to $x_m^{-0.9}$. 

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We have now all the ingredients required for assessing the exergy replacement costs of the minerals analyzed. This is done with the procedure shown in Fig. 1. Table 3 shows a summary of the replacement, mining & concentration and refining costs of the minerals considered. The exergy replacement costs of the considered deposit is expressed as “Bonus” in the table. The crustal, average mineral concentration of the deposits and average grade before the refining stage are represented by $x_c$, $x_m$ and $x_r$, respectively. For those substances where no data was found concerning average refining grades, we have assumed a value of $x_r = 0.9$. The energy consumption trend as a function of the ore grade $E(x_m)$ requires that the ore grade is expressed in mass percentage of the metal considered if not otherwise specified. With Eq. 5, the unit exergy replacement costs $k(x_c)$ and $k(x_m)$ are obtained, assuming that the same energy trend applies for the whole concentration grade (from $x_c$ to $x_r$). Finally, the mineral bonus is obtained with Eq. 4. As stated before, the bonus represents the natural exergy of the deposit which is gradually being lost when the mine is exploited (replacement costs). To the latter, we have to add the conventional mining & concentration and refining costs presented in the table. From Table 3 we can extract some conclusions.

The empirical data found for minerals gold, copper, nickel, cobalt and uranium suggest that the energy required for mining follows an exponential growth with the ore grade. This observed fact which is in accordance with the Second Law of Thermodynamics, has allowed us to make a general approximation of the exponential energy trend with the ore grade for the rest of minerals where no empirical data was available.

As was explained previously, unit exergy costs are calculated as the ratio between the real energy required for mining and concentrating a substance and the minimum thermodynamic energy (exergy) required to achieve the same process. This means that they provide a measure for the irreversibility (or technological ignorance) of the process. The closer is the value of $k$ to 1, the less irreversible is the process and hence, less energy is required. But $k$ is also a function of the ore grade. The smaller the ore grade, the greater the unit exergy cost of the mineral.

For instance, gold has the highest $k(x = x_m)$ unit exergy cost values associated to the deposits of the metals analyzed in this work, attributable to its low concentration in mines and the consequent amount of energy needed to concentrate it. Besides, the actual ore grade in mines is close to that in Crepuscular Earth’s crust. The opposite examples are silicon or lime which have a lower $k(x = x_m)$ value ascribed to their actual high ore grade in mines.

But the state of technology plays also an important role. This fact is highlighted with aluminium. Even if its ore grade is similar to that of chromium or manganese, the elevated value of $k(x = x_m)$ is an indicator of the significant irreversibility of the production process. The same thing happens with tantalum, which has a high unit exergy cost value compared to other minerals with similar ore grades such as tin or tungsten ( wolfram). This can be attributed to the elevated energy intensity in the mining and concentration steps of tantalum.

A particular case is that of nickel and its ores. Historically, the metal was likely obtained from sulphide ores due to the major energy requirement of laterites in the refining process. Nevertheless, more Ni resources are in the form of laterites than of sulphides (around 60% for laterite ores vs. 40% for sulphide ores). But focusing only in the concentration energy, sulphide ores have larger concentration requirements than lateritic ores, as revealed by the larger unit exergy costs.

Of special interest is the value of $k(x = x_m)$. The latter multiplied by the minimum exergy required to concentrate the mineral from $x_c$ to $x_m$ represents the amount of energy required to mine and concentrate a substance from the bedrock (Crepuscular Earth) to the current conditions in the mineral deposits and provides a measure of the mineral exergy bonus on Earth. The value of the

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2 Here, only the concentration term is considered since Thanatia contains all considered minerals but at a lower concentration. This means that there would be no need to produce them chemically as they are already available with the same chemical structure.
crepuscular unit exergy cost of the different minerals is always greater than that of the current mineral deposits. And the difference increases generally with the separation between the crepuscular grade and the average grade in the deposits. For instance, the crepuscular $k$-value of silicon, lime or titanium is in the same order of magnitude than the mine $k$-value, because their average ore grades are close to those of the Crepuscular Earth. The opposite happens with antimony, bismuth or tantalum, which have a very small crepuscular grade compared to current average ore grades, therefore its crepuscular $k$-value is considerably much larger compared to their unit exergy cost when the average ore grade in the mines are taken into account.

Considering all these facts, the exergy bonus provides hints about which are those minerals that would be difficult to replace after complete dispersion. Extracting and dispersing a mineral with a great exergy bonus implies losing irreversibly a natural capital that mankind could barely replace and if so, with huge amounts of energy. The minerals with the highest exergy replacement costs according to our calculations are gold, tantalum, mercury, silver, cobalt, cadmium or tungsten. This means that a good management of the latter metals becomes especially critical.

It should be stated that the values obtained are first assessments. Important assumptions have been made, such as assuming that the same technology is applied for the whole range of grades analyzed, including the crepuscular ore grade. One of the major limitations found is the lack of real data over time. So estimation of future trends of this issue without real and reliable information becomes subjective. Therefore, the results and data provided are an attempt to afford indicators based on physical facts rather than on subjective market policies for identifying challenges and opportunities in the mining sector and should not be taken as final and closed.

4. The decrease of the mineral capital endowment due to rawmaterial production

The method outlined in this study could be used to assess both the mineral capital endowment of the Earth’s crust and its yearly depletion due to mining. However some additional remarks need to be done. The mining process does not imply an immediate loss of the mineral exergy bonus of the material itself. On the contrary, once extracted, it is elevated from R#1 to R#2 through further concentration and refining processes. The same happens when the material goes to landfills (R#2 to R#3). We only lose this bonus when materials cannot be recovered again, i.e. when a material goes from R#i to R#0. This is the case of metallic pigments in paintings, zinc in tyres, phosphorous in car surface treatments, lead in gasoline, phosphates in agriculture, metals as additives in steels, cadmium and other metal dispersion in waste incineration, many electroplating materials, mine tailings and hundreds of more examples. Also, all fossil fuels required to elevate the exergy of materials, from R#1 and R#3 to R#2, become degraded and slowly but irreversibly contribute to form Thanatia (R#0).

Taking these considerations into account, we can now assess the yearly depletion of the mineral capital endowment due mineral production. For that purpose, world primary production figures such as those reported by the Mineral Commodity Summaries 2008 [35] are required. Table 1 shows the total exergy costs of the studied production chains. According to our calculations, the exergy replacement costs (bonus) associated to the 2008 production of the studied minerals is equal to 5.3 Gtoe.

It is worth to note that conventional economics only accounts for the energy required in the extraction and refining processes. In the case of the materials studied, these account for around 9%
of the total world fossil fuel produced\(^3\) in year 2008 (see Fig. 2). The latter value is in the range reported by the World Watch Institute (up to 7% of the total world energy consumption) and by the International Energy Agency (up to 10% also of the world energy consumption).

Nevertheless a fair accountability of resources should also take into account the use and the decrease of the non-fuel mineral capital endowment. This means that the true yearly balance of the exergy decrease in the mineral endowment of the planet should account for at least, the exergy of fossil fuels world production plus the loss of the mineral exergy bonus of the non-fuel minerals. As can be seen in Fig. 2, this accounts for 32\% of the whole energy stages, if the cradle to grave stage is taken into account and is in the same order of magnitude as the yearly loss of coal, oil or natural gas.

Fig. 3 also shows in a schematic way the gross mineral exergy bonus of the extraction of the considered minerals for year 2008. But this bonus is not entirely lost. As explained above, only that part that is not recycled becomes in reality lost. The USGS reports recycling ratios for some important minerals in the US [35] (see Table 2).

We will assume the same recycling ratios for the whole world as in the US, which means that from the total mineral bonus extracted, only 72\% is practically lost. Consequently, the exergy bonus lost due to mineral production in 2008, represents a decrease of the planetary mineral endowment of around 3.8 Gtoe. Adding the exergy of the fossil fuels used in the extraction and processing of the minerals, we obtain that the total exergy loss due to mineral production in 2008 was equal to 5.3 Gtoe. This represents around 41\%, of the overall decrease respectively (taking into account fossil fuels and the mineral bonus lost). It should be stated that only 37 minerals have been considered.

Hence, the previous reported value would increase, if all mineral commodities were to be included in the analysis.

Figure 2. Distribution of the exergy costs associated to the 2008 world production of the main mineral commodities

\(^3\) In Fig. 2, the energy associated to the mining and concentration, smelting and refining has been depicted as if it would come from coal. This is obviously a simplification, since that energy can come from other fossil fuels or even from renewable resources.
Table 1. Total exergy costs of 2008 world production. Values are expressed in Mtoe if not specified

<table>
<thead>
<tr>
<th>Substance</th>
<th>2008 Production, t</th>
<th>Bonus</th>
<th>Mining &amp; conc.</th>
<th>Smelting &amp; refining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>2.05E+08</td>
<td>3.06E+03</td>
<td>5.15E+01</td>
<td>1.16E+02</td>
</tr>
<tr>
<td>Antimony</td>
<td>1.97E+05</td>
<td>2.23E+00</td>
<td>6.57E-03</td>
<td>5.63E-02</td>
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<tr>
<td>Arsenic</td>
<td>5.27E+04</td>
<td>5.02E-01</td>
<td>1.13E-02</td>
<td>2.38E-02</td>
</tr>
<tr>
<td>Beryllium</td>
<td>1.38E+02</td>
<td>8.30E-04</td>
<td>2.37E-05</td>
<td>1.48E-03</td>
</tr>
<tr>
<td>Bismuth</td>
<td>7.70E+03</td>
<td>8.97E-02</td>
<td>6.60E-04</td>
<td>9.68E-03</td>
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<tr>
<td>Cadmium</td>
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<td>2.75E+00</td>
<td>1.23E+01</td>
<td>1.30E+01</td>
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<tr>
<td>Chromium</td>
<td>6.98E+06</td>
<td>7.54E-01</td>
<td>1.40E+02</td>
<td>6.03E+00</td>
</tr>
<tr>
<td>Cobalt</td>
<td>7.59E+04</td>
<td>1.96E+01</td>
<td>1.66E-02</td>
<td>2.33E-01</td>
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<tr>
<td>Copper</td>
<td>1.54E+07</td>
<td>4.05E+01</td>
<td>1.06E+01</td>
<td>7.86E+00</td>
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<tr>
<td>Fluorspar</td>
<td>6.04E+06</td>
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<td>Gold</td>
<td>2.26E+03</td>
<td>3.14E+01</td>
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<tr>
<td>Iron</td>
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<tr>
<td>Lead</td>
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<td>3.35E+00</td>
<td>8.16E-02</td>
<td>3.00E-01</td>
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<td>Limestone</td>
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<td>9.97E-01</td>
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<tr>
<td>Molybdenum</td>
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<td>3.98E+00</td>
<td>5.96E-01</td>
<td>5.26E-02</td>
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<tr>
<td>Nickel-laterites</td>
<td>1.19E+06</td>
<td>4.76E+00</td>
<td>4.89E-02</td>
<td>1.17E+01</td>
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<tr>
<td>Nickel-sulfides</td>
<td>1.00E+06</td>
<td>1.82E+00</td>
<td>3.71E+01</td>
<td>2.39E+00</td>
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<tr>
<td>Phosphate rock</td>
<td>1.61E+08</td>
<td>1.35E+00</td>
<td>1.10E+00</td>
<td>1.77E+01</td>
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<tr>
<td>Potash</td>
<td>3.48E+07</td>
<td>1.01E+03</td>
<td>2.54E+00</td>
<td>-</td>
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<tr>
<td>Rhenium</td>
<td>5.65E+01</td>
<td>1.38E+01</td>
<td>2.10E-04</td>
<td>2.02E-05</td>
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<tr>
<td>Silicon</td>
<td>2.83E+06</td>
<td>4.92E-02</td>
<td>4.85E-02</td>
<td>5.12E+00</td>
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<tr>
<td>Silver</td>
<td>2.13E+04</td>
<td>3.74E+00</td>
<td>6.50E-01</td>
<td>1.44E-01</td>
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<tr>
<td>Sodium</td>
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<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
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<tr>
<td>Tantalum</td>
<td>1.17E+03</td>
<td>1.35E+01</td>
<td>8.59E-02</td>
<td>2.27E-04</td>
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<tr>
<td>Tin</td>
<td>2.99E+05</td>
<td>3.04E+00</td>
<td>1.08E-01</td>
<td>3.82E+01</td>
</tr>
<tr>
<td>Titanium-rutile</td>
<td>6.21E+05</td>
<td>1.30E+01</td>
<td>2.04E-01</td>
<td>3.61E+00</td>
</tr>
<tr>
<td>Titanium-ilmenite</td>
<td>6.79E+06</td>
<td>7.29E-01</td>
<td>1.17E+00</td>
<td>2.07E+01</td>
</tr>
<tr>
<td>Uranium</td>
<td>6.09E+04</td>
<td>1.31E+00</td>
<td>2.74E-01</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>Vanadium</td>
<td>5.61E+04</td>
<td>1.41E+00</td>
<td>1.82E-01</td>
<td>5.09E-01</td>
</tr>
<tr>
<td>Wolfram</td>
<td>5.59E+04</td>
<td>9.89E+00</td>
<td>2.83E-01</td>
<td>1.92E-01</td>
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<tr>
<td>Zinc</td>
<td>1.16E+07</td>
<td>6.85E+00</td>
<td>4.13E-01</td>
<td>1.12E+01</td>
</tr>
<tr>
<td>Zirconium</td>
<td>1.28E+06</td>
<td>1.99E+01</td>
<td>2.25E-01</td>
<td>1.93E+01</td>
</tr>
</tbody>
</table>

TOTAL          2.98E+09  5.307.97  137.87  1.335.97

Table 2. US recycling rates of selected metals in 2008 [35]

<table>
<thead>
<tr>
<th>Substance</th>
<th>Recycling Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>48%</td>
</tr>
<tr>
<td>Chromium</td>
<td>34%</td>
</tr>
<tr>
<td>Copper</td>
<td>32%</td>
</tr>
<tr>
<td>Tin</td>
<td>34%</td>
</tr>
<tr>
<td>Lead</td>
<td>61%</td>
</tr>
<tr>
<td>Titanium-rutile</td>
<td>77%</td>
</tr>
<tr>
<td>Titanium-ilmenite</td>
<td>43%</td>
</tr>
<tr>
<td>Zinc</td>
<td>30%</td>
</tr>
</tbody>
</table>

5. Conclusions

The extraction of materials from the Earth’s crust implies a net reduction of the natural’s exergy stock.
This is because we are unable to recycle all materials we mine. Consequently, the Earth approaches gradually to a degraded planet of minimum exergy, with the absence of fuel and non-fuel mineral deposits. And this is a consequence of the Second Law of Thermodynamics.

We have presented in this paper a methodology for measuring the mineral bonus that Nature grants us for providing the minerals concentrated in mines and not dispersed throughout the crust. The exergy replacement costs account for the actual exergy required to extract and concentrate the materials from the Crepuscular Earth to the conditions found in Nature, with current available technologies. Hence, the knowledge of mining practices of extraction and refining of minerals is a fundamental key for assessing them.

The obtained values give an idea of the great amount of exergy that man saves thanks to the existence of the concentrated mineral capital on Earth. The analyzed substances represent only a part of the globally used mineral resources, so the complete analysis including all minerals is even larger.

Furthermore, as the mines become depleted, the obtained number will continue to increase and presumably in an exponential way, coinciding with the exponential trend of extraction throughout history.

Our analysis enhances and puts numbers to the importance and necessity of material reuse and recycling.

The accuracy of the numbers to be obtained with this methodology relies strongly on the quality of the data used. The knowledge of metallurgical processes that imitate Nature in creating minerals is required. But most importantly, we need to know precisely geological facts on how our mineral wealth is being altered by man. Unfortunately, there is an enormous lack of information about our mineral capital.

The obtained values should serve as an assessment tool for decision-makers in the mineral industry. Because, how can we effectively manage our resources if we do not even know which is the cost of the mineral capital that we are irremediably destroying?

![Figure 3. The decrease of the world mineral capital endowment due to raw-material production in 2008.](image)
6. Acknowledgment

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References


A new polygeneration system for methanol and power based on coke oven gas and coal gas

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Abstract:
Polygeneration system for chemical and power co-production has been regarded as one of promising technologies to use fossil fuel more efficiently and cleanly. In this paper, a novel polygeneration system, with both coal-based syngas and coke oven gas inputs for methanol and power production, is proposed. New system demonstrates the superior performance to the single-product systems, whose energy saving ratio is as high as 15%, and exergy efficiency can reach about 65%. To clarify the characteristic of the new system, exergy balance sheet and Energy Utilization Diagrams (EUDs) are applied to reveal the essence of performance improvement. The results show the following reasons: Firstly, pressure swing absorption is used to remove the hydrogen from the coke oven gas, by which, the concentration of reformed methane is gone up, which reduces exergy destruction. Secondly, the thermal energy for partial methane reforming is supplied by syngas out of coal gasifier instead of fuel gas, which not only save chemical energy of fuel, but also recover the sensible thermal energy of the syngas. Finally, the mixed gas by coke-oven gas and coal syngas can make the composition more fit for chemical synthesis even without any energy consumption. This novel system has the capability of both effectively utilizing the coke-oven gas and developing coal based polygeneration system, which leads to a new direction for clean energy technology.

Keywords:
Coke oven gas, Syngas, Dual-gas complement, System integration, Performance character.

1. Introduction

Multi-energy complement and coproduction have been a main character and direction of energy system sustainable development. China is a country with abundant of coal but short of oil. Coal is the main energy resource in primary energy resource. The complement problem between coal and the second energy resource by-produced during coal utilization has been paid more attention. In traditional development, power system focuses on improvement of thermal energy utilization, and chemical production focuses on max product outputs. Both of the development directions could not break through the problems of higher energy consumption, chemical energy destruction and pollution [1-9]. Therefore, polygeneration system, integrating between chemical and power productions, has attracted more attention, and some science researches and demonstration projects have been carried out.

In China, coke production was about half of the total in the world, which by-produces about 36 billion cubic meters per year of coke oven gas (COG). But only 10 % of it has been utilized, and most of it was burned in the air, it is obvious that leads to good energy waste and air pollution [10-11]. So its effective utilization is necessary. Because hydrogen and methane are the main components of COG, and syngas from coal is rich in CO, syngas from coal or COG must be adjusted to fit for chemical production with large energy consumption, which is the critical point when system integration.

This paper is to integrate a new polygeneration system with syngas from coal and COG. The performance of the system is identified, and the characteristics of the new system are disclosed by exergy analysis with EUD method.
2. New polygeneration system based on COG and coal gas

2.1. A new approach for integrated utilization between COG and coal-based syngas

In this paper, we chose the coal, whose base analysis (weight, %) is as follows: 68.54%C, 3.97%H, 6.85%O, 0.74%N, 1.08%S, 9.98%Ash, and 8.84%W, and LHV was 26710 kJ/kg. The syngas produced by a Texaco gasifier was composed of 44.0%CO, 30.8%H₂, 10.5%CO₂, 12.7%H₂O, and 1.8% others, which comes from industrial data. In order to convert almost all syngas into methanol, H₂/CO ratio of fresh gas should be adjusted to the stoichiometric ratio. But the H₂/CO ratio in syngas is about 0.69, so the syngas is always been adjusted by shift reaction. Another way, coke-oven gas is rich in H₂ and CH₄ (about 8.8%CO, 57.3%H₂, 2.8%CO₂, 20.5%CH₄, and 10.8% others in volume). Traditionally, COG is reformed with steam firstly, by which, CH₄ is converted into CO and H₂, leading to much higher H₂/CO ratio in syngas. Furthermore, because of being rich in hydrogen, if CH₄ is reformed completely, much more energy is needed, which always supplies by COG or/and other fuel gases combustion.

Synergetic considering the characters of coal syngas and COG, the new energy utilization mode is concept as shown in Fig.1. COG is put into pressure swing absorb process (PSA) to separate H₂ firstly, and then put into the reformer. The thermal energy is not supplied by fuel combustion but the high temperature syngas out of the coal gasifier, whose temperature can be higher than 1200°C. Furthermore, CH₄ in COG don’t need to be totally converted into CO and H₂. And the two flows of syngas out of reformer are mixed as fresh gas for methanol synthesis.

![Fig. 1 Concept of complementation between coke oven gas and coal syngas](image)

2.2. Description of the new polygeneration system

The flow sheet of the new system is shown in Fig 2. Through PSA process, 90% hydrogen is separated, and the rich-methane gas is put into the reformer. The syngas out of gasifier is put into the reactor as the thermal energy donor. In the reformer, about 70% of methane is reacted, which is more different from that mentioned in reference [12]. After clean-up unit, the low temperature coal gas is mixed with the product gas of the reformer. Then the mixed gas is put into the methanol synthesis reactor. There are about 80% un-reacted syngas is recycled to the reactor. And after recycled pressure energy, the excess un-reacted syngas and hydrogen out of PSA are put into combined cycle as fuel for power generation.
3. System simulation

3.1. Reference systems

The polygeneration system, based on COG and coal syngas input, is the complicated system with dual-energy inputs and dual-product outputs. When thermodynamic performance is analysed via contrast method, two or more conference systems must be chosen. In the paper, integrated coal gasification combined cycle (IGCC) system and methanol production system with COG input, which shown in Fig. 3, are chosen as reference systems. In Fig. 3, after being cleaned up and preheated at about 550 °C, COG is reformed by steam to convert CH₄ into H₂ and CO. Then the reformed gas is sent to the methanol production subsystem. Some of purge gas in methanol synthesis unit is sent to reformer as fuel, and the rest is sent to a captive power plant. The energy consumption is about 40 GJ/t-CH₃OH.

3.2. Simulation results

Mainly parameters of the processes come from industrial data. All the systems, including conference systems and the new system, are simulated by Aspen Plus. The thermodynamic properties of syngas and methanol were evaluated by the PR and RK equations respectively. The gas turbine was simulated basing on the technical level of 9FA class. The HRSG of the combined cycle works at two difference pressure levels. The turbine inlet temperature was 1260 °C, and the pressure ratio in the gas turbine was 16. The isentropic efficiencies of the gas turbine, the high-
pressure steam turbine and the low-pressure steam turbine were 0.9, 0.88 and 0.86, respectively. With Aspen Plus simulation, the parameters of critical points (shown in Fig.2) are shown in Tab.1. Point 4 denotes the fresh gas for methanol synthesis, ratio of H2/CO is much closer to the stoichiometric ratio of methanol production.

### Tab.1 Critical point parameters of the polygeneration system

<table>
<thead>
<tr>
<th>Point</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<table>
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<th>H2O</th>
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</table>

To evaluate the performance of the polygeneration system, the proposed system was compared with the reference single systems (including the COG-based methanol production system and IGCC system). The thermodynamic performance of the systems is shown in Tab.2. IGCC system and COG-based methanol production system have the same outputs as those of the polygeneration system, 300 MW power and 58.2 t/h methanol respectively. In the table, \( R_c \) denotes the ratio of methanol (in low heat value) to power output; \( E_c \) is the energy consumption for 1 ton methanol production; \( \eta_p \) and \( \eta_m \) symbol the thermal efficiencies of power generation and the total system. And we also chose primary energy saving ratio \( (PES) \) as a criterion to evaluate the thermodynamic performance of the new system. \( PES \) is defined as:

\[
PES = \frac{W}{\eta_p + Q_{ME}/\eta_{ME} - (Q_c + x \cdot Q_{COG})} \frac{W}{\eta_p + Q_{ME}/\eta_{ME}}
\]

Where \( W \) and \( Q_{ME} \) are the network output and methanol(LHV); \( \eta_p \) and \( \eta_{ME} \) are the efficiencies of power generation in IGCC system and methanol production system respectively; \( Q_c \) and \( Q_{COG} \) are the low heat value of coal gas and COG. Because the energy level of COG is higher than that of coal gas, we chose \( x \) as a coefficient to deal with this difference, as 1.1 in the paper [13].

The polygeneration system shows its better thermodynamic performance, whose primary energy saving ratio can reach about 15 %, thermal efficiency for power generation is about 10 percentage points higher than that of IGCC system, and energy consumption for methanol production is about 70 % of that in COG-based methanol production system.

To disclose the energy utilized advantage, exergy destructions of processes are shown in Tab. 3. The exergy efficiency of the proposal system is higher than 60%, which is much higher than those in the reference systems. The exergy destruction of reforming process is only about 1/15 of that in the COG based methanol production system. 367
Tab. 2 Main thermodynamic performance of the polygeneration system

<table>
<thead>
<tr>
<th></th>
<th>PG</th>
<th>Single-product system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>IGCC</td>
</tr>
<tr>
<td>Coal MW</td>
<td>710.6</td>
<td>683.4</td>
</tr>
<tr>
<td>Coke-oven gas MW</td>
<td>405.8</td>
<td>606.2</td>
</tr>
<tr>
<td>Network output MW</td>
<td>300.0</td>
<td>300.0</td>
</tr>
<tr>
<td>MEOH output t/h</td>
<td>58.2</td>
<td>58.2</td>
</tr>
<tr>
<td>$R_c$</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>$\eta_P %$</td>
<td>58.8</td>
<td>43.9</td>
</tr>
<tr>
<td>$E_C \text{GJ/t}$</td>
<td>26.8</td>
<td>37.5</td>
</tr>
<tr>
<td>$\eta_{th} %$</td>
<td>55.7</td>
<td>43.9</td>
</tr>
<tr>
<td>$PES %$</td>
<td>14.3</td>
<td></td>
</tr>
</tbody>
</table>

Tab. 3 Exergy balance of the polygeneration system and single-product systems

<table>
<thead>
<tr>
<th>System</th>
<th>PG</th>
<th>COG ME</th>
<th>IGCC</th>
</tr>
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<tbody>
<tr>
<td>Unit</td>
<td>MW %</td>
<td>MW %</td>
<td>MW %</td>
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<tr>
<td>Exergy input</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Fuel exergy</td>
<td>1134.4</td>
<td>100.0</td>
<td>718.5</td>
</tr>
<tr>
<td>Coal</td>
<td>727.8</td>
<td>64.2</td>
<td>698.7</td>
</tr>
<tr>
<td>Coke oven gas</td>
<td>406.6</td>
<td>35.8</td>
<td>718.5</td>
</tr>
<tr>
<td>Exergy destruction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASU</td>
<td>19.3</td>
<td>1.7</td>
<td>12.0</td>
</tr>
<tr>
<td>Gasification</td>
<td>104.4</td>
<td>9.2</td>
<td>106.2</td>
</tr>
<tr>
<td>PSA</td>
<td>5.7</td>
<td>0.5</td>
<td></td>
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<tr>
<td>Coke-oven gas reform</td>
<td>7.9</td>
<td>0.7</td>
<td>103.8</td>
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<tr>
<td>MEOH synthesis and distillation</td>
<td>43.6</td>
<td>3.8</td>
<td>47.2</td>
</tr>
<tr>
<td>Power system and others</td>
<td>230.3</td>
<td>20.3</td>
<td>131.6</td>
</tr>
<tr>
<td>Product exergy output</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Network output</td>
<td>300.0</td>
<td>26.4</td>
<td>300.0</td>
</tr>
<tr>
<td>MEOH</td>
<td>423.2</td>
<td>37.3</td>
<td>423.2</td>
</tr>
</tbody>
</table>

4. Discussion

4.1. EUD analysis of reforming process

From the results shown in tab.3, the new approach for integrated utilization between COG and coal syngas leads to less exergy destruction in reforming process. To disclose the reason of exergy destruction decrement, Energy Utilization Diagrams was used to analyze the process [14]. In Fig.4, $ed$ means the energy donating side, and $ea$ symbols the energy accepting side. $A_{esal}$ is the energy
degree of air heated process during fuel combustion, $A_{ea2}$ and $A_{ea3}$ are the energy degree of fuel and coke oven gas reheated processes respectively, $A_{ea4}$ is the energy degree of reforming process. The area between energy donated side and accepted side is the exergy destruction of the total reforming process, including reheating and reacting processes. Fig. 5 shows the exergy loss of the new reforming process. Compared Fig. 4 with Fig. 5, with system integration, the steam for reforming process in new system comes from power cycle, because of partial CH$_4$ reforming, the reforming temperature can be decreased, which means that the energy degree of steam much closer to that of the reforming process, and the energy denoted side is the syngas out of gasifier, then the fuel reheated process is cancel, which means that the processes 1 and 2 are deleted. Furthermore, partial reaction and different energy donated side make the exergy destruction decrease.

**Fig. 4 EUD of the conventional coke oven gas reforming**

**Fig. 5 EUD of coke oven gas reforming in dual-gas polygeneration system**
4.2. Analysis of thermodynamic performance

From the flow sheet shown in Fig. 2, the methane partial reform configuration determines the complement between COG and coal gas from the aspect of energy integration, and the syngas out of separator partial recycled to the methanol reactor directly decides the energy into the power combined cycle, which determines the chemical energy integration between chemical process and power cycle. So the methane reformed ratio \( (R_f) \) of reformed methane to all methane and the ratio \( (R_u) \) of recycled gas to the syngas out of separator are the main critical variable to determine the whole system performance.

Fig. 6 shows \( R_f \) how to impact on \( PES \), the system thermodynamic performance. In the figure, \( R_u \) is defined as the ratio of recycled gas to the syngas out of separator. With certain \( R_u \) (as 2.2, un-reacted syngas about 80% recycled to methanol reactor) and mixed ratio of COG to coal gas, when \( R_f \) increasing, \( PES \) goes up quickly first, and has a highest value, about 15%. But with \( R_f \) continuously increasing, \( PES \) decreases. For every \( PES \) line with certain \( R_u \), there is a \( R_f \) value corresponding to the best thermodynamic performance, with highest \( PES \), which results from the effective components in fresh gas increased and \( H_2/CO \) much closer to stoichiometric ratio of methanol synthesis with \( R_f \) going up, but when \( R_f \) comes to a certain value, \( H_2/CO \) in fresh gas deviates the stoichiometric ratio, which results from more coal gas required for reforming. As about 70% methane reformed, because the concentration of methane is lower, much more reforming energy is needed, which means that the ratio of coal gas to coke oven gas is much higher. Therefore, with certain system configuration, there is an optimal reforming ratio \( (R_{f, opt}) \) couple with recycled ratio and ratio of coal gas to coke oven gas resulting in the couple between chemical side and power generation side of the system, which leads to optimal thermodynamic performance.

![Fig. 6 Thermodynamic performance change with reforming ratio](image)

**Fig. 6 Thermodynamic performance change with reforming ratio**

Fig. 7 shows \( R_u \) how to impact on \( PES \), the system thermodynamic performance. With certain coke oven gas reforming ratio (70%) and \( H_2/CO \) (1.15) in refresh gas, \( PES \) goes up with \( R_u \) increasing first. This is because the effective components and chemical energy in fresh gas are utilized efficiently. But when \( R_u \) gone up to certain value, more recycled work is needed, and the synthesis ratio of methanol increases slowly, in the distillation unit, more energy consumption is needed too, so \( PES \) goes down. With every \( R_f \), there is a \( R_u \) corresponding to the optimal \( PES \), as optimal thermodynamic performance. Therefore, there is an optimal recycling ratio \( (R_{u, opt}) \). Appropriate
unreacted syngas recycle, methane reforming, and mixed ratio of coal gas to coke oven gas lead to couple of chemical side and power generation system, which results in optimal thermodynamic performance.

![Graph showing thermodynamic performance change with syngas recycling ratio](image)

*Fig.7 Thermodynamic performance change with syngas recycling ratio*

### 5. Conclusions

Based on polygeneration definition and dual-fuel gas complement, a new polygeneration system for methanol and power has been proposed, which primary energy saving ratio can reach about 15%. And the thermodynamic performance has also been analyzed by EUD method, the conclusions can be drawn from the results as follow: 1) with coke oven gas and coal-based syngas integrating utilization, and methane partial reform, chemical exergy destruction of reforming process is reduced obviously; 2) with partial recycle configuration of methanol synthesis, chemical exergy destruction is decreased too; 3) the decrement of chemical exergy destruction in the chemical process make more energy into the power island and realizes couple between chemical process and power generation, which leads to improvement of the system thermodynamic performance. The polygeneration system shows the integrating cascade utilization between chemical energy and physical energy.

This novel system has the capability of both effectively utilizing the coke-oven gas and developing coal-based polygeneration system, which leads to a new direction for clean energy technology.

### Acknowledgments

This study has been supported by China National High-Tech Research and Development Projects (2011AA050606).

### References


Abstract:

In the 40 forthcoming years, a substantial reduction of the electric energy production from oil and natural gas is expected; these sources are going to run out and therefore their price is going to increase markedly; the certain increase of the energy request will be met by a limited percentage increase of renewable energies, above all from coal and, despite the current situation, from the nuclear energy.

Due to technical-economic reasons, coal seems to be more recommended to meet the oscillations of the power request while the basic production is devolved upon the nuclear, in particular upon the fourth generation liquid metal reactors.

Super-hypercritical steam generators which are powered by coal have been reached a net output equal to 45%; leading companies research and development are oriented to the detection of high resistance metal alloys allowing to increase pressures and temperatures of operating fluid and therefore to increase the plant output from the current 45% to 50%; leading companies (i.e. Hitachi Power Europe GmbH) have been passed trials on pressurized parts in order to produce superheated steam at 350 bar and 700°C in coal fired boilers (Ref. http://www.hitachi-power.com/en/materials.html).

Against this background, the coal fired closed gas cycle, can become an important option for the electric power production thanks to its intrinsic advantages.

1. Introduction

The closed gas cycle works with fluid invariable both in nature and mass, excepting functional replenishments with an heat transfer to and from the cycle by heat exchangers. The disadvantage of the huge dimensions of these components is counterbalanced by some advantages; the most relevant ones are:

- The possibility of the gas choice
- The starting from initial thermodynamic condition independent on the environment, particularly for the pressure value
- Favourable effects deriving from employing a clean fluid.

It is important to consider also the favourable effects deriving from a clean fluid.

Regarding to the fossil fuel fired closed gas cycles, one of the main limits is represented by the low heat transfer capacity of the gas compared to the water in steam cycles; this results in a low value of the cross loading of the combustion chambers, which is expressed, as well known, by the ratio of input energy to the cross area of the chamber. For example, in the combustion chambers for air closed TG built in Germany in 1960-80, there were 1,2÷1,6 MW/m² against 6÷7 available in the steam power plants.

As a consequence the combustion chamber of Gelsenkirchen plant having volume of 500 m³ was producing 17,25 MWe while a steam generator of the same dimensions can attain 75 MWe. (Ref. ...
Actually, an efficiency enhancement is achievable either by increasing the cross sectional loading or by an enlargement of the combustion chamber. Using air as fluid these measures undergo some difficulties caused by its low heat transfer coefficient; in fact with a too high cross load, two different situations can occur: either the chamber temperature increases, and then the temperature of the exchange surfaces may become too high or increases the thermal content of the gas output, with an increase in energy losses and with imbalance of the entire downstream system. On the other hand with a lower cross load the chamber dimension get prohibitive for unit power nowadays requested for large plant.

2. The fluid choice

In order to overcome the difficulties encountered in the design and operation of the closed gas cycles, we focused our attention on gas-water mixtures. The injection of an appropriate amount of water in the gas downstream of the compressor allows to limit the temperature of the tube walls of the combustion chamber; the high heat transfer coefficient of boiling water vaporized in the tubes can significantly increase the thermal flow.

Moreover, the water in the mixtures leads to the increase the cycle work ratio.

To achieve this objective, in addition to the economic availability, the mixture should have the following two main properties:

- High density
- Specific heat at constant pressure lower than steam

The former allows to have comparable volumetric flow rates of the two fluids starting from an appropriate choice of the mass flow rate ratios in the tubes of the combustion chamber; the latter widens the gap between the $P_T$ power of the turbine and compressor mechanical power $P_C$, which is expressed by the following (1) and (2):

$$P_C = M_G \times c_{pG} \times (T_{2r} - T_1) \quad (1)$$

$$P_T = (M_G + M_W) \times c_{pGW} \times (T_1 - T_{2r}) \quad (2)$$

where $M_G$ and $M_W$ are the gas and water mass flow rate, and $c_{pGW}$ the specific heat at constant pressure of the steam-gas mixture.

The effect of the condition $c_{pG} < c_{pW}$ is higher in the reduction of the gas compression work compared to the lower contribution which gives to the expansion work of the mixture, with benefits to the useful work; substantially, the useful power $P = P_T - P_C$ increases because the turbine, in addition to working with a greater mass flow rate, develops an even higher mass work due also to the condition $c_{pGW} > c_{pG}$ (Ref. LOZZA, G., Gas Turbines and Combined Cycles, Esculapio, Bologna, 2006 – CAPETTI, A., Thermal Engines, UTET, Torino, 1964).

The gas which we think the best to meet the foreside requirements is the Argon, with a molecular mass of 40 and then a normal density of 1,786 kg/Nm$^3$ and $C_{pA} = 0.52$ kJ/(kg K) i.e. $1/4$ of that of the superheated steam at high temperature; the ratio $C_p/C_v$ is equal to 1.667.

The ratio $\gamma = C_{pAW}/C_{vAW}$ of the mixture is calculated as weighted average on the mass flow rate of the two fluids. To this regard, it should be noted that since $\gamma_{AW} < \gamma_A$ for a given expansion ratio, the output mixture temperature from the turbine is higher than Argon. This is a thermodynamic disadvantage of the mixture, however mild compared to the above-mentioned benefits.
The properties $C_p$ and $\gamma$ of both components and consequently this of the mixture, particularly their dependence on the pressure are very important not only for the nominal performances of the plant but also for their variation at partial load as specified speaking on the power plant regulation.

3. The proposed cycle

The proposed Argon-water closed cycle is characterized at full load by the following thermodynamic features:

- Maximum pressure: 343 bar
- Minimum pressure: 1 bar
- Maximum temperature: 700 °C
- Minimum temperature: 40 °C
- Inter-refrigerated three-stage compression
- Two reheaters

As an optimal Argon-Water mass ratio of the mixture, the value $2/3$ was chosen ($M_A/M_W=2/3$). Actually, if the percentage of water of the mixture is higher, the total efficiency decreases owing to a lower inlet temperature in the boiler; if the percentage of water in the mixture is lower, the result is the same because the cycle work ratio becomes too low.

The choice was also supported by the fact that, with a view to implementing a plant of unit power which can be compared to that of the current coal-fired supercritical groups, the chosen mass flow rate of the two fluids are 320 and 480 kg/s, respectively ($M_A=320$ e $M_W=480$ kg/s) for a full load of 800 kg/s.

The proposed cycle is shown in figure 1.

3.1 Plant machinery

Referring to the Argon compression, the increase from 1 bar to 343 bar is obtained by three compressor each having the same compression ratio equal to 7. Enormous flow rate at the beginning leads to an axial compressor (1,7 Mm$^3$/h) leads to an axial compressor which is a feasible solution also for the second compressor (246000 m$^3$/h). As regard the third compression we think it could be preferable a centrifugal machine because of the very low height of the axial blades (about 15 mm). The centrifugal compressor could be a two-stage machine each having 2,65 compression ratio. We assumed efficiencies 89 % and 84 % for axial and centrifugal machine respectively.

For the Argon Water mixture expansion we have a Curtis wheel for the high pressure turbine followed by a reaction medium and low pressure turbines. We assumed efficiencies 75 % for the Curtis turbine and 90 % for the reaction turbines.

The boiler feedwater pump is a variable centrifugal multistage machine electric motor driven with an efficiency of 70 %.

3.2 Plant heat exchangers

Main plant heat exchangers are the regenerator, the two compressor intercooler including the argon cooling exchangers by service water, the mixer and the condenser. Figures 2-3-4-5 show the working conditions of the condensate regenerator, of the A e B exchangers, of the inter-refrigerator and of the mixer.
Fig. 2 – Condensate regenerator

Fig. 3 – Intercooler 1 exchanger A
Fig. 4 – Intercooler 1 exchanger B

Fig. 5 – Intercooler 2 exchanger A
Figure 8 shows schematically the thermodynamics of the mixture in T-S plan.
3.3 The boiler

The combustion chamber is fuelled by coal (6000 Kcal/kg); the boiler is composed by a combustion chamber which is cooled by wall screen with Argon water mixture coming from the mixer. After gas tempering fuel gases cross the RH2 then RH1-HT then SH-HT then RH1-LT then SH-LT. At this point we have a flue gas extraction for the gas tempering and finally the air-preheater.

The RH2 as the first heat exchanger because of the favourable low pressure considering the thermo-mechanical stress. Similar consideration have been taking in mind for the all other exchanger positioning.

Mixture inlet temperature even at partial load is about 170 °C; Argon water mixture exit from the combustion chamber at 400 °C. A schematic view of the boiler is showed in Fig. 9.

Because of the particular position and configuration of the various heat exchanger the mixture pressure drop is increasing from the RH2 to SH; it is a pressure drop distribution which is favourable for turbine power because leads to larger expansion ratio in the three turbines and then to plant efficiency enhancement.

4. Performances of the cycle

The proposed system efficiency is calculated as ratio between the alternator power output, reduced of the power consumed by the extraction and feeding pumps, and the thermal power of the fossil fuel.

The power output by the three turbines and the power input by the two compressors and the pumps are shown in table 1 together with the plant electrical power.

The contributions of the various machines to the above total values for both the expansion and compression are specified in table 2 and 3.
Table 1.

<table>
<thead>
<tr>
<th>P HP Turbine [MW]</th>
<th>P MP Turbine [MW]</th>
<th>P LP Turbine [MW]</th>
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<tbody>
<tr>
<td>368.2</td>
<td>356.6</td>
<td>626.1</td>
</tr>
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<td><strong>P Tot Turbine [MW]</strong></td>
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<thead>
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<th>P MP Compr. [MW]</th>
<th>P HP Compr. [MW]</th>
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<tr>
<td>69.0</td>
<td>69.0</td>
<td>73.1</td>
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<tr>
<td><strong>P Tot Compr. [MW]</strong></td>
<td><strong>211.0</strong></td>
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</table>

| P Pumps [Mwe] | 24.5           |

| Plant Power [Mwe] | 1081.2         |

Table 2.

<table>
<thead>
<tr>
<th>T1(°C)</th>
<th>T-HP</th>
<th>T-MP</th>
<th>T-LP</th>
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<tr>
<td></td>
<td>700</td>
<td>700</td>
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<th>βt</th>
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<table>
<thead>
<tr>
<th>cpAW (kJ/kgK)</th>
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</table>

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<thead>
<tr>
<th>γAW</th>
<th>1.513</th>
<th>1.448</th>
<th>1.443</th>
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<table>
<thead>
<tr>
<th>T2,is (°C)</th>
<th>363</th>
<th>387</th>
<th>115</th>
</tr>
</thead>
</table>

| T2 (°C) | 447   | 419   | 173   |

Table 3.

<table>
<thead>
<tr>
<th>T1(°C)</th>
<th>C-LP</th>
<th>C-MP</th>
<th>C-HP</th>
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<tbody>
<tr>
<td></td>
<td>40</td>
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<table>
<thead>
<tr>
<th>βt</th>
<th>7</th>
<th>7</th>
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</table>

<table>
<thead>
<tr>
<th>cpAW (kJ/kgK)</th>
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</table>

<table>
<thead>
<tr>
<th>γAW</th>
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</table>

<table>
<thead>
<tr>
<th>T2,is (°C)</th>
<th>408</th>
</tr>
</thead>
</table>

| T2 (°C) | 454  | 454  | 479  |

380
The thermal power $Q_{TOT}$ received in total by the fluid, calculated by the sum of thermal power in the plant exchangers (vaporizer, SH, RH1, RH2) amounts to $Q_{TOT}=2232.8$ MW.

The thermodynamic efficiency of the $\eta_{TER}$ cycle is therefore given by the Eq. (3):

$$\eta_{TER} = \frac{(P_{T-TOT} - P_{C-TOT}) \times \eta_0 - P_p}{Q_{TOT}}$$

(3)

where $\eta_0$ includes the mechanical and electrical efficiency of the group. Assuming $\eta_0=97\%$, $\eta_{TER}=48.4\%$ is obtained.

Finally, assuming an efficiency of the boiler $\eta_{GV} = 93.5\%$ the plant efficiency results $\eta_{IMP} = \eta_{GV} = 45.3\%$. We note that this efficiency has been obtained on the basis of the efficiencies assumed for the turbomachinery whose value could be slightly enhanced with benefit of plant efficiency aiming at achieve $\eta = 50\%$.

4.1 Performances and mixture composition

We examined the variations of the plant performances at full load as the dosage of the two components of the mixture changes. Figures 10-11-12-13 show in the order the cycle efficiency, the cycle work ratio, the electrical power of the plant and the boiler inlet temperature.

Fig. 10 – Plant efficiency VS mixture dosage change
Fig. 11 – Work ratio VS mixture dosage change

Fig. 12 – Plant power VS mixture dosage change

Fig. 13 – Boiler inlet temperature VS mixture dosage
5. Partial load performances

Finally, we examined the plant performances as the mixture nominal (2/3) mass flow rate changes. The results are gathered in figures 14-15-16-17-18 showing the cycle efficiency, the plant electrical power, the boiler inlet temperature, the heat specific at constant pressure and the outlet temperature of the turbines. As regards the efficiency we observed that its decreasing at lower loads is due to the diminution of the Cp and of the mixture flowing in the turbine.

In effect while Argon Cp is constant the steam one lowers, at constant temperature when the pressure decreases with the load.

Fig. 14 – Plant efficiency VS mixture mass flow

Fig. 15 – Plant power VS mixture mass flow
**Fig. 16 – Boiler temperature VS the mixture mass flow rate**

**Fig. 17 – Mixture Cp VS the mixture mass flow rate**

**Fig. 18 – Turbines outlet temperature**

384
6. Conclusions

The proposed thermodynamic cycle is presented as a suitable alternative for the generation of electrical power compared both to coal fired supercritical steam cycles that have to supply load variation, and the gas combined cycles if the fuel price gets prohibitive. Concerning with the boiler design, it would be necessary to investigate experimentally the critical thermal flow of the argon-water mixture; particularly, for the design of the superheater and reheaters, the gas tempering has been considered in order to control the thermo-mechanical stress of the heat exchangers.

From our analysis the following features of the proposed plant can be focused:

- Cycle efficiency remains practically constant with load
- The maximum temperature of 700 °C in the turbine is permitted by available steel alloys and therefore do not require blade refrigeration; moreover turbines operate without moisture even at partial load.
- The absence of mass extraction in the turbine leads to simplification of the plant; concerning this we note that the utilization of mass extraction in the turbines could lead to an efficiency enhancement but with disadvantages of higher complexity power plant configuration and operation.
- Plant turbomachinery do not meet particular design problems being the Argon thermophysical properties similar to the air; on the other hand, the higher Cp/Cv ratio, under the same condition and compression ratio and axial velocity, Argon undergoes a minor flow area variation in comparison with air obtaining a better flow pattern.
- The results obtained in the analysis of the proposed plant lead to dimensions of the boiler comparable to the current supercritical steam power plant

References

Fig. 1 – The proposed Argon Water cycle
Fig. 9 – Schematic view of the boiler
Binary Alkane Mixtures as Fluids in Rankine Cycles

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Abstract:
Waste heat recovery from the exhaust gases of gas turbines, geothermal resources, and from industrial plants offers a great opportunity for energy conservation by productively using the waste energy. Organic Rankine cycles (ORC) have been used to convert low grade heat available as waste from exhaust gases from turbines and engines as well as from industrial plants. Different working fluids (generally pure substances) have been investigated and in part used for this purpose. This was also the theme of our previous work. Among others the efficiency of the process depends on the extent of losses from irreversible heat transfer from the source and to the sink. The losses depend on the levels of matching of T-H curves of heat source, working fluid and the heat sink. This can be achieved by matching the corresponding T-H curves. One way to tune the properties is to use a suitable mixture in place of pure substance. There are only a few studies which report the use of fluid mixtures as the working fluid for ORC. In the present communication we report the results of model calculations of binary mixtures of one short chain alkane with one long chain alkane (hexane + decane, hexane + dodecane) at different compositions. The upper pressure levels were selected up to 20 bar for safety reasons and the cooling temperatures were selected at levels suitable for co-generation. At a fixed condenser pressure the mixtures perform better than the pure components (20-50% higher efficiencies). At a fixed condenser temperature the efficiency varies with the condensation pressure and is higher at lower condenser pressures. The exergy losses occurring at various stages were also investigated. The results for the total heat recovery efficiency, second law efficiency and the surface area of the heat exchanger have been discussed.

Keywords:
ORC; Rankine cycle; Exergy loss; Thermal efficiency; T-H Diagrams

1. Introduction

The utilization of low, medium and high temperature heat has been studied extensively in the past [1-10]. The choice of working fluids is of key importance for the performance of an organic Rankine cycle (ORC). The number of working fluids which can be used in ORC systems is countless. The most important criteria for the selection of ORC working fluid are the high efficiency and low exergy loss which are basically governed by the thermodynamic properties. The efficiency of an ORC system depends on the entropy changes in the working fluid as well as in the environment during various stages. Thus it depends on the working fluid as well as on the working conditions (the temperature at which heat is available and the temperature at which it is rejected).

In our previous publications [11, 12] the results for some representative substances e.g. hydrocarbons, refrigerants, aromatics, were presented for the case of waste heat availability at 773.15 K, 623.15 K and 523.15 K. In contrast to most previous publications the combined generation of heat and power (CHP) using ORC is studied in our work, which is continued here, meaning that the heat rejection of the cycle shall be used for heating purposes. Such systems can be used as the energy supply for hospitals, small industries etc. Thus, to be useful for this purpose, a heating of the cooling water to 85°C was studied. The previous studies were limited to pure
substances. An important limitation of an ORC with a pure working fluid is the isothermal boiling, which often leads to a bad thermal matching between the working fluid and the heat source as well as between the working fluid and the cooling water stream due to pinch point limitations which again lead to large irreversibilities. A \( T-H \) diagram helps to visualise [13] the complete process, as an example the heat transfer from hot air to two different fluids is depicted in Figure 1. In this case not only the ORC, but also the process lines for the hot exhaust gas and the cooling water are included and thus the whole process can be visualised. Any pinch point breach can be seen on it and the temperature differences along the heat transfer processes can easily be seen as a direct measure of thermodynamic irreversibilities. Fig.1 shows qualitatively the temperature variation in boiler in ORC with pure substance (full line) and a binary mixture (dashed line). Since the temperature difference between the heat source and the fluid mixture is throughout smaller than between the pure fluid and the heat source, the irreversibilities in the former case are smaller. This could lead to improved second law efficiencies. Also, similar losses from irreversible heat transfer to the sink will be observed.

![Temperature variation in boiler for pure fluid and fluid mixture.](image)

Some studies with binary and ternary mixtures of non-azeotropic working fluids featuring evaporation/condensation at different temperatures, i.e. non isothermal (variable) heat addition and rejection have been reported from time to time [7, 14-18]. However, the studies are limited and report the results obtained under quite different conditions. Due to the numerous parameters involved, a comparison of the performance of mixtures as working fluids to pure substances is difficult. In the present study it is attempted to systematize such a comparison. The results of model calculations of binary mixtures of one short chain alkane with one long chain alkane (hexane + decane, hexane + dodecane etc.) at different compositions are reported here. The model calculations have been performed keeping fixed as many parameters as possible and study the performance by varying only a limited number of parameters. Apart from the first law and the second law efficiencies, the required surface area for the heat exchanger and the condenser is roughly estimated for each process since this is an important factor regarding the investment costs. The cycles are studies for different evaporator pressures of up to 2000 kPa, which is a reasonable value for single stage turbines and also for safety reasons in small devices.
2. Method

ORC is a Rankine cycle in which the working fluid is not water but an organic fluid. The working fluids for Rankine cycle are classified in literature as dry with positive slope (dT/dS) or isentropic with infinitely large slope depending on the shape of temperature-entropy (T-S) diagram. A detailed description is found in [1]. Water (and Ammonia) with negative slope (dT/dS) have been termed as wet fluids. The model used for the calculations and the numbering of the different states is shown in Figure 2(a) for a ready reference.

Fig. 2. The ORC system used in this study (a) and the related schematic T-s diagram (b), the entropy scales will differ for the three different fluids.

The system consists of:

a) hot gas that enters the system boundary at $T_{\text{air},3}$ transfers energy via heat exchanger to the working fluid (its temperature drops to $T_{\text{air},0}$) and leaves the system boundary at $T_{\text{air,surr}}$.

b) working fluid that enters the system boundary at $T_{\text{F},0}$ at a high specified pressure (state 0), is heated to $T_{\text{F},3}$ by the heat energy delivered by the air, drives the turbine to produce electricity, passes through a condenser thereby delivering the rest heat energy to a cold water stream. It leaves the condenser at $T_{\text{F},5}$. The working fluid is brought back to the initial state 0 through a pump. The difference between the temperatures $T_{\text{F},5}$ and $T_{\text{F},0}$ is very small (max. 0.7K). The power of the pump has been taken into account while calculating the net power of the ORC cycle or of the complete process.

c) cold water stream that enters the system boundary at $T_{\text{W},5}$ is heated to a higher temperature $T_{\text{W},4}$ for further use.

The temperature $T_{\text{air},0}$ is at least 10 K higher than $T_{\text{F},0}$ in all the cases.

The related qualitative T-s diagram is also drawn in Figure 2(b). An enthalpy stream of hot air, simulating an exhaust gas at a definite temperature, is available from an industrial process or an engine. Energy will be transferred as heat to the working fluid of a Rankine cycle. The Rankine
cycle produces electricity and rejects the heat at a lower temperature which can be used further for the heating of cold water (W). The equations used for the model process calculations are summarized below.

The working fluid which leaves the condenser as boiling liquid at a lower pressure (state 5, \( p = p_{\text{cond}} \)) is brought to a higher pressure (\( p = p_{\text{boiler}} \), state 0) with the help of a feed pump. The specific work of the feed pump is then

\[
w_{50} = \frac{v(p_{\text{boiler}} - p_{\text{cond}})}{\eta_p} \quad (1)
\]

where \( v \) is the specific volume of the saturated liquid in state 5. Thus

\[
h_{F,0} = h_{F,5} + w_{50} \quad (2)
\]

The subscript F refers to the fluid of the Rankine cycle and the numbers refer to different states.

The working fluid receives energy from the hot gas stream via a counter current heat exchanger and is vaporized in three stages:

a) Heating of the working fluid up to boiling (state 0 \( \rightarrow \) state 1)

b) Complete vaporization of the working fluid (state 1 \( \rightarrow \) state 2)

c) Superheating of the fluid (state 2 \( \rightarrow \) state 3).

The energy balance across the heat exchanger gives:

\[
\dot{m}_F \cdot (h_{F,3} - h_{F,0}) + \dot{m}_{\text{air}} \cdot (h_{\text{air},0} - h_{\text{air},3}) = 0 \quad (3)
\]

The heat exchanger, which is assumed to be adiabatic towards the surrounding, may be thought to be made up of three parts and in each part one of the above operations takes place. So the first part, i.e. the heat transfer needed for raising the temperature of the working fluid to the boiling temperature can be written as:

\[
\dot{Q}_{add,01} = k_0 \cdot A_0 \cdot \Delta T_{\text{LMTD,01}} = \dot{m}_F \cdot (h_{F,1} - h_{F,0}) \quad (4)
\]

The logarithmic mean temperature difference \( \Delta T_{\text{LMTD}} \) is defined as:

\[
\Delta T_{\text{LMTD,01}} = \frac{\Delta T_0 - \Delta T_1}{\ln(\Delta T_0/\Delta T_1)} \quad (5)
\]

The pinch point for the heat exchanger (states: 0-3) restricts the maximum mass flow rate in the cycle, while the pinch point in the heat rejection from the cycle limits the maximum cooling water flow rate.

The temperature of air in state 1 is written as

\[
T_{\text{air,1}} = T_{\text{air,0}} + \frac{\dot{m}_F \cdot (h_{F,1} - h_{F,0})}{\dot{m}_{\text{air}} \cdot c_{p,\text{air}}} \quad (6)
\]

Similar equations hold for the second and the third part of the heat transfer.

The superheated vapour is then expanded in a turbine (state 3 \( \rightarrow \) state 4) to the pressure of the condenser, \( p_{\text{cond}} \):

\[
w_{34} = \eta_T \cdot (h_{F,4s} - h_{F,3}) \quad (7)
\]
The isobaric condensation of the vapour to the state of boiling liquid (state 4 → state 5):

The heat will be transferred from the cycle to the cold water (Index: W) running in the condenser.

\[
\bar{Q}_{\text{cond}} = -\dot{m}_v \cdot (h_{F,5} - h_{F,4}) = \dot{m}_w \cdot (h_{F,4} - h_{F,5}) \tag{8}
\]

Various parameters (e.g. the thermal efficiency of the cycle \(\eta_{\text{th,ORC}}\), the total efficiency \(\eta_{\text{th,total}}\), net power of the process \(P_{\text{net}}\), the exergy loss of the hot stream and the \(T\text{--}\dot{H}\) diagram for the process) are used to evaluate system performance.

The thermal efficiency of a Rankine cycle is defined as \([9]\)

\[
\eta_{\text{th,ORC}} = \frac{|w_{50} + w_{34}|}{q_{03}} = \frac{|w_{50} + w_{34}|}{(h_{F,3} - h_{F,0})} \tag{9}
\]

The net power delivered by the system is

\[
P_{\text{net}} = |\dot{m}_v \cdot (w_{50} + w_{34}) + \dot{m}_w \cdot w_{p,W}| \tag{10}
\]

with

\[
w_{p,W} = \frac{\Delta p_{p,w}}{\eta_{p,w}} \tag{11}
\]

The efficiency of the Rankine cycle given by equation (9) does not take into account any losses due to the release of the exhaust gases at temperatures which are higher than the one of the surroundings. However, the exhaust gas at the exit of the heat exchanger cannot be cooled down to the temperature of the surroundings due to the pinch point restriction and thus contributes to the exergy loss. A more realistic approach will be to consider this enthalpy loss and define the thermal efficiency of the complete process, viz. \(\eta_{\text{th,total}}\),

\[
\eta_{\text{th,total}} = \frac{P_{\text{net}}}{\dot{m}_{\text{air}} \cdot c_{p,\text{air}} \cdot (T_{\text{air,3}} - T_{\text{air,surr}})} \tag{12}
\]

In order to make the comparisons easier the mass flow rate of the air was chosen such that the term in the denominator gives 1000 kW. This means that the maximum possible heat transfer to the cycle would correspond to this value.

If the air is cooled up to \(T_{\text{air,surr}}\) the exergy (loss+destruction) rate for the complete process can be calculated

\[
\dot{I}_{\text{Process}} = \Delta \dot{E}_{\text{Process}} = \dot{E}_{\text{air,3}} - P_{\text{net}} - \Delta \dot{E}_{\text{acc,water}} = \Delta \dot{E}_{\text{air,3,0}} + \dot{E}_{\text{loss,Exhaust}} - P_{\text{net}} - \Delta \dot{E}_{\text{acc,water}} \tag{13}
\]

with

\[
\Delta \dot{E}_{\text{air,3,0}} = \dot{m}_{\text{air}} \cdot [(h_{\text{air,3}} - h_{\text{air,0}}) - T_{\text{air,surr}} \cdot (s_{\text{air,3}} - s_{\text{air,0}})] \tag{14}
\]

\[
\dot{E}_{\text{loss,Exhaust}} = \dot{m}_{\text{air}} \cdot [(h_{\text{air,0}} - h_{\text{air,surr}}) - T_{\text{air,surr}} \cdot (s_{\text{air,0}} - s_{\text{air,surr}})] \tag{15}
\]

\[
\Delta \dot{E}_{\text{acc,water}} = -\dot{m}_w \cdot [(h_{w,4} - h_{w,5}) - T_{\text{air,surr}} \cdot (s_{w,4} - s_{w,5})] \tag{16}
\]

This formula assumes that the air exhausted to the atmosphere will be equilibrated with the surrounding without further usage (\(\dot{E}_{\text{loss,Exhaust}}\)). This is termed as exergy loss in the following, coming due to the unavoidable exhausting of the air at a higher temperature than ambient. Also some exergy is gained (accumulated) in the water stream which is used further for heating purposes.
\( \Delta E_{\text{acc,water}} \). The thermal efficiencies defined by equation (9) and equation (12) do not reflect the ability to energy from low grade waste heat into usable work. Therefore, the exergy efficiency (i.e. the second law efficiency), which can evaluate the performance of the waste heat recovery is needed. The second law efficiency for the process \( \psi_{\text{total}} \) is calculated as
\[
\psi_{\text{total}} = \frac{\Delta E_{\text{acc,water}} + P_{\text{net}}}{E_{\text{air,3}}} \quad (17)
\]

Another way to analyse the exergy loss for the complete process is to sum up the exergy destruction rates in all parts and the other exergy loss rates \( (\dot{j}) \):
\[
\dot{i}_{\text{Process}} = \Delta E_{\text{Process}} = \dot{i}_{\text{Boiler}} + \dot{i}_{\text{Turbine}} + \dot{i}_{\text{Condenser}} + \dot{E}_{\text{h,Exhaust}} + \dot{i}_{\text{Pump}} + \dot{i}_{\text{PR}} \quad (18)
\]
where \( \dot{i}_{s} \) denote the exergy destruction rate in boiler, turbine or condenser. These have been calculated from the difference of the exergy streams flowing into the device and out of the device:
\[
\dot{i}_{\text{Device}} = \dot{E}_{\text{in}} - \dot{E}_{\text{out}} \quad (19)
\]
The exergy destruction rates in the two pumps are the power consumed by the pumps. These exergy losses/destruction rates with different working fluids will be discussed later in this paper.

Besides this, the surface area of the heat exchanger \( A \) and of the condenser \( A_{\text{Condenser}} \) required for the complete heat transfer is also very important from the point of view of its cost. This may be estimated using equation (4) for the three parts of the heat exchanger as well as of the condenser using typical values for the overall heat transfer coefficient \( k \).

**Description of the model process:** The properties of working fluids needed for the calculations were taken from [19]. The isentropic efficiencies of the turbine and the pump were taken as 0.85. The model process was described by the following parameters:

**Surroundings:** \( T_{\text{surr}} = 298.15 \) K, \( p_{\text{surr}} = 101.3 \) kPa

**Gas Stream:** Air, ideal gas \( [c_{p} = 1.004 \text{ kJ/(kg K)}] \) entering at 773.15 K or 623.15 K. The mass flow rate was constant at 2.097 kg/s or 3.0647 kg/s resulting in a maximum possible heat flow rate of 1000 kW. The exit temperature of the gas stream from the heat exchanger was calculated according to a pinch point analysis for the studied maximum temperature and pressure of the cycle fluid, leading to gas exhaust temperature \( T_{\text{surr}} \).

**Heat Exchanger:** The ideal heat exchanger with 100% effectiveness was considered to be adiabatic towards the surrounding and isobaric. The heat is transferred in three stages from hot gas to the working fluid. The overall heat transfer coefficients, gas to liquid: \( k_{l,g} = 40 \text{ W/(m}^2 \text{ K)} \) [state 0 \( \rightarrow \) state 1, heat transfer between liquid and gas; state 1 \( \rightarrow \) state 2, heat transfer between evaporating liquid and gas (in 2-phase region)] and \( k_{g,g} = 20 \text{ W/(m}^2 \text{ K)} \) [state 2 \( \rightarrow \) state 3, heat transfer between two gases] were assumed. \( \Delta T_{\text{pinch}} = 10 \) K was taken as temperature difference at the pinch point for most of the cases. In a few cases \( \Delta T_{\text{pinch}} \) was higher than 10 K. Thus, the temperature of the hot exhaust gas at the exit of the heat exchanger is throughout higher than the ambient temperature.

**Condenser:** The condenser was also treated as ideal with 100% effectiveness were considered to be adiabatic towards the surrounding and isobaric. As considered above for heat exchangers the
heat is transferred in three stages from superheated vapour to cold liquid water and different overall heat transfer coefficients were used [gas to liquid: $k_{l,g} = 40 \text{ W/(m}^2\text{K)}$, liquid as well as 2-phase region to liquid: $k_{l,l} = 1000 \text{ W/(m}^2\text{K)}$] were assumed. The cooling water entered the condenser at $T_{W,5} = 298.15 \text{ K}$. The efficiency of the cold water pump $\eta_{P,W}$ was taken to be 0.7. The pressure increase due to the cold water pump was taken as 600 kPa. The mass flow rate was adjusted to ensure total heat transfer. The temperature of cold water at the exit $T_{W,4}$ was 358.15 K if not specified.

The boiler pressure was varied between 500 and 1500 kPa. The turbine entrance temperature $T_{F,3}$ was varied from the saturation temperature of the investigated fluid up to the maximum temperature calculated according to the pinch point analysis. At higher pressures the design of the turbine gets complex due to the flow velocities at the turbine exit more than one stage is needed.

### 3. Results and Discussions

Calculations were performed for n-hexane, n-decane, n-dodecane and the mixtures n-hexane(1) + n-decane(2), and n-hexane(1) + n-decane(2) having different concentrations (mass fraction of hexane = $\xi_1$). These were considered as the working fluid for the above mentioned ORC. The needed thermodynamic parameters, viz. the enthalpies and entropies for fluids and their mixtures in different states were adopted [19] or calculated using method [20] from software [19].

#### 3.1. Calculations at constant condenser pressure

The first set of calculation was performed at a constant condenser pressure for all the working fluids. The condenser pressure ($p_{\text{cond}}$) was chosen as 37.389 kPa for n-hexane (1) + n-decane (2) mixtures. This is the saturation pressure for a mixture of 50% mass fraction of n-hexane ($\xi_1 = 0.5$) at $T_{F,\text{sat}} = 323.15 \text{ K}$. For n-hexane (1) + n-dodecane (2) mixtures the condenser pressure was chosen as 40.864 kPa [the saturation pressure for a mixture with $\xi_1 = 0.5$ at $T_{F,\text{sat}} = 323.15 \text{ K}$]. The parameters defined by equations (9) – (19) and the required surface areas for the heat exchanger and the condenser were calculated. The pinch point temperature difference was kept 10 K. Some representative results for the various efficiencies obtained for n-hexane, n-decane and two of the representative mixtures without superheating for the case that the energy is available at the high temperature 773.15 K are summarized in Table 1 together with important process parameters. The values refer to a boiler pressure of 1500 kPa, hot air inlet temperature of 773.15 K and condenser pressure of 37.389 kPa. The high temperature of the cycle was dependent on the fluid and the boiler pressure and is also reported.
Table 1. Comparison of different parameters of ORC systems with hexane(1), decane(2) and their mixtures as working fluid.

<table>
<thead>
<tr>
<th></th>
<th>$\xi_1 = 0.0$</th>
<th>$\xi_1 = 0.5$</th>
<th>$\xi_1 = 0.9$</th>
<th>$\xi_1 = 1.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{F,3}$ (K)</td>
<td>593.141</td>
<td>529.931</td>
<td>476.831</td>
<td>461.72</td>
</tr>
<tr>
<td>$m_c$ (kg/s)</td>
<td>1.080</td>
<td>1.238</td>
<td>1.476</td>
<td>1.561</td>
</tr>
<tr>
<td>$\eta_{th,ORC}$</td>
<td>0.128</td>
<td>0.143</td>
<td>0.175</td>
<td>0.183</td>
</tr>
<tr>
<td>$\eta_{th,total}$</td>
<td><strong>0.092</strong></td>
<td><strong>0.130</strong></td>
<td><strong>0.162</strong></td>
<td><strong>0.141</strong></td>
</tr>
<tr>
<td>$P_{Turbine}$ (kW)</td>
<td>97.3</td>
<td>135.5</td>
<td>169.0</td>
<td>177.3</td>
</tr>
<tr>
<td>$P_{Pump}$ (kW)</td>
<td>2.9</td>
<td>3.2</td>
<td>3.9</td>
<td>4.2</td>
</tr>
<tr>
<td>$P_{net}$ (kW)</td>
<td>92.2</td>
<td>129.6</td>
<td>161.9</td>
<td>141.3</td>
</tr>
<tr>
<td>$P_{P,W}$ (kW)</td>
<td>2.2</td>
<td>2.7</td>
<td>3.2</td>
<td>3.18</td>
</tr>
<tr>
<td>$A$ (m$^2$)</td>
<td>364.5</td>
<td>384.7</td>
<td>332.0</td>
<td>319.4</td>
</tr>
<tr>
<td>$\Delta E_{air,330}$ (kW)</td>
<td>358.9</td>
<td>397.8</td>
<td>399.4</td>
<td>399.7</td>
</tr>
<tr>
<td>$\dot{i}_{Boiler}$ (kW)</td>
<td>46.7</td>
<td>97.6</td>
<td>133.3</td>
<td>142.7</td>
</tr>
<tr>
<td>$\dot{i}_{Turbine}$ (kW)</td>
<td>9.6</td>
<td>15.4</td>
<td>22.2</td>
<td>24.5</td>
</tr>
<tr>
<td>$\dot{i}_{Condenser}$ (kW)</td>
<td>147.9</td>
<td>78.6</td>
<td>16.0</td>
<td>48.6</td>
</tr>
<tr>
<td>$\Delta E_{air,ex}$ (kW)</td>
<td>57.4</td>
<td>70.6</td>
<td>58.8</td>
<td>6.6</td>
</tr>
<tr>
<td>$\dot{E}_{lost,Exh}$ (kW)</td>
<td>43.0</td>
<td>4.1</td>
<td>2.5</td>
<td>2.2</td>
</tr>
<tr>
<td>$\Delta E_{process}$ (kW)</td>
<td>252.4</td>
<td>201.7</td>
<td>181.2</td>
<td>254.0</td>
</tr>
<tr>
<td>$A_{Condenser}$ (m$^2$)</td>
<td>67.8</td>
<td>97.9</td>
<td>229.5</td>
<td>192.2</td>
</tr>
<tr>
<td>$T_{F,5}$ (K)</td>
<td>411.84</td>
<td>323.15</td>
<td>314.84</td>
<td>313.22</td>
</tr>
<tr>
<td>$\Psi_{total}$</td>
<td><strong>0.372</strong></td>
<td><strong>0.498</strong></td>
<td><strong>0.549</strong></td>
<td><strong>0.368</strong></td>
</tr>
</tbody>
</table>

The increase of $\eta_{th,ORC}$, $\eta_{th,total}$ and $\Psi_{total}$ with the increasing boiler pressure was reported when pure alkanes were used as working fluids in ORC [12]. The same trend is observed when their mixtures are used as working fluid. Also similar to pure organic substances the efficiency dropped with increasing temperature level and was highest without superheating. Similar observations have been reported in literature [21]. The decrease of efficiency with increasing turbine entrance temperature can be explained by the shape of the T-s diagram [compare Figure 2(b)]. An increased average temperature for the heat rejection is observed. This is not balanced by the increased average temperature of heat addition to the cycle. This is discussed in detail in [12].

It is observed from Table 1 that for under these conditions the thermal efficiency for the complete process, $\eta_{th,total}$ is lowest for decane (0.092 for $\xi_1=0.0$) and highest for a mixture (0.162 for $\xi_1=0.9$). The second law efficiency $\Psi_{total}$ is also higher for mixtures (0.549 for $\xi_1=0.9$ and 0.498 for $\xi_1=0.5$) and low (0.368 or 0.372) when pure substances are used as working fluids. This means that when mixtures are used as working fluids the efficiency increases by 33% to 48.5% compared to pure n-decane or pure n-hexane, respectively. Obviously the exergy loss rate for the complete process is least for the case when the second law efficiency has a maximum.
A comparison of the exergy loss rates at various stages show that the exergy loss rates in exhaust is highest for decane as it leaves the system at a high temperature due to pinch point restrictions. The exergy destruction in the boiler is higher for n-hexane followed by mixtures ($\xi_1=0.9$), ($\xi_1=0.5$) and n-decane, while the losses in the condenser show the opposite tendency, leading to a minimum in the losses for the mixture with $\xi_1=0.9$. The losses in the turbine are comparatively low. The required surface areas for the heat exchanger do not differ much from each other. However, the required surface areas for condenser in case of n-hexane and the mixture ($\xi_1=0.9$) are higher than those required when n-decane and ($\xi_1=0.5$) mixtures are used.

The performance of an ORC system can be visualized by T-H diagrams [13]. For the description of the complete process not only the Rankine cycle, but also the process lines for the air and the cooling water are to be included. Any pinch point breach can be seen on it and the temperature differences along the heat transfer processes can easily be seen as a direct measure of thermodynamic irreversibilities. Figure 3 shows the T-H diagram for n-hexane, mixture ($\xi_1=0.5$) and n-decane under the conditions given in Table 1. The full line shows the step in which turbine produces power. It is noticed that the area bounded by the enthalpy lines is least for the system with n-decane as working fluid. This is also reflected in the values of the efficiency of the process which is lowest for n-decane. The best thermodynamic case would be when the lines along the heat transfer from and to the cycle would fall on each other, although the heat exchanger area would then increase towards infinity.

![T-HT Diagram](image-url)

*Fig. 3. T-H diagram n-hexane, n-decane and the mixture ($\xi_1=0.5$) at 1500 kPa without superheating (source temperature =773.15K).*
Qualitatively the same trend in the values of exergy loss/destruction rates and the efficiencies was observed for the n-hexane (1) + n-dodecane (2) system. Here too, the highest second law efficiency is achieved ($\Psi_{\text{total}} = 0.561$) for ($\xi_1 = 0.9$) mixture and lowest ($\Psi_{\text{total}} = 0.343$) for n-dodecane as working fluid. A comparison of the results for the mixture of n-hexane + n-decane with the pure fluid n-octane showed that the mixtures always performed better than the equivalent pure fluid as working medium.

### 3.2. Calculations at constant condenser temperature

Calculations were performed for n-hexane, n-decane, n-dodecane and the mixtures n-hexane(1) + n-decane(2), and n-hexane(1) + n-decane(2) having different concentrations (mass fraction of hexane = $\xi_1$) as working fluid at a constant condensation temperature ($T_{f,s} = 323.15$ K). The saturation pressure for the liquid state varied from 0.88 kPa (n-decane) to 54.09 kPa (n-hexane). The parameters defined by equations (9) – (18) and the required surface areas for the heat exchanger and the condenser were calculated. Using the thermodynamic parameters from [19] the efficiencies and the required surface areas for the heat exchanger and the condenser were calculated. Some typical results are summarized in Table 2 together with important process parameters. The values refer to a boiler pressure of 1500 kPa and the hot air inlet temperature of 773.15 K.

The increase of $\eta_{\text{th,ORC}}$, $\eta_{\text{th,total}}$ and $\Psi_{\text{total}}$ with the increasing boiler pressure was observed for n-hexane, n-decane and their mixtures. Also both the first law and second law efficiencies dropped with increasing temperature level and was highest without superheating. Hence the results without superheating for the case that the energy is available at the high temperature 773.15 K (range c from above) are reported here.
Table 2. Comparison of different parameters of ORC systems with hexane(1), decane(2) and their mixtures as working fluid.

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<td>461.72</td>
</tr>
<tr>
<td>(m_r (kg/s))</td>
<td>1.025</td>
<td>1.238</td>
<td>1.494</td>
<td>1.587</td>
</tr>
<tr>
<td>(\eta_{th,ORC})</td>
<td>0.201</td>
<td>0.143</td>
<td>0.165</td>
<td>0.171</td>
</tr>
<tr>
<td>(\eta_{th,total})</td>
<td><strong>0.182</strong></td>
<td><strong>0.130</strong></td>
<td><strong>0.150</strong></td>
<td><strong>0.150</strong></td>
</tr>
<tr>
<td>(P_{Turbine}(kW))</td>
<td>188.9</td>
<td>135.5</td>
<td>156.8</td>
<td>162.3</td>
</tr>
<tr>
<td>(P_{Pump}(kW))</td>
<td>2.6</td>
<td>3.2</td>
<td>4.0</td>
<td>4.3</td>
</tr>
<tr>
<td>(P_{net}(kW))</td>
<td>182.4</td>
<td>129.6</td>
<td>149.7</td>
<td>150.2</td>
</tr>
<tr>
<td>(P_{P,W}(kW))</td>
<td>3.8</td>
<td>2.7</td>
<td>3.2</td>
<td>7.9</td>
</tr>
<tr>
<td>(A (m^2))</td>
<td>465.9</td>
<td>384.7</td>
<td>324.7</td>
<td>311.3</td>
</tr>
<tr>
<td>(\Delta \dot{E}_{air,3,0}(kW))</td>
<td>397.8</td>
<td>397.8</td>
<td>397.8</td>
<td>397.8</td>
</tr>
<tr>
<td>(\dot{\dot{E}}_{\text{boiler}}(kW))</td>
<td>59.2</td>
<td>97.6</td>
<td>130.3</td>
<td>138.8</td>
</tr>
<tr>
<td>(\dot{\dot{E}}_{\text{turbine}}(kW))</td>
<td>20.2</td>
<td>15.4</td>
<td>20.4</td>
<td>22.0</td>
</tr>
<tr>
<td>(\dot{\dot{E}}_{\text{condenser}}(kW))</td>
<td>84.1</td>
<td>78.6</td>
<td>31.8</td>
<td>50.1</td>
</tr>
<tr>
<td>(\Delta \dot{E}_{acc,water}(kW))</td>
<td>45.6</td>
<td>70.6</td>
<td>58.4</td>
<td>24.5</td>
</tr>
<tr>
<td>(\dot{\dot{E}}_{\text{net,exhaust}}(kW))</td>
<td>4.2</td>
<td>4.2</td>
<td>4.2</td>
<td>4.2</td>
</tr>
<tr>
<td>(\Delta \dot{E}_{\text{process}}(kW))</td>
<td>173.9</td>
<td>201.7</td>
<td>193.8</td>
<td>227.2</td>
</tr>
<tr>
<td>(A_{\text{condenser}}(m^2))</td>
<td>233.7</td>
<td>97.9.0</td>
<td>164.5</td>
<td>196.4</td>
</tr>
<tr>
<td>(p_{\text{condenser}}(kPa))</td>
<td>0.88053</td>
<td>37.389</td>
<td>50.81</td>
<td>54.087</td>
</tr>
<tr>
<td>(\Psi_{\text{total}})</td>
<td><strong>0.567</strong></td>
<td><strong>0.498</strong></td>
<td><strong>0.518</strong></td>
<td><strong>0.435</strong></td>
</tr>
</tbody>
</table>

It is observed from Table 2 that under the conditions that the temperature of the condenser is held constant at 323.15 K the thermal efficiency for the complete process, \(\eta_{th,total}\) is lowest for the mixture (\(\xi_1=0.5\)) and highest for n-decane. The second law efficiency \(\Psi_{\text{total}}\) is also highest for n-decane (0.567) followed by the mixtures (0.518 for \(\xi_1=0.9\) and 0.498 for \(\xi_1=0.5\)). The second law efficiencies for different mixtures at constant condenser temperature (solid line) and constant condenser pressure (dashed line) are shown in Fig. 4. N-decane has the highest boiling temperature at a fixed boiler pressure while the condenser pressure is now very low for the fixed condenser temperature case, thus, the heat addition occurs at the highest average temperature and the heat rejected is same for all fluid compositions. The lowest second law efficiency is found with n-hexane as working fluid. The exergy loss for the process was lowest for n-decane followed by the different mixtures and by n-hexane. The exergy loss with the exhaust is very small in all the cases. The main difference in the exergy loss arises due to large exergy destruction in the boiler for n-hexane and for the mixtures.
3.3. Calculations for heat source at 623.15 K

An examination of $T - \dot{H}$ diagram given in Figure 3 shows a parallel course of the enthalpy curves for the heat source at 773.15 K and the working fluid. One observes also some free space above the heating line of the working fluid. The heating line for the heat source will have smaller slope and will be nearer to working fluid line for a heat source at a lower temperature, e.g. 623.15 K. In this case a good thermal match between the heat source line and the working fluid line (where a mixture is used) will be achieved and thus a better utilization of energy should be possible. Therefore, some exemplary calculations were performed with heat source at 623.15 K at constant condensation temperature of 323.15K. As expected higher second law efficiencies were obtained for mixtures as working fluid. The results are shown in Table 3. The values refer to a boiler pressure of 1500 kPa, hot air inlet temperature of 623.15 K.
Table 3. Comparison of different parameters of ORC systems with hexane(1), decane(2) and their mixtures as working fluid.

<table>
<thead>
<tr>
<th></th>
<th>$\xi_1 = 0.0^{(a)}$</th>
<th>$\xi_1 = 0.5$</th>
<th>$\xi_1 = 0.9$</th>
<th>$\xi_1 = 1.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{F,3}$ (K)</td>
<td>522.691</td>
<td>529.931</td>
<td>476.831</td>
<td>461.72</td>
</tr>
<tr>
<td>$\dot{m}_f$ (kg/s)</td>
<td>1.175</td>
<td>1.192</td>
<td>1.438</td>
<td>1.528</td>
</tr>
<tr>
<td>$\eta_{th,ORC}$</td>
<td>0.193</td>
<td>0.143</td>
<td>0.165</td>
<td>0.171</td>
</tr>
<tr>
<td>$\eta_{th,total}$</td>
<td><strong>0.163</strong></td>
<td><strong>0.125</strong></td>
<td><strong>0.144</strong></td>
<td><strong>0.145</strong></td>
</tr>
<tr>
<td>$P_{Turbine}$ (kW)</td>
<td>171.7</td>
<td>130.5</td>
<td>151.0</td>
<td>156.3</td>
</tr>
<tr>
<td>$P_{Pump}$ (kW)</td>
<td>1.0</td>
<td>3.1</td>
<td>3.9</td>
<td>4.1</td>
</tr>
<tr>
<td>$P_{net}$ (kW)</td>
<td>163.4</td>
<td>124.7</td>
<td>144.1</td>
<td>144.6</td>
</tr>
<tr>
<td>$P_{P,W}$ (kW)</td>
<td>7.4</td>
<td>2.6</td>
<td>3.1</td>
<td>7.6</td>
</tr>
<tr>
<td>$A$ (m$^2$)</td>
<td>1332.2</td>
<td>1127.5</td>
<td>644.3</td>
<td>581.4</td>
</tr>
<tr>
<td>$\Delta\dot{E}_{air,3,0}$ (kW)</td>
<td>317.8</td>
<td>317.7</td>
<td>317.6</td>
<td>317.6</td>
</tr>
<tr>
<td>$\dot{E}_{Boiler}$ (kW)</td>
<td>22.8</td>
<td>28.8</td>
<td>60.2</td>
<td>68.3</td>
</tr>
<tr>
<td>$\dot{E}_{Turbine}$ (kW)</td>
<td>20.2</td>
<td>14.8</td>
<td>19.6</td>
<td>21.2</td>
</tr>
<tr>
<td>$\dot{E}_{Condenser}$ (kW)</td>
<td>80.1</td>
<td>75.7</td>
<td>30.7</td>
<td>48.2</td>
</tr>
<tr>
<td>$\Delta\dot{E}_{air,steam}$ (kW)</td>
<td>23.1</td>
<td>68.0</td>
<td>56.2</td>
<td>23.6</td>
</tr>
<tr>
<td>$\dot{E}_{Sat.,Exhau}$ (kW)</td>
<td>5.9</td>
<td>6.1</td>
<td>6.1</td>
<td>6.1</td>
</tr>
<tr>
<td>$\Delta\dot{E}_{turbine}$ (kW)</td>
<td>137.3</td>
<td>131.0</td>
<td>123.4</td>
<td>155.6</td>
</tr>
<tr>
<td>$A_{Condenser}$ (m$^2$)</td>
<td>169.0</td>
<td>94.2</td>
<td>158.4</td>
<td>189.0</td>
</tr>
<tr>
<td>$p_{Condenser}$ (kPa)</td>
<td>0.88053</td>
<td>37.389</td>
<td>50.81</td>
<td>54.087</td>
</tr>
<tr>
<td>$\Psi_{total}$</td>
<td><strong>0.576</strong></td>
<td><strong>0.595</strong></td>
<td><strong>0.619</strong></td>
<td><strong>0.519</strong></td>
</tr>
</tbody>
</table>

(a) For n-decane the calculations were performed only at 500 kPa boiler pressure due to pinch point restrictions. These are reported here.

As the same amount of power is to be transferred over a small temperature range the required mass flow rate of air is higher and so are the mass flow rates of the fluids. For heat transfer from the hot air to the working fluid it is necessary that the temperature of air is higher than the temperature of working fluid throughout the corresponding stages. Hence the temperature of air at state 1 ($T_{air,1}$) must be higher than the saturation temperature of fluid at the given turbine pressure ($T_{F,1}$). This is now the pinch point. $T_{air,1}$ had to follow the pinch point restrictions. It has to be increased. This is achieved by increasing $T_{air,0}$. The thermal efficiencies of the organic Rankine cycles $\eta_{th,ORC}$ do not change if the other conditions are kept the same [refer to equation (9)]. It is observed that both $\eta_{th,total}$ and $\Psi_{total}$ with the heat source at 623.15 K is lower than that at 773.15 K. The highest total thermal efficiency is obtained with n-decane as working fluid. The second law efficiencies follow the order:

$$\Psi_{total}(\xi_1 = 0.9) > \Psi_{total}(\xi_1 = 0.5) > \Psi_{total}(\text{n-decane}) > \Psi_{total}(\text{n-hexane}).$$

Fig. 5 shows the $T$-$H$ diagram for n-hexane, n-hexane + n-decane mixture ($\xi_1 = 0.9$) and n-decane at saturation vapour pressures at 1500 kPa boiler pressure and 323.15 K condenser temperature.
Fig. 5. T-H diagram n-hexane, n-decane and the mixture ($\xi_1=0.9$) at 1500 kPa without superheating (source temperature =623.15K).

Conclusions

Organic Rankine cycles working with pure fluids or their mixtures were investigated for their usage in combined heat and power generation systems, utilizing low grade heat available either at 773.15 K or at 623.15K from exhaust gases from turbines and engines as well as from industrial plants. Model calculations of binary mixtures of different compositions of one short chain alkane with one long chain alkane (hexane + decane, hexane + dodecane) were performed at a certain condenser pressure or temperature and different boiler pressures and temperatures. The usefulness of binary mixtures compared to pure fluids depends strongly on the parameters which are fixed. For pure fluids as well as for the mixtures higher first law ($\eta_{th,\text{total}}$) and second law efficiencies ($\Psi_{\text{total}}$) were obtained at higher boiler pressures. At a fixed boiler pressure the efficiencies decreased with increasing boiler temperatures due to the fact that the fluid left the turbine as superheated vapour. At a fixed condenser pressure the mixtures performed better than the pure fluids. The second law efficiency increased by 20-50%. The exergy destruction rate in the boiler is higher for small chain alkanes followed by the mixtures ($\xi_1=0.9$), ($\xi_1=0.5$) and the long chain alkanes. The exergy destruction rates in the turbine are comparatively low. The required surface areas for the heat exchanger do not differ much from each other. However, the required surface area in case of n-hexane and ($\xi_1=0.9$) mixture are higher than those required when n-decane and ($\xi_1=0.5$) mixtures are used. At a fixed condenser temperature which results in different pressure the first law efficiency with pure long chain alkane is much higher than that obtained with mixtures or short chain alkane. The second law efficiencies achieved with long chain alkane and mixtures do not differ much but the efficiency with pure short chain alkane n-hexane is lower. The required surface area for the heat exchanger and condenser was highest for long chain alkane. By using the heat source at 623.15 K and taking advantage of the non-isothermal boiling of fluid mixtures a better
thermal match between the working fluid and the heat source as well as between the working fluid and the cooling water stream could be obtained. A comparison of the results for the mixture of n-hexane + n-decane with the pure fluid n-octane showed that the mixtures always performed better than the equivalent pure fluid as working medium.

**Nomenclature**

\( A \)  
area (surface area for heat exchanger), \( \text{m}^2 \)

\( \Delta \dot{E}_{\text{air}} \)  
total exergy loss rate air, kW

\( \dot{E}_{\text{air},3} \)  
exergy of air stream, kW

\( \Delta \dot{E}_{\text{air},3,0} \)  
exergy loss rate of air stream from state 3 to state 0, kW

\( \dot{E}_{\text{Exhaust}} \)  
exergy in exhaust, kW

\( \Delta \dot{E}_{\text{water}} \)  
exergy gain (accumulation) rate in water, kW

\( c_{p,\text{air}} \)  
specific heat capacity of air, \( \text{kJ/(kg K)} \)

\( H \)  
enthalpy stream, kW

\( h_{\text{air},i} \)  
specific enthalpy of air in state \( i \), \( \text{kJ/kg} \)

\( h_{F,i} \)  
specific enthalpy of fluid in state \( i \), \( \text{kJ/kg} \)

\( \dot{i}_{\text{Boiler}} \)  
exergy destruction rate in boiler, kW

\( \dot{i}_{\text{Condenser}} \)  
exergy destruction rate in condenser, kW

\( \dot{i}_{\text{Process}} \)  
exergy (loss+destruction) rate for the process, kW

\( \dot{i}_{\text{Pump}} \)  
exergy destruction rate in pump, kW

\( \dot{i}_{\text{W,W}} \)  
exergy destruction rate in cold water pump, kW

\( \dot{i}_{\text{Turbine}} \)  
exergy destruction rate in Turbine, kW

\( k_{i,j} \)  
heat transfer coefficient \( i \rightarrow j \), \( \text{kJ/(m}^2\text{ K)} \)

\( \dot{m}_{\text{air}} \)  
mass flow rate of air, kg/s

\( \dot{m}_{F} \)  
mass flow rate of fluid, kg/s

\( \text{ORC} \)  
organic Rankine cycle

\( P_{\text{Turbine}} \)  
turbine power, kW

\( P_{\text{Pump}} \)  
\( \text{ORC} \) pump power, kW

\( P_{\text{net}} \)  
the net power of the process, kW

\( P_{\text{P,W}} \)  
power of cold water pump, kW

\( P_{\text{Boiler}} \)  
pressure in boiler, kPa

\( P_{\text{Cond}} \)  
pressure in condenser, kPa

\( \dot{Q}_{\text{add}} \)  
rate of heat addition, kW

\( \dot{Q}_{\text{rem}} \)  
rate of heat removal, kW

\( T \)  
temperature, K

\( T_{\text{air},i} \)  
temperature of air in state \( i \), K

\( T-H \)  
temperature-enthalpy diagram

\( T-S \)  
temperature-entropy diagram

\( T_{F,i} \)  
temperature of fluid in state \( i \), K

\( T_{F,sat} \)  
saturation temperature of fluid at condenser pressure, K

\( T_{W,i} \)  
temperature of cold water in state \( i \), K

\( v \)  
specific volume of saturated liquid, \( \text{m}^3/\text{kg} \)
\( W_{s,0} \)  
specific work of ORC pump, kJ/kg

\( W_{P,W} \)  
specific work of the pump for cold water, kJ/kg

**Greek symbols**

- \( \eta_{s,P} \)  
  isentropic efficiency of pump
- \( \eta_{P,W} \)  
  efficiency of cold water pump
- \( \eta_{th,ORC} \)  
  thermal efficiency of ORC
- \( \eta_{th,total} \)  
  total thermal efficiency of the process
- \( \Delta p_{P,W} \)  
  pressure drop in cold water pump, kPa
- \( \Delta T_{LMTD,ij} \)  
  logarithmic mean temperature difference between state \( i \) and \( j \), K
- \( \Delta T_i \)  
  difference between the temperature of air and that of fluid in state \( i \), K
- \( \Delta T_{pinch} \)  
  difference between the temperature of hot air and the fluid at pinch point, K
- \( \Psi_{total} \)  
  second law efficiency
- \( \xi_i \)  
  mass fraction of component \( i \) of a mixture

**Subscripts and superscripts**

- \( air \)  
  air
- \( cond \)  
  condenser
- \( Device \)  
  device such as boiler, condenser, pump
- \( F \)  
  fluid
- \( i,j \)  
  state points 0,1,2,3,4,5
- \( LMTD \)  
  logarithmic mean temperature difference
- \( ORC \)  
  organic Rankine cycle
- \( P,W \)  
  cold water pump
- \( pinch \)  
  pinch point
- \( s \)  
  isentropic
- \( sat \)  
  saturated
- \( surr \)  
  surroundings
- \( th \)  
  thermal
- \( W \)  
  water, cold water

**References**


Excess Enthalpies of Second Generation Biofuels

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Abstract:
The use of biofuels is increasing in the EU with the target of decrease the dependency of the petroleum and also to reduce CO\textsubscript{2} emissions and to support the agricultural community. A wide variety of biogenic products is added to fuels and the quality of these products becomes more important requiring an accurate knowledge of the thermodynamic properties of the new fuel blends. Between these properties the heats of mixing or the excess enthalpies are needed to calculate the energy balances.

The 1-pentanol is considered an alcohol of the second generation of biofuels, it has some advantages in comparison with ethanol such as a lower vapour pressure and higher heating values, quite similar to the gasoline.

In this work the experimental values of the excess enthalpies for the binary mixtures containing 1-pentanol and hydrocarbons as hexane, 1-hexene and 1,2,4-trimethyl benzene at 25°C and 40°C and atmospheric pressure are reported. A flow calorimeter developed in our laboratory was used for the measurements.

Keywords:
Biofuels, 1-pentanol, excess enthalpy, hexane, 1-hexene, 1,2,4-trimethyl benzene.

1. Introduction

The European Union is strongly dependent on fossil fuels for its transport needs so that the EU has adopted measures to encourage the production and use of sustainable biofuels because they can provide a very significant contribution in the short to medium term. Furthermore, biofuels can contribute to the EU’s objectives of securing the EU fuel supply while improving the greenhouse gas balance and fostering the development of a competitive European (biofuels and other) industry.

To facilitate the wider use of biofuels in road transport, biofuels and blends need to become increasingly compatible with existing logistics as well as future ones but a good characterization of the thermodynamic properties is needed to obtain an in-depth understanding for example of the relationship between biofuel quality and engine performance.

In this context, 1-pentanol is a very important compound in the second generation of biogasolines due to the fact that it has high octane rating, up to 100 Research Octane Number (RON), better water tolerance and very high heat of combustion.

In this perspective and due to the fact that the new ‘blends’ of the second generation biofuels require reference materials with well-characterized reference values, our group decided to do a complete study of the mixtures 1-pentanol + hydrocarbons behaviour, as part of a research project. In this paper excess molar enthalpies measurements for the systems 1-pentanol with hydrocarbons as hexane, 1-hexene and 1,2,4-trimethyl benzene are reported. They have been measured at two different temperatures (298.15 to 313.15) K and at atmospheric pressure.
2. Experimental section

2.1. Materials

The compounds were purchased from Sigma-Aldrich and were of the highest purity available, chromatography quality reagents with a purity >0.99 (GC) for 1-pentanol, >0.99 (GC) for hexane, >0.97 (GC) for 1-hexene and >0.98 (GC) for 1,2,4-trimethyl benzene. Their purities were also checked by gas chromatography and all were found to be >0.997.

2.2. Apparatus and procedure

An automated quasi-isothermal flow calorimeter has been developed in our laboratory[1] for the accurate measurement of excess enthalpies at atmospheric pressure. It is based on the accurate measurement of the energy required to maintain the mixing vessel at a constant temperature. To achieve this condition, a Peltier cooler removes, at constant rate, energy from the flow cell and a control-heater compensates this energy and additionally the energy liberated (exothermic mixing) or absorbed (endothermic mixing) by the mixing process. Excess enthalpy is calculated by the determination of the net power exchanged.

A schematic view of the calorimeter is shown in Figure 1. Two precision isocratic pumps with dual floating pistons in series, (Agilent 1100 used in HPLC chromatography) delivers the pure compounds through the cell at a programmable constant flow rate. The fluids pass through a loop immersed in the bath (Hart Scientific, model 7041) to ensure that it reaches the bath temperature prior to entering the cell. The mixing point is at the bottom of the cell and it is made of two concentric tubes.

![Figure 1. Schematic view of the calorimeter.](image)

The cell is a stainless steel vessel containing a copper block where all the energy in the process is exchanged by conduction. The liquid flows through a stainless steel tube which is coiled around the copper block. The fluid inlet and outlet temperature has to be the same, and it is the bath temperature in which the cell is immersed.
At the top of the copper block is the Peltier cooler to remove at constant rate energy from the flow cell and the heater (100 Ω resistance used as a control heater). Refrigeration power is set and held constant through a DC power supply (Agilent E3640A) during the experiments and the control heater is connected to a function generator (Agilent 33220A) of arbitrary waveform, to change the power input into the cell.

The calorimeter is controlled using the value of an NTC thermistor connected to a multimeter (Agilent 3458 A) and located at the top of the flow cell, which is also used to measure the exit temperature. The cell is shown in Figure 2.

![Figure 2. Photograph of the measuring cell.](image)

A complete automation system supplies everything needed such as data acquisition, monitoring, and controlling to operate the calorimeter and take measurements from a single personal computer. The automation program has been done using Agilent-VEE language. The optimum total flow rate ranges from (0.5 to 1) ml/min which depends on the effect of mixing.

An electrical calibration of the calorimeter is carried out using the calibration resistance located on the bottom of the cell. It consists of the simulation of different energies in a calibration resistance by Joule effect at the same conditions as in the experimental measurements. The Peltier cooler, the control-heater and the calibration heater are each connected to their own DC power supplies. These devices are controlled using a computer with a GPIB connection and specific software developed in our laboratory.

The measuring procedure starts with a flow of one pure compound to set up the power input to maintain the gradient temperature \(Q_{\text{base}}\), it indicates the energy losses in the system. After that we program the different volumetric flows to measure the energy of the excess enthalpy at different compositions \(Q_{\text{measured}}\). Then you can calculate the net power \(Q_{\text{net}}\) with the difference between \(Q_{\text{measured}}\) and \(Q_{\text{base}}\). Finally the excess enthalpy is calculated using net power, electrical calibration and molar flow.

The properties measured directly and their corresponding uncertainties are: flow rate ± 0.15% (1-10 mL/min); temperature ± 10 mK; the heating and cooling systems have an stability better than 2.4 μW, and it results in an uncertainty of ± 0.0001 in the composition of the mixture and the extended uncertainty in the excess molar enthalpy is better than ± 1% for a covar factor of 2 which means a confidence level of 0.95.

3. Results

For the same three binary mixtures the excess enthalpies were measured at T= (298.15 and 313.15) K, these experimental data as a function of the composition and the calculated results are given in Figure 3. Density values and molecular weight of pure compounds, needed to compute mass flow from volumetric flow, it has been obtained from the literature. These data are given in Table 1.
Table 1. Density and molecular weight of pure compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Density at 293.15 K (kg·m⁻³)</th>
<th>Density at 303.15 K (kg·m⁻³)</th>
<th>Molecular Weight (g·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Pentanol</td>
<td>815.10ₐ</td>
<td>807.90ₐ</td>
<td>88.149</td>
</tr>
<tr>
<td>Hexane</td>
<td>659.33ₐ</td>
<td>650.18ₐ</td>
<td>86.177</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>673.00ₐ</td>
<td>663.70ₐ</td>
<td>84.159</td>
</tr>
<tr>
<td>1,2,4-Trimethyl benzene</td>
<td>873.66ₐ</td>
<td>867.61ₐ</td>
<td>120.19</td>
</tr>
</tbody>
</table>

ₐReference 2. ₉Reference 3. ₈Reference 4. ₅Reference 5

The data have been correlated using Redlich-Kister equation:

\[
H^E_m(J \cdot mol^{-1}) = x \cdot (1-x) \cdot \sum_{i=1}^{n} A_i \cdot (2x-1)^{i-1} \sqrt{1+C(2x-1)}
\]  

(1)

and the standard deviations \( \sigma (H^E_m) \) were calculated by:

\[
\sigma (H^E_m) = \left[ \sum_{i=1}^{N} \left( H^E_{m,exp} - H^E_{m,calc} \right)^2 / (N-n) \right]^{1/2}
\]

(2)

where \( N \) is the number of experimental points and \( n \) is the number of coefficients \( A_i \). The calculated parameters of the equation, standard deviations and absolute maximum deviation are summarized in Table 2.

Table 2. Parameters of Redlich-Kister equation, standard deviation of excess molar enthalpies \( \sigma \) and, absolute maximum deviation \( (|\Delta H^E_{m,\text{max}}|) \) for the measured systems.

| T (K) | A₁ | A₂ | A₃ | A₄ | A₅ | C   | \( \sigma \) | \( |\Delta H^E_{m,\text{max}}| \) |
|-------|----|----|----|----|----|-----|------------|----------------|
|       |    |    |    |    |    |     |            |                |
| 298.  |    |    |    |    |    |     |            |                |
| 15    | 191| 589.| 973.| 530.| 228.| 3.   | 74 8.40    |
|       | 6.5| 23 | 47 | 22 | 83 | 0.98 |           |
| 313.  |    |    |    |    |    |     |            |                |
| 15    | 262| 771.| 119.| 320.| 516.| 2.   | 55 4.25    |
|       | 0.0| 09 | 4.9| 28 | 14 | 0.93 |           |
| 298.  |    |    |    |    |    |     |            |                |
| 15    | 213| 408.| 112.| 174.| 154.| 1.   | 74 3.10    |
|       | 3.6| 47 | 7.0| 68 | 42 | 0.96 |           |
| 313.  |    |    |    |    |    |     |            |                |
| 15    | 288| 745.| 907.| 520.| 180.| 3.   | 95 8.70    |
|       | 1.9| 68 | 45 | 79 | 92 | 0.93 |           |
| 298.  |    |    |    |    |    |     |            |                |
| 15    | 374| 126.| 988.| 438.| 441.| 3.   | 97 3.92    |
|       | 8.7| 9.3| 91 | 13 | 08 | 0.87 |           |
| 313.  |    |    |    |    |    |     |            |                |
| 15    | 473| 176.| 502.| 566.| 87.1| 1.   |           |
|       | 4.3| 7.6| 14 | 25 | 7 | 0.82 |           |

2/1
The experimental data as a function of the composition and the calculated results with Redlich-Kister equation are represented in Figure 3.

Figure 3. Experimental excess molar enthalpies as function of the composition for the binary systems 1-pentanol(1) + hexane(2) (○) at 298.15 K and (●) at 313.15 K; 1-pentanol(1) + 1-hexene(2) (△) at 298.15 K and (▲) at 313.15 K; and 1-pentanol(1) + 1,2,4-trimethyl benzene(2) (□) at 298.15 K and (■) at 313.15 K.

4. Discussion and Conclusions

We have chosen for this study a paraffin, an olefin and an aromatic hydrocarbon because these type of hydrocarbons are the most representative in the composition of any gasoline. We want to know the behavior of the blending with a second generation biofuel such as 1-pentanol. In this case we studied the excess enthalpies as function of the composition for the binary systems 1-pentanol with hexene, 1-hexene or 1,2,4-trimethyl benzene.

Concerning the effect of mixing, all systems have a strong endothermic behaviour which increases at higher temperatures, this behaviour is coherent with the results for the systems 1-pentanol with cyclehexane or toluene measured in our laboratory [6].

All the systems have a strong endothermic behaviour (positive excess enthalpy), the highest excess enthalpy is observed for the system 1-pentanol + 1,2,4-trimethyl benzene at 313.15 K. The maximum value is $H^E_m = 1257$ J·mol$^{-1}$ for a mole fraction of 1-pentanol of 0.35 at $T= 313.15$ K and it decreases to $H^E_m = 1015$ J·mol$^{-1}$ at the same composition at $T= 298.15$ K.
On the other hand, the binary mixture 1-pentanol + 1-hexene shows the maximum excess enthalpy at a mole fraction of 1-pentanol of 0.30 and the corresponding values are $H_m^E = 829 \text{ J} \cdot \text{mol}^{-1}$ at 313.15 K and $H_m^E = 617 \text{ J} \cdot \text{mol}^{-1}$ at 298.15 K.

Finally the binary mixture 1-pentanol + hexane presents the maximum excess enthalpy at a mole fraction of 1-pentanol of 0.35 and the corresponding values are $H_m^E = 724 \text{ J} \cdot \text{mol}^{-1}$ at 313.15 K and $H_m^E = 538 \text{ J} \cdot \text{mol}^{-1}$ at 298.15 K.

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**References**


**Responsibility notice**

The authors are the only responsible for the printed material included in this paper.
Local stability analysis of a Curzon-Ahlborn engine considering the Van der Waals equation state in the maximum ecological regime

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Abstract:
In this work we analyze the stability of an endoreversible Curzon-Ahlborn-Novikov engine, using Van der Waals gas as a working substance and the corresponding efficiency for this engine working at temperatures within the maximum ecological regime. From the local stability analysis we find that a critical point of an almost linear system is stable and analytically expressed in eigenvalues. After an arbitrarily small perturbation, the system state exponentially decays to a critical point, with either of two characteristic relaxation times, which are a function of the thermal conductance ($\alpha$), heat capacity ($C$) and $\tau=T_2/T_1$. The behavior of relaxation times and solution of the systems are qualitatively shown by sketching its phase portrait, which results susceptible to operating regimes, i.e. the eigenvectors in the maximum ecological regime have a clockwise rotation with respect to the eigenvectors in the regime of maximum power. Finally, we have to observe that after the approximation $\lambda_{VW} = 1$, we obtain $\eta_{VWE} = \frac{3}{4} \eta_C$, where $\eta_{VWE}$ is the van der Waals efficiency at maximum ecological regime and $\eta_C$ is Carnot’s efficiency. Finally we discuss the local stability and steady state of the energetic properties of the endoreversible engine.

Keywords:
Endoreversible, Ecological Regime, Dynamics, Van der Waals equation, Stability, Steady State.

1. Introduction

One of the important topics in thermodynamics has been the formulation of the criteria for comparing the performance of real processes. For example, the Carnot engine provides an upper bound on the efficiency of all heat engines operating between two fixed-temperature thermal-reservoirs. Clausius, Kelvin and others carried out pertinent studies by identifying limits on works, heat input and efficiency of various heat engines. The use of reversible processes as standards of performance is no desirable because a reversible process must be carried out at an infinitesimally-slow pace, or requires an infinitely-large heat-exchanger surface-area. Since power produced by a heat engine is work divided by time, a finite time amount of work produced by the engine over an infinite time delivers no power. The need to produce a finite amount of power in a real heat-engine is one of the reasons why the performance criterion of an ideal, reversible heat-engine is seldom used. There is a strong need in industry to find new bounds in power and efficiency for comparing the performances of thermal-power cycles. In this direction a new branch of irreversible thermodynamics, called finite time thermodynamics (FTT) has been developed during the last pastyears [1-9]. This FTT originated from the pioneering Curzon-Ahlborn (CA) [10] as a non-equilibrium approach to systems undergoing irreversible processes; which are visualized as
networks of internally reversible (endoreversible [10]) subsystems exchanging energy in an irreversible fashion among themselves and with the environment. Perhaps the simplest and most extensively studied FTT system is the so-called Curzon-Ahlborn-Novikov (CAN) engine [5,6,8-10]. This engine consists on a Carnot engine which exchanges heat with thermal baths $T_1$ and $T_2$ ($T_1 > T_2$) through thermal conductors governed by the linear Newton heat transfer law. The CAN engine has non-zero power output, a positive entropy production and a more realistic efficiency (in terms of $T_1$ and $T_2$) than of the Carnot engine.

It is important to mention that this theory has been heavily criticized, partially because of the mainframe thermodynamics community who does not consider this theory as an extension of irreversible thermodynamics. However, Salamon P.[11] and Andresen B.[12] have perfectly established the application of the FTT. In fact, Andresen B.[12] said that at least 597 papers have been written in the context of this branch of thermodynamics. The subject has also made its way into textbooks [13, 14].

Most of the studies of FTT have been concerned with their steady-state energetic properties, which are important from the designed point of view. On the other hand, only a few of these studies have dealt with the system’s dynamic properties, such as the response to noisy perturbation or the stability of the system’s steady-state.


In 1991, Angulo-Brown [21] developed an ecological optimization criterion for FTT-thermal cycles. This criterion consists on the maximization of a function $E$ that represents a good compromise between high power output and low entropy production. This function is given by $E = P - T_2 \sigma$, where $P$ is the power output of the cycle, $\sigma$ the total entropy production (system plus surroundings) per cycle, and $T_2$ the temperature of the cold reservoir. When function $E$ is maximized, the CA cycle has a configuration that produces around 80% of the maximum power and only about 30% of the entropy produced in the maximum power. Another important property of the maximum ecological regime is that the CA-engine’s efficiency in this regime $\eta_E$, is given by $\eta_E \approx \frac{1}{2} (\eta_C + \eta_{CA})$, where $\eta_C$ is the Carnot efficiency and $\eta_{CA}$ is the CA efficiency.

The paper is organized as follows. In section 2, we describe the local stability analysis method applied to a two-dimensional system. In section 3, a brief description of an endoreversible engine is presented. In section 4, the local stability analysis of a CAN engine using a Van der Waals gas as working substance in the maximum power regime is presented. In section 5, we discuss our results in context of the thermodynamic. Finally, in section 6 we write some comments.

In this work we present a local stability analysis to an endoreversible CAN engine using a Van der Waals gas as working substance in the maximum ecological regime.

2. Linearization and stability analysis

In this section, we show a brief description of both the linearization technique for two-dimensional dynamical systems, and the fixed point local stability analysis [17]. Consider a dynamical system

$$\frac{dx}{dt} = f(x,y)$$

(1)
\[
\frac{dy}{dt} = g(x,y).
\]  \hspace{1cm} (2)

Let \((\bar{x}, \bar{y})\) be a fixed point such that \(f(\bar{x}, \bar{y}) = 0\) and \(g(\bar{x}, \bar{y}) = 0\). Consider a small perturbation around this fixed point and write \(x = \bar{x} + \delta x\) and \(y = \bar{y} + \delta y\), where \(\delta x\) and \(\delta y\) are small disturbances from the corresponding fixed point values. By substituting equations (1) and (2), expanding \(f(\bar{x} + \delta x, \bar{y} + \delta y)\) and \(g(\bar{x} + \delta x, \bar{y} + \delta y)\) in a Taylor series and using the fact that \(\delta x\) and \(\delta y\) are small to neglect quadratic terms, the following equations are obtained for the perturbations:

\[
\begin{pmatrix}
\frac{d\delta x}{dt} \\
\frac{d\delta y}{dt}
\end{pmatrix} = \begin{pmatrix} f_x & f_y \\
g_x & g_y \end{pmatrix} \begin{pmatrix} \delta x \\
\delta y \end{pmatrix},
\]  \hspace{1cm} (3)

where \(f_x = \frac{\partial f}{\partial x}|_{\bar{x}, \bar{y}}\); \(g_x = \frac{\partial g}{\partial x}|_{\bar{x}, \bar{y}}\); \(f_y = \frac{\partial f}{\partial y}|_{\bar{x}, \bar{y}}\) and \(g_y = \frac{\partial g}{\partial y}|_{\bar{x}, \bar{y}}\).

Equation (3) is a linear system of differential equations. Thus, we assume that the general solution of the system is

\[
\delta \vec{r} = e^{\lambda t} \vec{u},
\]  \hspace{1cm} (4)

with \(\delta \vec{r} = (\delta x, \delta y)\) and \(\vec{u} = (u_x, u_y)\). Substitution of the solution \(\delta \vec{r}\) into equation (3) yields the following eigenvalue equation:

\[
A \delta \vec{r} = \lambda \delta \vec{r},
\]  \hspace{1cm} (5)

where \(A\) is the matrix given by the first term on the right-hand side equation (3). The eigenvalues of this equation are the roots of the characteristic equation.

\[
|A - \lambda I| = 0
\]  \hspace{1cm} (6)

or

\[
(f_x - \lambda) (g_y - \lambda) - g_x f_y = 0.
\]  \hspace{1cm} (7)

If \(\lambda_1\) and \(\lambda_2\) are solutions of equation (7), the general solution of the system is

\[
\delta \vec{r} = c_1 e^{\lambda_1 t} \vec{u}_1 + c_2 e^{\lambda_2 t} \vec{u}_2,
\]  \hspace{1cm} (8)

where \(c_1\) and \(c_2\) are arbitrary constants and \(\vec{u}_1\) and \(\vec{u}_2\) are the eigenvectors corresponding to \(\lambda_1\) and \(\lambda_2\), respectively. To determine \(\vec{u}_1\) and \(\vec{u}_2\) we use the equation (5) again for each eigenvalue. Information about the stability of the system can be obtained from the eigenvalues \(\lambda_1\) and \(\lambda_2\). In general, \(\lambda_1\) and \(\lambda_2\) are complex numbers. If both \(\lambda_1\) and \(\lambda_2\) have negative real parts, the fixed point is stable. Moreover, if both eigenvalues are real and negative, perturbations decay exponentially. In this case, it is possible to identify characteristic time scales for each eigendirections as

\[
t_1 = \frac{1}{|\lambda_1|},
\]  \hspace{1cm} (9)

and

\[
t_2 = \frac{1}{|\lambda_2|}.
\]  \hspace{1cm} (10)

### 2.1 Van der Waals Model

To describe the behavior of real gases, Van der Waals proposed two corrections for the thermal equation of ideal gases \(pV = RT\). The first idea was that one has to correct the “volume” of molecules, which cannot be treated as points. Roughly speaking, the molecules can be visualized as little hard spheres. Therefore there is a minimum volume \(b\) (for 1 mole) which cannot be passed even by applying very large pressures. The quantity \(b\) can be regarded as the volume of 1 mole of molecules in a closed-packed arrangement. An obvious and simple way to correct this behavior is to replace \(V\) by \(V - b\), in the equation of ideal gases. The second correction is due to mutual attraction of the molecules. This attraction tends to decrease the volume or acts like an additive pressure. If
we consider a small surface layer of the gas, its attraction by the inner molecules should be proportional to the square of the density, i.e., proportional to 

3. The Curzon-Ahlborn-Novikov engine using a Van der Waals gas as working substance

Consider the endoreversible CAN heat engine Fig.1. This engine works between the heat reservoirs $T_1$ and $T_2$ ($T_1 > T_2$). The working temperatures at steady state are $T_1$ and $T_2$. Heat flows from $T_1$ to $T_2$ and from $y$ to $T_2$ through the thermal resistances are governed by the Newton’s heat transfer law, with a thermal conductance denoted by $\alpha$. Using the endoreversibility hypothesis, an engine working between the reservoirs $T_1$ and $T_2$ acts like a Carnot engine, although it works in finite time cycles, i.e.

\[ - \]

and

\[ - \]

\begin{equation}
T_1
\end{equation}

\begin{equation}
T_2
\end{equation}

\begin{equation}
\alpha
\end{equation}

\begin{equation}
C \cdot x
\end{equation}

\begin{equation}
C \cdot y
\end{equation}

\begin{equation}
P
\end{equation}

\begin{equation}
J_1
\end{equation}

\begin{equation}
J_2
\end{equation}

Fig.1 Schematic representation of a CAN engine consists of a Carnot engine (Ca) and the heat reservoirs $T_1$ and $T_2$. The heat exchange $J_1$ and $J_2$ takes place through both thermal conductors with the same conductance $\alpha$.

1 and 2 are the steady-state heat flows from $T_1$ to the engine, and from the engine to $T_2$ respectively. $\alpha$ is the engine power output.

The CA engine works usually in steady state, so that the heat flux from a reservoir at temperature $T_1$ is $J_1$, and the heat flux from the engine to the reservoir at temperature $T_2$ is $J_2$.

\begin{equation}
J_1
\end{equation}

\begin{equation}
J_2
\end{equation}

From equations (11) – (14), and from the definition of efficiency,
it follows that
\[ \bar{x} = \frac{T_1}{2} \left( 1 + \frac{T_2}{T_1} \right) \]  
\[ \bar{y} = \frac{T_1}{2} \left( 1 - \bar{\eta} \right) \left( 1 + \frac{T_2}{T_1} \right) \].  

The efficiency of a Curzon-Ahborn-Novikov engine working at maximum ecological regime using a Van der Waals gas as working substance was found by Ladino-Luna [22]

\[ \eta_{VWE} = 1 - \frac{1}{\sqrt{2}} \left( \tau + \tau^2 \right) \left\{ 1 + \left[ \frac{4}{3} \left( 1 + 3\tau \right) \frac{2}{\tau + \tau^2} - 1 \right] \lambda_{VW} + \left[ \frac{1}{16} \ln \left( 1 + 3\tau \right) - \frac{1}{2} \sqrt{\frac{2}{\tau + \tau^2}} \ln \sqrt{\frac{1}{2} \left( \tau + \tau^2 \right)} \right] \left[ 1 + 3\tau - 4 \frac{1}{\sqrt{2}} \left( \tau + \tau^2 \right) \lambda^2 v_w \right] \right\} + O(\lambda^3 v_w), \]  

(18)

where:

\[ \lambda_{VW} = \frac{1}{\gamma - 1} \left( \ln \frac{V_{\max} - b}{V_{\min} - b} \right)^{-1}, \]  

(19)

where \( b \) is a constant which depends on the gas, \( \gamma \) is the ratio of the constant-pressure and constant-volume heat capacities \( \gamma = C_p/C_v \), \( V_{\max} \) and \( V_{\min} \) are the subtended volumes, maximum and minimum respectively, by the gas in a cycle. Now if we consider that \( b \) is smaller than \( V_{\max} \) and \( V_{\min} \), table 13.1 [23], then the ratio \( (V_{\max} - b)/(V_{\min} - b) \) is approximately \( V_{\max}/V_{\min} \), this ratio is called volumetric compression ratio \( r_c \), for Diesel cycle the typical values are 12-15, table 10.1 [24], so we do the calculus using (19) obtaining \( \lambda_{VW} = 1.006 \), which shows that we can use for purposes of calculus \( \lambda_{VW} = 1 \), equation (19) give more values to \( \lambda_{VW} \), but are all not have physically mean. If \( \lambda_{VW} = 1 \) we obtain the approximate expression,

\[ \eta_{VWE} = \frac{3}{4} \eta_C. \]  

(20)

In the above approximation, we observe a relation between Carnot’s efficiency and Van der Waals’s efficiency at maximum power, which is \( \eta_{VWE} = 3 \eta_C/4 \). It is reasonable because \( \eta_{VW} \) is smaller than \( \eta_C \), so the efficiency of a CA engine working in the maximum power regime using a Van der Waals gas working substance is given by (20), with \( \tau = T_2/T_1 \).

Now, substituting this efficiency (20), into equations (16) and (17) renders

\[ \bar{x} = \frac{T_1}{2} \left( 1 + \frac{T_2}{T_1} \right) \]  
\[ \bar{y} = \frac{T_1}{2} \left( 1 + 7\tau \right). \]  

(21)

(22)

From (13), (15), (16) and (17) we can write the power output of the steady-state in terms of \( T_1 \) and \( T_2 \) and \( \tau \) and it becomes

\[ \bar{p} = \frac{3\tau T_1 \left( 1 - \tau \right)^2}{8 \left( 1 + 3\tau \right)}. \]  

(23)

Solving for \( T_1 \) and \( T_2 \), from equations (21) and (22) gives

\[ T_1 = -\frac{6\bar{x}\bar{y}}{\bar{x} - 7\bar{y}}, \]  

(24)

and

\[ T_2 = 2 \left( \frac{\bar{x}\bar{y} + 4\bar{y}^2}{\bar{x} + 7\bar{y}} \right). \]  

(25)

Finally substituting (24) and (25) in (23) we obtain the power output in steady-state \( \bar{p} \) as function of \( \bar{x} \) and \( \bar{y} \),

\[ \bar{p} = -\frac{a(x - y)^2}{x - 7y}. \]  

(26)
4. Local stability of an endoreversible CAN engine

Following Santillán et al [15], a system of differential equations that provides information about how the stability engine is constructed. Santillán et al. developed a system of coupled differential equations to model the rate of change of intermediate temperature. Assuming that the temperatures $x$ and $y$ correspond to macroscopic objects with heat capacity $C$, the differential equations for $x$ and $y$ are given by [15]

$$\frac{dx}{dt} = \frac{1}{C} [\alpha(T_1 - x) - J_1]$$

and

$$\frac{dy}{dt} = \frac{1}{C} [\alpha(J_2 - (y - T_2))]$$

(27)

(28)

Both derivatives cancel when $x$, $y$, $J_1$, and $J_2$ take their steady state values. Under the endoreversibility assumption, the heat flux from $x$ to the working fluid is $J_1$ and the heat flux from the Carnot engine to $y$ is $J_2$, so $J_1$ and $J_2$ are given in terms of $x$ and $y$, and the power output $P$ as,

$$J_1 = \frac{x}{x-y} P$$

(29)

and

$$J_2 = \frac{y}{x-y} P.$$  

(30)

It seems reasonable to assume that the power output produced by the CA engine is related to temperature $x$ and $y$ in the same way that the power output at steady state $\bar{P}$ depends of $\bar{x}$ and $\bar{y}$ in the maximum power regime (see equation (23)), i.e.,

$$P = -\frac{a(x-y)^2}{x-y}.$$  

(31)

The substitution (29)- (31) in (27) and (28) leads to the following set of differential equations for temperatures $x$ and $y$ of a CA engine performing in maximum-power regime and using a Van der Waals gas as working substance.

$$\frac{dx}{dt} = \frac{a[T_1(x-7y)+6xy]}{C(x-7y)}$$

(32)

and

$$\frac{dy}{dt} = \frac{a[T_2(x-7y)-2y(x-4y)]}{C(x-7y)}.$$  

(33)

To analyze the stability’s system near to the steady state, we proceed by following the steps described in section 2. First we define

$$f(x, y) = \frac{a[T_1(x-7y)+6xy]}{C(x-7y)}$$

(34)

$$g(x, y) = \frac{a[T_2(x-7y)-2y(x-4y)]}{C(x-7y)}.$$  

(35)

Now the matrix $A = \begin{pmatrix} f_x & f_y \\ g_x & g_y \end{pmatrix}$, where $A$ is the matrix given by the first term on the right-hand side equation (3) where

$$f_x = \frac{\partial f}{\partial x} = -\frac{14a(1+3\tau)^2}{3C(1+7\tau)^2}$$

(36)

$$f_y = \frac{\partial f}{\partial y} = 2a(1+3\tau)$$

(37)

$$g_x = \frac{\partial g}{\partial x} = \frac{2a(1+3\tau)^2}{3C(1+7\tau)^2}$$

(38)

$$g_y = \frac{\partial g}{\partial y} = -\frac{8a(1+3\tau)(2+7\tau)}{3C(1+7\tau)^2}$$

(39)

with $\tau = T_2/T_1$.

Due to the substitution (36)-(39) in equation (7), we found that both eigenvalues $\lambda_1$ and $\lambda_2$, are given as

$$\lambda_1 = \frac{-1\alpha 11+66\tau+147\tau^2+\sqrt{73+492\tau+774\tau^2-756\tau^2+441\tau^4}}{3C(1+7\tau^2)}$$

(40)
and
\[ \lambda_2 = \frac{-\alpha \left[ 11+66\tau+147\tau^2-\sqrt{73+492\tau+774\tau^2-756\tau^3+441\tau^4} \right]}{3C (1+7\tau^2)}, \tag{41} \]
since both are real and negative, it follows from equation (8) that any perturbation decays exponentially with time and thus that steady state is stable for every value of \( \alpha, C \) and \( \tau = T_2/T_1 > 0 \).

5. Systems stability characteristics

The decay time depends on the absolute value of \( \lambda_1 \) and \( \lambda_2 \). Indeed, we can define two relaxation times \( t_1 \) and \( t_2 \) as
\[ t_1 = -\frac{1}{\lambda_1} = \frac{3C \alpha}{\alpha \left[ 11+66\tau+147\tau^2+\sqrt{73+492\tau+774\tau^2-756\tau^3+441\tau^4} \right]} \tag{42} \]
and
\[ t_2 = -\frac{1}{\lambda_2} = \frac{3C \alpha}{\alpha \left[ 11+66\tau+147\tau^2-\sqrt{73+492\tau+774\tau^2-756\tau^3+441\tau^4} \right]} \tag{43} \]

Note that both relaxation times are proportional to \( C/\alpha \). This means that in order to improve the system’s stability, we can either increase \( \alpha \) or decrease \( C \). Both of the relaxation times depend on \( \tau \). The smaller \( \lambda_1 \) and \( \lambda_2 \) are then \( t_1 > t_2 \), where \( t_1, t_2 \) correspond to the slow and fast direction, respectively. Thus the steady state is stable because any perturbation would be decayed exponentially. The plot of \( t_1 \) and \( t_2 \) versus \( \tau \) is shown in figure 2. We notice that in the limit \( \tau \to 1 \), both relaxation times tend to be closer to one another, indicating that the stability is preserved, but in the limit \( \tau \to 0 \) the stability is not preserved.

![Fig. 2 Plots of the CAN engine relaxation times \( t_1 \) and \( t_2 \), after a small perturbation, versus \( \tau \).](image)

Equations (20) and (23), respectively, determine the steady-state efficiency \( (\bar{\eta}) \) and power output \( (\bar{P}) \), as functions of \( \tau = T_2/T_1 \) and \( \alpha \), of an endoreversible Curzon-Ahlborn engine using a Van der Waals gas as working substance. It is easy to show that both \( \bar{\eta} \) and \( \bar{P} \) are decreasing functions of \( \tau \) see Fig. 3 and Fig. 4, for every fixed values of \( \alpha \) and \( C \).
We conclude from the assertions in the previous paragraph that energetic properties of a Curzon-Ahlborn-Novikov engine using a Van der Waals gas as working substance, working in the maximum ecological regime worsen as $\tau$ decreases to zero and improve as $\tau$ increases to one. In Fig. 5 is shown the phase portrait for an endoreversible CAN engine working maximum power regime and maximum ecological regime and we can see that the trajectories approach the origin tangent to slow eigendirections which are susceptible to work regime.
Fig. 5 Behavior of the portrait phase for an endoreversible CAN engine using a Van der Waals gas as working substance, working in the maximum ecological regime and the maximum power regime.

6. Comments

We obtain the same behavior at a CAN engine working at maximum power regime, see Santillán et al.[15]. In Fig. 2 the range where the engine has good thermodynamic and dynamic properties is shown similar to Santillán’s results. From Figure 5 it is clear that all trajectories approach the origin tangentially to slow eigendirection, i.e. we can say that it is a stable point. In addition, it is shown that eigendirections are susceptible to both the heat transfer law and the work regime [17, 20], because the eigenvectors in the ecological regime have different angles with the maximum power regime. It is important to point out that we obtain an analytical expression to both eigenvalues, which depend of $\alpha$, $C$ and $\tau$. Finally, we highlight the fact that the approach used $\lambda_{vW} = 1$, leads to the known relationship $\eta_{vWE} = \frac{3}{4}\eta_C$.

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References


Some Remarks on the Carnot’s Theorem

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Abstract:
It is common in many thermodynamics textbooks to illustrate the Carnot’s theorem through the usage of diverse equations of state for gases, paramagnets, and other simple thermodynamic systems. As it is well-known, the universality of the Carnot efficiency is easily demonstrated in a temperature-entropy diagram. In fact, any thermodynamic cycle depicted in a \((T,S)\) diagram, being the inexact differential of work, can be mapped into a \((w,z)\) diagram. In this work we show that this property is consistent with a preserving area map with Jacobian \(\left[\frac{\partial (w,z)}{\partial (T,S)}\right] = -1\), and that any equation of state satisfying this Jacobian transformation fulfills the Carnot’s theorem.

Keywords:
Second law of thermodynamics, Carnot’s theorem, Legendre transformation, preserving areas transformation.

1. Carnot’s Theorem

It is well known the limit imposed by the second law of thermodynamics about the maximum efficiency of any energy converter (thermodynamic cycle, heat engine, and so on) working between two extreme absolute temperatures \(T_1\) and \(T_2\), that is, the efficiency of the Carnot cycle, which is the following,

\[
\eta = 1 - \frac{T_1}{T_2}
\]

where \(T_1 < T_2\) are the temperatures of the cold and the hot reservoirs at which the thermodynamical engine operates. This upper limit works for both, reversible and irreversible processes. There exist several possible demonstrations of this fact, but perhaps the most compact and easy way to do this is on the \((T,S)\) plane, where \(S\) denotes the entropy. Such a demonstration can be easily found on any thermodynamics textbook. Although the Carnot’s theorem is accompanied with (1), the original statement was that the efficiency was function solely of the temperature at which heat is respectively received and emitted and independent of the nature of the working substance. However it should be mentioned that it was Rankine who obtained the explicit form of equation (1) [1].

It is well known that any cycle on the \((T,S)\) plane (the heat-plane) has a corresponding cycle on a \((w,z)\) plane, where \(w\) and \(z\) are some conjugate variables in such a way that the inexact differential of work \(dW\) can be written as \(wdz\) (the work-plane).

Several examples are in the literature on the independency of (1) from any working substance and some of them are based on gases obeying the equation of state of the ideal gas, Van der Waals and other equations of state [2-7]. Some of the authors ask themselves about the validity of (1) for non ideal substances [6,7]. In fact [7] answers this question by introducing a general method to obtain the efficiency of the Carnot’s cycle for an arbitrary equation of state. It is also common that in some textbooks (1) is found by using other simple thermodynamic systems as the working substance, for instance, a stretched elastic wire, a surface film [8] and ideal paramagnets [2-5].
2. Consistency of equations of state with thermodynamics

Equations of state for several thermodynamic systems (as fluids, paramagnets, etc.) are built following empirical and semiempirical procedures, or methods based in first principles stemming from statistical mechanics, as is the case of the Virial equation for example. Despite this there are no much efforts on explaining if the many existing equations of state are compatible with first and second laws of thermodynamics (because it is not expected that these equations describe the behavior of gases near zero temperature, compatibility with third law can be relaxed).

About this subject Tykodi and Hummel [9] proposed a way to verify the thermodynamic validity of any gas state equation. The result obtained was that if any equation of state of the form \( p = p(T,V) \) is expected to be in agreement with the first and the second laws of thermodynamics, where \( p \) is the pressure, \( T \) the temperature and \( V \) the volume, the equation of state should be expressible as,

\[
[p + \xi(T,V)] \phi(V) = RT. \tag{2}
\]

where \( \phi(V) \) is a function of the volume, \( R \) the universal gas constant and \( \xi(T,V) \) is a function of the temperature and the volume defined as follows,

\[
\xi(T,V) = -T \int T^{-2} \left( \frac{\partial U}{\partial V} \right)_T \, dT, \tag{3}
\]

integrated at constant \( V \) and \( U \) is the total internal energy. (2) and (3) stem from well-known simple thermodynamic identities. From the Gibbs’ equation,

\[
dU =TdS - pdV, \tag{4}
\]

it immediately follows that,

\[
\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - p. \tag{5}
\]

by using the Maxwell relation,

\[
\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V, \tag{6}
\]

and replacing (6) into (5) one obtains,
that can be written as,

$$ \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p. $$

Integration of (8) at constant temperature gives (2) and (3). In addition, it is expected that in the limit of a very dilute gas, it behaves as an ideal gas, that is,

$$ \lim_{V \to \infty} p = p_{\text{ideal gas}}, $$

in other words,

$$ \lim_{V \to \infty} \frac{V}{\phi(V)} = 1, $$

and

$$ \lim_{V \to \infty} V \xi(T,V) = 0. $$

Substitution of (7) into (3) gives the following relation,

$$ \xi(T,V) = -T \int (T \left( \frac{\partial p}{\partial T} \right)_V - p) \, dT. $$

In this way, all we need is to know the equation of state to evaluate (12) and to obtain the function $\phi(V)$ to determine whether such equation of state is thermodynamically consistent or not. Some work has been made on equations of state like the ideal gas, Van der Waals, Dieterici and Redlich-Kwong[9].

In 1990 Agrawal and Menon [6] calculated the expression of the Carnot efficiency for the Van der Waals gas, pointing out that typically in textbooks [2-5] this treatment is only made with the ideal gas as a working substance. These authors emphasize the fact that for non ideal substances the calculation of (1) is not a trivial task, alluding that in general the heat capacities present a dependence on the volume. Later, in 2006 Tjiang and Sutanto [7] demonstrated that an arbitrary gas state equation fulfills (1). Recently, Penrose [10] has asserted that: “this law (the second law of thermodynamics) has a universality that goes beyond any particular system of dynamical rules that one might be concerned with… It applies also to hypothetical dynamical theories that we have no good reason to believe have relevance to the actual universe that we inhabit...”.

3. Carnot’s theorem for equations of state which do not fulfill the Tykodi-Hummel consistency criterion.

More can be said about the generality of (1). Since Carnot’s theorem is a thermodynamical principle, it is not expected that an equation in a non-agreement with the thermodynamics, that is a “non-thermodynamical” equation of state should fulfills this theorem. At first sight the statement that “any working substance reproduces the Carnot efficiency” should apply only to well behave thermodynamical equations of state seems reasonable, however, surprisingly (at least for the authors of this work) it is not the case, because even those equations not consistent with thermodynamics (see Appendix A) reproduce (1). The general method that we used in the calculation of the efficiency is an analogue to the one used in [7]. Some more about the mathematics of this method can be found in Appendix B.
In particular, the equation in a non-agreement with the first and the second laws of thermodynamics shown in Appendix A, reproduce (1). As much as we would like to prove this for every single equation of state one by one, we consider that it is more convenient do it with a general equation. The proposal is the following,

\[ p = \sum_{j=-m}^{n} \sum_{i=-m}^{m} a_{ij} T^i v^j, \]  

(13)

\( p \) is the pressure, \( T^i \) and \( v^j \) are the temperature and the volume elevated to the \( i \) and \( j \) power respectively and \( a_{ij} \) are the constant coefficients of the series (equation (A1) is a particular case of equation (13)). This equation is general enough to cover any analytical function. For example, the virial equation which has the following form,

\[ p = RT \left( \frac{1}{v} + \frac{B_2}{v^2} + \frac{B_3}{v^3} + \ldots \right), \]  

(14)

where \( v \) is the molar volume and \( B_2, B_3, \text{etc.} \) are the second, the third, etc. virial coefficients and are functions of the temperature only. Since the virial coefficients \( B_j \) are related to the Mayer cluster integrals, which are integrals of an exponential function, then they are infinitely derivable on the variable \( T \) and then they are analytic functions and by the Taylor theorem they accept a power series representation. That means that one can write each \( B_j \) as follows,

\[ B_j = \sum_{i=2}^{\infty} b_{ij} T^i, \]  

(15)

where each \( b_{ij} \) are the constant coefficients of the series. Then (14) is now written as,

\[ p = RT \left( \frac{1}{v} + \frac{1}{v^2} \sum_{j=2}^{\infty} b_{ij} T^i + \frac{1}{v^3} \sum_{j=3}^{\infty} b_{ij} T^i + \ldots \right). \]  

(16)

that can be rearranged as,

\[ p = \frac{RT}{v} + RT \sum_{j=2}^{\infty} \sum_{i=0}^{\infty} \frac{b_{ij} T^i}{i! v^i}, \]  

(17)

by grouping one obtains the same kind of function as (13). For this equation, the total internal energy \( U \) is obtained according to (B7) and (B8) giving the following result,

\[ U = \sum_{i=-m}^{m} (i - 1) T^i \left( \sum_{j=-n}^{n} i a_{ij} \frac{v^{j+1}}{j+1} + a_{i,-1} \ln v \right) + \alpha T + F(T), \]  

(18)

where \( \alpha \) is a constant and \( F(T) \) is an arbitrary function of the temperature only (for the ideal gas \( F(T) = 0 \) and \( \alpha = 3nR/2 \)). And from (B5) the entropy is,

\[ S = \sum_{i=-m}^{m} \left( \sum_{j=-n}^{n} i a_{ij} \frac{v^{j+1}}{j+1} + iT^{i-1} a_{i,-1} \ln v \right) + \alpha \ln T + \int \frac{F(T)}{\tau} dT + S_0. \]  

(19)

Equation (B12) is,

\[ \eta = 1 + \frac{T_k}{T_1} \left( \frac{\sum_{i=-m}^{m} \sum_{j=-n}^{n} i a_{ij} \frac{v^{j+1}}{j+1} + iT^{i-1} a_{i,-1} \ln v}{\sum_{i=-m}^{m} \sum_{j=-n}^{n} i a_{ij} \frac{v^{j+1}}{j+1} + iT^{i-1} a_{i,-1} \ln v} - \frac{\sum_{i=-m}^{m} \sum_{j=-n}^{n} i a_{ij} \frac{v^{j+1}}{j+1} + iT^{i-1} a_{i,-1} \ln v}{\sum_{i=-m}^{m} \sum_{j=-n}^{n} i a_{ij} \frac{v^{j+1}}{j+1} + iT^{i-1} a_{i,-1} \ln v} \right). \]  

(20)

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Subtracting (B13) from (B14) we have that,

\[
\begin{align*}
\text{m} \sum_{j=-m}^{m} \left( \sum_{i=-n}^{n} \alpha_{i,j} \gamma_{i-1}^{j-1} \nu_{i+1}^{j+1} \right) 
- \text{m} \sum_{j=-m}^{m} \left( \sum_{i=-n}^{n} \alpha_{i,j} \gamma_{i-1}^{j-1} \nu_{i+1}^{j+1} \right)
- \text{m} \sum_{j=-m}^{m} \left( \sum_{i=-n}^{n} \alpha_{i,j} \gamma_{i-1}^{j-1} \nu_{i+1}^{j+1} \right)
- \text{m} \sum_{j=-m}^{m} \left( \sum_{i=-n}^{n} \alpha_{i,j} \gamma_{i-1}^{j-1} \nu_{i+1}^{j+1} \right)
= -1. 
\end{align*}
\]

Then by the substitution of (22) in (20) we arrive to the final form given by (1). Now we have the certainty that any equation generated from (13) will reproduce (1).

At this point we can propose some equations of state that are physically strange and to use them as the working substance in a Carnot cycle. As an example, let be

\[
p = \frac{aV}{T},
\]

\[
(23)
\]

\[\alpha\] being a constant with the adequate units. From (13) we can see that the only non zero coefficient is the \(\alpha_{-1,1}\), then, from (18) its internal energy is,

\[
U = -\frac{aV^2}{T} + \alpha T + F(T).
\]

\[
(24)
\]

Which in the usual monoatomic case (\(\alpha = \frac{3}{2}nR\) and \(F(T) = 0\)) becomes

\[
U = -\frac{aV^2}{T} + \frac{3}{2}RT,
\]

\[
(25)
\]

by means of (19) its entropy is,

\[
S = -\frac{aV^2}{2T^2} + \frac{3}{2}R \ln T + S_0.
\]

\[
(26)
\]

At first glance this is a non-physical equation of state, because when \(T\) grows \(p\) diminishes and when the gas expands the pressure increase. Expressions (25) and (26) in the limit of large volumes do not reproduce the ideal gas case. It is not logical that increasing the temperature of a gas produces a decrease of the energy. Also it has a problem with the entropy when \(T \to 0\). In Fig. 2 it is shown the possible corresponding Carnot cycle for this equation of state.
Before moving to the next section we would like to mention that in the methods used in [7] and in Appendix A for finding the Carnot efficiency we use the well-known relation,

\[
\left( \frac{\partial U}{\partial V} \right)_{T} - T \left( \frac{\partial p}{\partial T} \right)_{V} - p. 
\] (27)

that can only be obtained if the Maxwell relation [2-5]

\[
\left( \frac{\partial S}{\partial V} \right)_{T} = \left( \frac{\partial p}{\partial T} \right)_{V}. 
\] (28)

is valid. It can be said that (1) is valid if (28) is also valid.

4. Legendre transformations and Jacobian identities

Maxwell relations, as it is well-known, come from Legendre transformations on the internal energy $U$. A highlight that has been left aside in textbooks is the connection between Maxwell relations and their little known and more compact form of Jacobian identities as it has been pointed by David Mermin and Vinay Ambegaokar in 2001[11], for example,

\[
\frac{\partial (p,V)}{\partial (T,S)} = 1. 
\] (29)

From this identity it follows immediately the Maxwell relation, (a problem that can be found in [5])

\[
\left( \frac{\partial S}{\partial V} \right)_{T} = \left( \frac{\partial p}{\partial T} \right)_{V}. 
\] (30)

Equation (30) is obtained from (29) by means of the Jacobian properties, that is, by using some called auxiliary variables $(T,V)$,

\[
\frac{\partial (p,V)}{\partial (T,S)} = \frac{\delta(p,V)}{\delta(T,V)} \frac{\partial (T,V)}{\partial (T,S)} - \left( \frac{\partial p}{\partial T} \right)_{V} \left( \frac{\partial V}{\partial S} \right)_{T} = 1. 
\] (31)

Now we will show a demonstration that we haven’t found in textbooks. This demonstration shows in a simple manner that Legendre transformations would produce mappings that preserve areas (with a suitable choice of the range of the coordinate system). Some general comments about the Legendre transformations and its definition can be found in Appendix C.
4.1. Mappings that preserve areas

Let’s take the function \( M \) defined in a subspace \( V \) of \( \mathbb{R}^2 \), then if \( \tilde{x} \in V \) with \( \tilde{x} = (x, y) \), then
\[
M(\tilde{x}) = M(x, y).
\]

(32)

Its differential is
\[
dM = m(x, y) \, dx + n(x, y) \, dy,
\]
where \( m \) and \( n \) are functions of \( x \) and \( y \), but for simplicity we’ll just denote them as \( m \) and \( n \), then,
\[
dM = m \, dx + n \, dy.
\]

(33)

Let’s take the Legendre transformation \( K \) of \( M \), which according to (C1) is,
\[
K = -xm + M,
\]
we are changing the variable \( x \) for the variable \( m \), that according to (C4), has the form
\[
m = -\left( \frac{\partial M}{\partial x} \right)_y.
\]

(34)

The differential of this new function is
\[
dK = -xdm + ndy,
\]
And because \( dK \) is exact, then by the Schwarz theorem,
\[
\left( \frac{\partial x}{\partial y} \right)_m = -\left( \frac{\partial n}{\partial m} \right)_y.
\]

(35)

Now let \( \Omega \) be a mapping with \( \Omega: (y, n) \mapsto (x, m) \) like the one illustrated in Fig. 3. It is easily shown that this mapping preserves areas (but changes orientations) given the fact that the Jacobian between this two coordinates systems is \( -1 \),
\[
\frac{\partial (ny)}{\partial (mx)} \frac{\partial (ny)}{\partial (mx)} - \frac{\partial (mx)}{\partial (my)} \frac{\partial (mx)}{\partial (my)} = \left( \frac{\partial n}{\partial m} \right)_y \left( \frac{\partial y}{\partial x} \right)_m = -\left( \frac{\partial x}{\partial y} \right)_m \left( \frac{\partial y}{\partial x} \right)_m = -1.
\]

(36)

Fig. 3. Preserving areas maps between the \((y, n)\) plane and the \((x, m)\) plane.

What this means is that if the contour in the \((y, n)\) plane is taken clockwise, then the corresponding contour in the \((m, x)\) plane should be taken counterclockwise. Then the area in the \((y, n)\) plane is the negative of the area in the \((m, x)\) plane.
4.2. Application to thermodynamics

In particular the heat-plane, that is, the \((T,S)\) plane and the work-plane \((w,z)\) are of the same kind of those studied in the last subsection. All that is left to do is make the correct associations. Let’s take the following substitution, in which the coordinate plane \((x,y)\) is now \((S,V)\),

\[(x, y) \rightarrow (S, V). \quad (40)\]

the function \(M\) is replaced by the total internal energy \(U\),

\[M(x,y) \rightarrow U(S,V). \quad (41)\]

following (C4) and (36),

\[m = \left( \frac{\partial M}{\partial x} \right)_y \rightarrow T = \left( \frac{\partial U}{\partial S} \right)_V, \quad (42)\]

\[n = \left( \frac{\partial M}{\partial y} \right)_x \rightarrow -p = \left( \frac{\partial U}{\partial V} \right)_S, \quad (43)\]

which are already familiar identities [2-5]. The Helmholtz potential \(F\) takes the place of \(K\) and it is given by,

\[F = U - TS, \quad (44)\]

and because of (38)

\[\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V. \quad (45)\]

That is to say, from an application that maps a thermodynamical process from the \((-p,V)\) plane to the same process but in the \((T,S)\) plane, it is possible to obtain the first law of thermodynamics for a cycle (see Fig. 4),

\[Q = -W, \quad (46)\]

\[\begin{align*}
&\text{Volume } V \\
&\text{Temperature } T \\
&\text{Entropy } S \\
&\text{Negative of the pressure } -p
\end{align*}\]

\[\text{Fig. 4. Preserving areas maps between the } (-p,V) \text{ plane and the } (T,S) \text{ plane.}\]

Note in Fig. 4 the direction of the process. Usually we are more familiar with the \((p,V)\) plane instead of the \((-p,V)\) plane. In Fig. 5 it is illustrated the trivial conversion from one another.
The generality of this result, which is purely mathematical in a certain manner is linked to the first law of thermodynamics. It is also connected directly to the second law of thermodynamics through the Carnot’s theorem and it seems to carry out a little bit more general property, since apparently extends Carnot’s theorem beyond thermodynamics because there are not physics involved. Uncovering a possible contradiction in the sense that we have a thermodynamical principle that should be obeyed by non-thermodynamical or even non-physical entities. We believe that this geometrical property is a link between some aspects of the thermodynamics that have remained dissociated, but we intuitively believed that are connected.

5. Conclusions

In this work we have proposed a gas state equation in a general form (see equation (13)). This equation embraces any known gas state equation, remarkably those compatible with the virial expansion. All these equations fulfill the Tykodi-Hummel criterion of thermodynamic self-consistency. However, (13) also can generate a subset of equations of state, which present a phenomenological anomalous thermodynamic behavior, and on the other hand, they do not fulfill the Tykodi-Hummel criterion. In Sect. 3, we have shown that (13) satisfies the Carnot theorem, thus, the subset of anomalous gas state equations also fulfill with Carnot’s theorem, nevertheless, they do not obey the Tykodi-Hummel criterion (see Appendix A). This result is in accordance with the Penrose’s comment mentioned at the end of Sect. 2. In the present work we have also shown that this great universality of Carnot’s theorem has to do with a geometrical property stemming from preserving areas maps between the work-plane and the heat-plane. As Mermin and Ambegaokar assert [11], this approach based in Jacobian transformations is apparently little known in the literature.

We believe that this geometrical property (preserving areas maps) has not been emphasized in most of standard thermodynamic textbooks. This approach can evidently enrich the conventional thermodynamic analysis.

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Appendix A

Let’s take the following ansatz as a possible equation of state,

\[ p(T,V) = \frac{a V}{T} \]  

(A1)
From (12), one can obtain that
\[ \xi(T, V) = -\frac{\alpha V}{T} = -p, \quad (A2) \]

and (2) yields to \( 0 = RT \), which is not possible. Then going on the other side, from (2)
\[ \xi(T, V) = \frac{RT}{\phi(V)} - p, \quad (A3) \]

if (5) is true then \( \lim_{V \to \infty} V / \phi(V) = 1 \), and applying (6),
\[ \lim_{V \to \infty} V \xi(T, V) = RT - \lim_{V \to \infty} \frac{\alpha V^2}{T} \neq 0, \quad (A4) \]

then this equation of state is not compatible with thermodynamics under the Tykodi-Hummel criterion.

**Appendix B**

The general method that we used in the calculation of the efficiency is the following:

Our aim is to obtain the efficiency, defined as,
\[ \eta = \frac{W}{Q_{in}} = 1 + \frac{Q_{out}}{Q_{in}}, \quad (B1) \]

where \( W \) is the total work, \( Q_{in} \) and \( Q_{out} \) are the input and output heats over the isothermal processes. Here we use the convention that \( Q_{out} \) is negative since the integration path is taken from \( 4 \to 1 \) (see Fig. 1).

One way to find the heat is using the equality \( \delta Q = T dS \) (because we have a reversible process), where \( \delta Q \) is the inexact differential of heat and \( dS \) the exact differential of entropy. As it is well known \( \frac{1}{T} \) is the integrating factor of \( \delta Q \). From (7)
\[ dS = \frac{1}{T} dU + \frac{p}{T} dV, \quad (B2) \]

because \( dU \) is exact, then,
\[ dS = \frac{1}{T} \left[ \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \right] + \frac{p}{T} dV. \quad (B3) \]

From (5) and (6) we have,
\[ \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p, \quad (B4) \]

then,
\[ dS = \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial p}{\partial V} \right)_T dV, \quad (B5) \]

and,
\[ dQ = \left( \frac{\partial U}{\partial T} \right)_V dT + T \left( \frac{\partial p}{\partial V} \right)_V dV. \quad (B6) \]
From (B4),
\[
\left( \frac{\partial^2 U}{\partial V \partial T} \right)_v = T \left( \frac{\partial^2 p}{\partial T^2} \right)_T, \tag{B7}
\]
an integration over the variables \(V\) and \(T\) yields to
\[
U = \iiint \left( \frac{\partial^2 U}{\partial V \partial T} \right)_v \, dV \, dT + \int f(T) \, dT + H(V), \tag{B8}
\]
where \(f(T)\) and \(H(V)\) are functions to determine. At this point we can impose the condition that for a very dilute monoatomic gas it behaves as the ideal gas, that is,
\[
\lim_{V \to \infty} U = \frac{3}{2} nRT, \tag{B9}
\]
where \(n\) is the molar number of the gas, then,
\[
f(T) = \frac{3}{2} nR, \tag{B10}
\]
all this to calculate \(\left( \frac{\partial U}{\partial T} \right)_v\) and to obtain from (B5) the entropy \(S(T,V)\). \(Q_{\text{in}}\) and \(Q_{\text{out}}\) are over isothermal processes, then
\[
\begin{align*}
Q_{\text{in}} &= T_2 \Delta S_{24} \\
Q_{\text{out}} &= T_2 \Delta S_{12},
\end{align*} \tag{B11}
\]
and (B1) becomes,
\[
\eta = 1 + \frac{T_2}{T_1} \frac{\Delta S_{24}}{\Delta S_{12}}, \tag{B12}
\]
where \(\Delta S_{12}\) denotes \(S(T_2,V_2) - S(T_2,V_1) > 0\), and \(\Delta S_{24} = S(T_1,V_4) - S(T_1,V_3) < 0\) \((S(T,V)\) is a state function). Over the adiabatic processes we also have the following conditions,
\[
\begin{align*}
S(T_1,V_2) &= S(T_2,V_2), \tag{B13} \\
S(T_1,V_4) &= S(T_1,V_4), \tag{B14}
\end{align*}
\]
the subtraction between (B13) and (B14) yields to
\[
\Delta S_{24} = -\Delta S_{12}, \tag{B15}
\]
then (B12) is exactly (1), so in this way it is possible to arrive directly from the equation of state to the entropy and finally to the efficiency of Carnot.

As a manner of example, consider the following equation of state (which satisfies the Tykodi-Hummel criterion),
\[
p(T,V) = \frac{\alpha T}{V} + \frac{bT^2}{V^3}, \tag{B16}
\]
From (B4) we have that,
\[
\left( \frac{\partial U}{\partial V} \right)_T = \frac{bT^2}{V^3}, \tag{B17}
\]
because of (B7),
\[
\left( \frac{\partial^2 U}{\partial V \partial T} \right)_V = 2 \frac{bT^2}{v^2}, \tag{B18}
\]
integration over the volume gives,
\[
\left( \frac{\partial U}{\partial T} \right)_V = - \frac{bT}{v^2} + f(T), \tag{B19}
\]
and integration over the temperature results in,
\[
U = - \frac{bT^2}{v^2} + \int \frac{3}{2} nRdT + H(V). \tag{B20}
\]
Then (B19) is,
\[
\left( \frac{\partial U}{\partial T} \right)_V = - \frac{bT}{v^2} + \frac{3}{2} nR, \tag{B21}
\]
and from (B5), (B21) and (B16) one obtains,
\[
dS = \left( - \frac{b}{v^2} + \frac{3}{2} \frac{nR}{T} \right) dT + \left( 2 \frac{bT}{v^2} + \frac{a}{v} \right) dV, \tag{B22}
\]
then,
\[
S = - \frac{bT}{v^2} + \frac{3nR}{2} \ln T + a \ln V. \tag{B23}
\]
Equation (B12) implies that
\[
\eta = 1 + \frac{T_2}{T_1} \frac{\text{aln} V_2}{\text{aln} V_3} - bT_2 \left( \frac{1}{V_2} - \frac{1}{V_1} \right) \tag{B24}
\]
from (B13) and (B14),
\[
aln \frac{V_4}{V_3} - bT_2 \left( \frac{1}{V_4} - \frac{1}{V_1} \right) = - \left( \text{aln} \frac{V_2}{V_1} - bT_1 \left( \frac{1}{V_2} - \frac{1}{V_1} \right) \right), \tag{B25}
\]
then,
\[
\eta = 1 - \frac{T_2}{T_1} \tag{1}
\]
\[\]
**Appendix C**

The Legendre transformation maps functions in a vector space into functions in the tangent space [12]. Let's take a function \( F(\mathbf{x}) \) with \( F: \mathbb{R}^n \rightarrow \mathbb{R} \). Its Legendre transformation named \( K \) to the variable \( \mathbf{p} \in \mathbb{R}^n \) is given by,
\[
K(\mathbf{x}, \mathbf{p}) = -\mathbf{x} \cdot \mathbf{p} + M(\mathbf{x}) \tag{C1}
\]
this function has the property that \( \forall \mathbf{p}, K(\mathbf{x}, \mathbf{p}) \) has a maximum with respect to \( \mathbf{x} \) in a point \( \mathbf{x}(\mathbf{p}) \), which is defined by the extremal condition of \( K(\mathbf{x}, \mathbf{p}) \) respect to \( \mathbf{x} \). In other words,
\( \vec{\nabla}_x K(\vec{x}, \vec{p}) = 0 \), \hspace{1cm} (C2)

then,
\( \vec{p} = \vec{\nabla} M(\vec{x}) \). \hspace{1cm} (C3)

If we now define the function \( n(\vec{p}) = K(\vec{x}(\vec{p}), \vec{p}) \), we have transformed the function \( M(\vec{x}) \) to a new function that has as a domain the tangent space to \( M(\vec{x}) \). The basis coordinates are the set,
\[ p_i = \frac{\partial M}{\partial x_i} \], \hspace{1cm} (C4)

which is an already familiar result from the classical mechanics used to go by means of this Legendre transformation from the Lagrangian function to the Hamiltonian function.

References

The Dead State

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Abstract:
The purpose of this paper is to provide guidance for the selection of the dead state for exergy analysis, guidance that is especially important in applications to energy-conversion and materials processing plant engineering, and to ecology. First, the general definition of the dead state is provided, based on the concept of ‘the available energy of a body’ as originally presented by Gibbs. Gibbs ‘body’ can be any overall system, no matter how complex, and a crucial point is that there is no need to include or have a ‘reference environment.’ On this groundwork, criteria underlying the selection of the appropriate dead state for a variety of practical engineering systems are referred to; while these cases are not exhaustive, they provide examples of the rationale for selection of an appropriate dead state for any case. Finally, the implications and relevance of the dead state on applications of exergy considerations to the issues of ecology and sustainability are discussed.

Keywords:
Dead State, Exergy, Reference Environment, Available Energy, Resource Assessment, Sustainability

1. Introduction

This paper has two principal parts: Fundamentals, and Practical Applications.

1.1 Fundamentals. Following Gibbs [1] the ‘available energy of a body’ is defined for any ‘body’ – i.e., for any overall system, no matter how complex the system’s structure. The structure generally includes several subsystems or processes and how they interact. While a subsystem may be an ‘environment’, an environment is not necessary. Given the structure, the ‘dead state’ of the system follows directly from this general definition of available energy. Moreover, the dead state of the overall system dictates the dead state of each subsystem. The overall dead state and hence dead states of the subsystems can change with time.

In practice, the overall dead state and hence the subsystem dead states depend upon underlying choices. Above all, the practitioner must delineate the makeup of the overall system. That is, given the purpose of the analysis, choose the parts of the ‘universe’ to be included in the overall system (as subsystems). Moreover, it is essential to choose ‘constraints’ placed upon (i) spontaneous processes allowed within each subsystem, (ii) modes of interaction between subsystems, (iii) modes whereby products are delivered from the overall system (to its ‘market’).

1.2 Applications. Exergy is an additive property. The exergy of a subsystem represents its contribution to the available energy of the overall system. Exergy is definable whether or not one of the subsystems is an ‘environment.’

In many if not most engineering applications of ‘exergy analysis’ to a conversion plant – for efficiency analysis and/or costing – an important subsystem is a local environment with which it interacts. The dead state of each plant subsystem and its contents depends upon the assumed constraints applied to it and to the environment. The choice of constraints can have a significant effect upon the conclusions drawn from the analysis.

Among the factors that are relevant to the choices of constraints (and hence to the outcome of an analysis) are:

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1 Interaction is synonymous with ‘exchange of additive property.’
• The projected time-period for which the analysis will be relevant
• The scope of the environment
  o Its breadth
  o The accessibility of materials therein
  o The stability of the materials
  o Relevance of variations with time
• The scope of technology – i.e., the ‘state of the art’ for the projected time period
• The scope of science – i.e., its ‘state of development’ for the period
These choices (relevant to engineering applications) are all the more important when exergy and ‘dead state’ considerations are applied to ecology and sustainability.

1.3 Closure. The fundamentals will be presented and illustrated in the context of simple examples. Nevertheless, these examples will be used to draw (convincingly, it is hoped) broad, general principles relevant to complex practical applications.

2. Gibbs Available Energy

In 1873 Gibbs [1] defines the available energy, for two cases.

2.1 Case 1. The first, more general case, is for that of a ‘body’ – any closed system which, overall, may have parts (subsystems). At any instant \( t \) the system has values of energy, entropy and of volume. Using different symbols than Gibbs, here they are denoted by \( E(t) \), \( S(t) \), \( V(t) \). Its available energy at \( t \), a characteristic of the system alone, is the maximum amount of energy deliverable with no net transfer of either entropy or volume to external systems. That is, during the hypothetical delivery, entropy and volume can be exchanged between its parts. External devices (‘technology’) may be employed to do so; but, in order to assure that no external object makes a net contribution to the energy delivered, the net change of every external device’s energy must be zero.

Shown in Figure 1 is a very simple example of an overall system, in this case consisting of two identical subsystems, 1 and 2. The subsystems are separated by an impermeable movable piston. Let us say that at an instant \( t \) each subsystem, by itself, is at equilibrium with a uniform temperature and pressure within. But, supposing \( p_1 - p_2 \) > 0 and \( T_1 - T_2 \) > 0, the overall system is not at equilibrium and has available energy. That is, energy could be delivered from the overall system by exchange of volume and/or entropy; the net amount of energy delivered would equal \( \int [p_1 \, dV_1 + p_2 \, dV_2 - (p_1 - p_2) \, dS_1 + (p_1 - p_2) \, dS_2] \). This net output of energy would be a maximum, equal to the available energy \( A \), when the entropy production \( dS_e \) is zero throughout the delivery, and the overall system has reached an equilibrium state, with \( p_1 - p_2 \) = 0 and \( T_1 - T_2 \) = 0. The remaining energy content of the overall system would be the minimum value reachable from the initial state with its volume \( V(t) \) and entropy \( S(t) \).

\[ \text{2 The existence of entropy (as well as energy and volume) is taken for granted here. See the Appendix for elaboration.} \]
\[ \text{3 Here, the equal sign depends upon volume and entropy balances for the case of no net transfers of volume or entropy to or from the overall system.} \]
At any particular state of any overall system, with its particular entropy $S$ and volume $V$, there is a minimum possible energy, $E_{\text{min}}$. That is, there is function $E_{\text{min}}(S, V)$. Thus, at any state of the system, the Gibbs available energy is given by $A = E - E_{\text{min}}(S, V)$. When the energy of the body equals $E_{\text{min}}(S, V)$, the body is at an equilibrium state at $(S, V)$, and there is no available energy. On Figure 2, from Gibbs [1], the curve through MBCN represents a hypothetical $E_{\text{min}}(S, V)$, at a fixed $V$. The location A represents an arbitrary nonequilibrium state of the system, and the distance AB is the available energy of that state. Figure 3 (from [2a]) shows a complete $E_{\text{min}}(S, V)$ surface and the points A and B. It is notable that Point A – with its unique values of $E$, $S$ and $V$ – does not represent a unique state of the overall system. For example, consider Figure 1 again. At any fixed $(S, V)$ there are many conceivable states of the overall system with the same energy $E$.  

2.1.1 The Dead State. When the overall system is at Point B, it is at a ‘dead state’ – a state of zero available energy. Whenever the overall system is at any condition vertically above B, Point B is the corresponding dead state.

Gibbs called $E_{\text{min}}(S, V)$ “the surface of dissipated energy”. If an overall system, like that in Figure 1, were allowed to reach equilibrium without delivering energy (say by letting entropy flow

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4 States with the same $E$ could differ as a result, simply, of disparities in pressure and temperature differences between the subsystems. Furthermore, many states with the same $E$ will differ because of gradients within a subsystem, and so on.
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through the piston and letting it oscillate, uncontrolled), entropy would be produced. The system would end up at Point C, another dead state.

### 2.1.2 Additional Measures of Potential Influence.

The available energy represents the system’s intrinsic potential to influence any other system. Gibbs defined other equivalent measures of disequilibrium and potential to influence. The distance AC on either figure (2 or 3) represents the system’s ‘capacity for entropy’ – at least that amount of entropy could be extracted from any system (at T > 0), no matter how cold. AF on Figure 3 is Gibbs ‘available vacuum.’ At least this amount of volume increase could be imposed upon any system no matter how low its pressure.

These three characteristics (represented by AB, AC and AF) are measures of a system’s disequilibrium and potential to influence any object; they are attributes of the system alone. Gibbs also described the potential influence upon specific objects. For example consider a large object at any temperature $T$, represented by the slope of the straight line MAN on Figure 2. The distance QA on the figure is the amount of entropy that could be extracted from the object; starting at A the system would end up at N. AR is the amount of entropy that could be imposed upon the object.

### 2.2 Case 2.

This special case presented by Gibbs, is for a circumstance where one part of the overall system is a ‘medium’ – a large subsystem which has a constant temperature and a constant pressure. In Gibbs’ terminology the overall system consists of a ‘body’ (any body) and the ‘medium’ (made up of the same components as the body). In both cases, 1 and 2, his development is for circumstances where the overall system reaches equilibrium without net transports of entropy or volume between the overall system and its surroundings. In Case 2, net exchanges of entropy and volume between the body and the medium (two subsystems) are allowed. Figure 4 (from [2a]) shows two surfaces, the curved surface for the body alone, and a planar surface. The plane is tangent to the curved surface at the location where the body and the medium have the same temperature and pressure – namely the constant $T$ and $p$ of the medium. If the body is at internal equilibrium at B (of Figures 3 and 4), the vertical distance from B to the planar surface represents the available energy of the composite system of body and medium together. If the body is at A, the available energy from the composite equals that vertical distance plus AB. (As explained below, the available energy can be attributed to the body, and called the ‘exergy’ of the body. The exergy of the medium is zero.)

At the dead state of the overall system (body and medium) the body will be at the location where its $T$ and $p$ are equal to that of the medium – where the body’s surface is tangent to that of the medium.

#### 2.2.1 Gibbs Available Energy with Variable Composition.

Subsequently, in 1875, Gibbs [3] presented – implicitly – the available energy of a body and medium for the case of open systems, where exchanges with a ‘medium’ include not only entropy and volume but also chemical components.

### 3. Generalized Available Energy

In the foregoing review of Gibbs’ 1873 development of available energy, leading to $A = E - E_{\text{min}}(S, V)$, the entropy and volume were ‘constrained’. That is, the hypothetical process that delivers available energy is carried out with limitations: no net transport of volume or entropy to or from the surroundings of the overall system. Such limitations will, herein, be called constraints. This word will be used not only for limitations upon transports but also for restrictions on spontaneous changes (such as changes of composition by chemical reactions within a subsystem).

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5 The word ‘component’ is to be understood as distinct from ‘constituent’. Constituents are species actually present; components are species from which the constituents could be composed (e.g., see Hatsopoulos and Keenan [4]). In the case at hand, components are constituents of the ‘medium’ from which the constituents of the ‘body’ could be composed.
3.1 Constraints. To illustrate the concept of constraints, consider Figure 1 again. Suppose the piston to be fixed in place (or replaced by an immovable wall). This additional constraint upon the overall system could be represented by the symbol $V_f$ (for the volume of $f$). When $V_f$ is constrained, interchanges of volume between the two subsystems would be precluded, and full advantage of pressure difference between the two could not be taken. In general the available energy from the composite of $I$ and $2$ would be less. Because, the minimum energy reachable would in general be greater than that reachable if the constraint on $V_f$ were removed: $E_{\text{min}}(S, V, V_f) > E_{\text{min}}(S, V)$, and so $A(E, S, V, V_f) = E - E_{\text{min}}(S, V, V_f) < A(E, S, V) = E - E_{\text{min}}(S, V).$

This example illustrates that the existence of additional constraints changes the amount of available energy, and it changes the dead state. While additional constraints may seem to be 'strictly theoretical' and even questionable, later in this article it will be illustrated that it has important consequences in practice. There are relevant effects on delivery of available energy, on subsystem dead states, on calculated exergy values, and on costing.

Moreover, it is important to recognize that, in general, available energy is defined:

- For an overall system, consisting of specific relevant subsystems, and one subsystem may be a large 'medium',
- Subject to constraints, which may restrict
  - how subsystems can interact, and
  - spontaneous changes within a subsystem.
  - modes of interactions with external devices.

See [2b] for further elaboration on generalization of Gibbs available energy, including the relevance of constraints to equilibrium.

3.2 Exergy. Available energy is not an additive property, which is readily illustrated by considering Figure 1. Suppose that Subsystem 1, alone is at equilibrium; likewise for Subsystem 2. Then each, alone, has zero available energy. Whereas, when the two are not in equilibrium with each other, the composite of the two (the overall system) has available energy. The author [5] has derived 'subsystem exergy' such that (i) exergy is additive, (ii) the sum of the subsystem exergies is equal to the available energy of the overall system, (iii) hence each subsystem's exergy can be viewed as its contribution to the overall available energy, and (iv) because it is additive, an 'exergy balance' can be written for any subsystem, so that 'exergy analysis' can be carried out.

Unlike the usual, 'textbook' derivations for exergy equations, which depend upon having a 'reference environment', the derivation in [5] is for any overall system. No reference environment (reservoir) is required. In the derivation, the dead state of the overall system becomes relevant, in lieu of a reference environment. The dead state of each subsystem is dictated by the dead state of the overall system. Incidentally, these dead states can change with time, when $E_{\text{min}}$ increases because of dissipations.

For the case when subsystems are free to exchange entropy $S$, volume $V$, and chemical components $N_i$, the expression for exergy content of a subsystem is:

$$X = E + p_f V - T_f S - \Sigma \mu_f N_i$$

The subscript $f$ denotes the pressure, temperature and component chemical potential at the dead state. The expressions for exergy transports follow directly from this expression for content.

When one of the subsystems is a 'medium', large and at equilibrium (or constrained equilibrium) – with pressure $p_0$, temperature $T_0$ and chemical potentials $\mu_0$ – it has zero exergy. The medium dictates the dead state of all the subsystems. Then, in the foregoing expression for exergy, the $f$'s
become the usual 0’s. However, as argued later, there are many practical instances where it is erroneous (if not presumptuous) to assume an equilibrium environment (or a finite, non-equilibrium environment with a quasi-stable equilibrium ‘dead state’).

Understanding (a) the meaning of ‘dead state’ in general (including in the absence of an ‘environment’) and (b) the relevance of constraints upon the dead state is important. In practice, the choices made to determine the overall dead state are effected (even when one subsystem is an ‘environment’).

The derivation of exergy in [5] is a simplification of one presented earlier with Wepfer [6]. (In [6], by the way, there is an error in line 2 of Eq. (14); the subscripts shown as B should be A.)

4 Practical Examples

4.1 Relevance to Subsystem Dead States for Engineering Exergy Analysis and Costing Applied to Conversion Systems and Plants.

What is meant here by Engineering Exergy Analysis is this: analysis of an existing, operating plant (or system), or analysis of a plant that is being designed. The intent is that all of the subsystems consist of technologies that are currently available. (Comments relevant to R&D and resource assessment are presented later.)

Before a plant (or system) is analyzed it is important to ascertain (or make reasonable assumptions) regarding the dead state of the materials in every subsystem. That is, the $p_f$, $T_f$, and $\mu_f$ need to be determined for each subsystem. (When a material flows between two subsystems, it of course has the same dead state in both.)

Given a plant and its surroundings, (a) the first step in determining appropriate subsystem dead states is to establish the relevant “composite system” (overall system, consisting of subsystems). That is, what parts of the ‘universe’ have significant effect on performance of the plant or system.

- Relevant: considering the purpose of the analysis.
- Significant effect: having an effect that influences the outcome of the analysis within the desired significant figures.

In turn, (b) the practical, technological constraints on the interactions between subsystems need to be specified.

These principles – (a) and (b) – are illustrated with several cases, in [6]. That article includes a section on “The selection of reference datums [dead states] for subsystem [exergy].” Rather than duplicate that section, here only one of those cases will be presented, in order to illustrate the application of principles.

One case that illustrates the relevance of constraints is the situation where a ‘working fluid’ is confined, within some of the subsystems. An example is the H$_2$O confined in the ‘cycle’ of a power plant. Another is the refrigerant confined in a vapor-compression refrigeration system. In these circumstances the total volume of the working fluid is fixed, constrained. As long as a refrigeration system is intact (working, practically) the refrigerant cannot equilibrate its pressure (or composition) with that of the surrounding environment. Its equilibration would be constrained, so that only thermal equilibration could occur. The appropriate dead state for the refrigerant is that which it would reach upon system shut-down; typically that would be a state at environmental temperature and the refrigerant’s saturation pressure at that temperature.

If one assumes that the dead state pressure should equal atmospheric pressure, erroneous subsystem efficiencies (and costs) will result. If the reader needs to be convinced that the correct dead state pressure should be the one recommended here, it is suggested that two exergy analyses be carried out. One with the recommended $p_0$ and one with $p_0$ equal to atmospheric. Then draw exergy flow diagrams for the two cases and compare – noting that all of the exergy enters as supply to the compressor, which then delivers exergy to the other subsystems. (By the way, if one argued
that atmospheric pressure is correct, then to be consistent the chemical exergy of the refrigerant
should also be taken into account."

Another, even more interesting, ‘refrigerant example’ would be for the case of a dual-purpose
vapor compression system; one which delivered cooling to a load at temperature less than ambient
and heating at a temperature higher than ambient (and with no interaction with the ambient). See
Paulus and Gaggioli [7] for the rationale for proper specification of $T_f$ and, hence, $p_f$.

Other circumstances discussed in [6], with different procedures for determining the dead states,
include:

- Multiple, stable surrounding media
- Circumstances when variations in the environment, with time, are significant
- Metastable and Unstable Ambient Environments; e.g.
  - inherently unstable (such as weather changes; see [8,9])
  - unstable because of the impact of effluents from the plant

One point that can be made regarding the choice of an environment for analyzing a plant is this:
*Alternative* choices may be appropriate, depending upon the purpose of the analysis. For example,
suppose one analysis is being made for the purpose of improving efficiency or economy of a plant
(which has state of the art equipment, and apparatus required in order to satisfy regulations and
codes). Then an appropriate environment would be that immediately surrounding the plant. On the
other hand, if a second analysis is to include assessment of environmental impact, then the selected
environment (or subsystems) will need to include chemical components for neutralizing the
emissions, to stable non-toxic conditions. Such components might exist only remotely from the
plant. (If costing were part of the analysis, emissions could have negative unit exergy costs – so
that the cost of bringing the neutralizing components would be charged to the plant.)

For further elaboration on selection of dead states, see [6] for details and examples.

### 4.2 Relevance to Analyses for R&D and for Resource and Sustainability Assessment

This section will be devoted to the importance of the constraint concept, and to the significance
of choosing a relevant dead state.

#### 4.2.1 Significance of Constraints. Again, consider a simple *example*, referred to earlier.
Suppose that the system in Figure 1 is at a condition like A in Figure 2, and consider a *real* process
that is striving to deliver the available energy represented by AB. Invariably there would be
entropy production, due to ‘mechanical friction’ and heat transfer through temperature differences.
As a result the system would end up at a condition to the right of B on the curve toward C; the more
the entropy production the closer to C (but never above C, which is the condition reached if the
system is allowed, uncontrolled, to equilibrate internally, so no energy is delivered).
Let us suppose that, with more or less well-controlled, but real equilibration the final condition reached is at $\alpha$, on Figure 5 (For convenience of the artwork the ordinate (for $E$) is not linear; $\alpha$ appears closer to C than if the ordinate were linear; i.e. the energy delivered ($E_A - E_\alpha$) is significantly greater than the dissipation of available energy ($E_\alpha - E_B$)). Moreover suppose that the entropy production is predominantly caused by mechanical, viscous friction. Consider the following alternative scheme, starting at A, for delivering available energy: If the piston were fixed in place (constraining $V_1$), and available energy were delivered with very little entropy production due to heat transfer, that delivery process would end up at a place like $\beta$, below and slightly to the right of A. Next, deliver more available energy by letting $V_1$ change by a modest amount (to $V_1'$), with some but less viscous friction (because of the controlling of $V_1$’s change). By repeating, once more, this procedure of fixing and then changing $V_1$, the path to equilibrium could be like that from A to $\gamma$ on Figure 5. More available energy, namely $E_A - E_\gamma$, would be delivered (less dissipated) than from the path A to $\alpha$. (By increasing the number of steps the delivery could be increased all the more so.) This is a simplistic example of how adding constraints, and controlling them, can improve the delivery of available energy. The general conclusion to be drawn therefrom (which may appear obvious) is that improving the control of available energy transfer processes – by adding, or by finding new constraints – can improve the efficiency.

The objective of additional constraints is control; that is accomplished by reducing states that otherwise would proceed more spontaneously, toward successive constrained-equilibrium states.

Adding effective constraints will generally depend upon advances in technology. Finding new constraints will often depend on scientific advancement as well. New constraints ‘produce’ new constrained-equilibrium states.

It can be surmised that there exists unknown constraints that could even ‘increase’ the available energy. That is, by allowing states that (at the current status of science) are believed to be at equilibrium but are at metastable equilibrium – such that the metastability could be overcome by manipulation of ‘newly discovered’ constraints. Moreover, if the new constraints can be controlled well, the delivery of the additional available energy can be improved.

From the vantage point of one or two hundred years ago, that ‘new’ available energy could be what we call nuclear today.

**4.2.2 Significance of the Dead State.** Consider the object of Figure 1 again, but this time in conjunction with a medium like that depicted by the flat surface in Figure 4. And, for simplicity, assume that the curve through BC in Figures 2 and 5 is for the constant volume passing through the point of tangency in Figure 4. That point of tangency represents the dead state of the object, at the overall dead state of the composite of object and medium. Shown on Figure 5 is the line that is in
the plane and passes, through the point of tangency at 0. The slope of that line is the temperature at that overall dead state located at 0.

If the object is at A, the available energy of the composite (the overall system including the object and the medium) is equal to the distance $E_A - E_H$ on Figure 5. If the object is at B (with no available energy of its own), the available energy of the composite is $E_B - E_H$.

When delivering available energy, entropy production within the object, when starting at A, is represented by the horizontal distance between A and $\gamma$. Further entropy production, as a result of interactions with the medium, is the horizontal distance between $\gamma$ and $\mu$. The overall delivery when proceeding from A to $\mu$ is $E_A - E_{\mu}$.

Finally, suppose there exists another medium at say a much lower temperature, represented by the tangent line through 0′ on Figure 6. Now the overall available energy for the composite is $[E_A - E_N]$; the delivery is represented by $[E_A - E_I]$. Clearly, these are greater than $[E_A - E_H]$ and $[E_A - E_P]$, respectively. (Again, consider the nonlinearity of the $E$ scale, and for example consider what the differences would be if the slope of the straight line through 0 were 273K and that through 0′ were 27.3K or 2.73K.)

4.2.3 Intermediate Conclusions. In general terms,

- Controlling with constraints that are available with current technology can improve the delivery of available energy (to desired products).
- Moreover, if additional constraints were found, it is conceivable that delivery can be improved.
  - An obvious, simple example is control of chemical composition. In the examples presented above, chemical composition of Subsystems 1 and 2 could have been changing, and there would have been associated entropy production during delivery. Inasmuch as only entropy and volume exchanges were allowed between 1 and 2 (and with the mediums), then:
    - If the compositions of 1 and 2 (when the object was at B) differed, there could be additional available energy deliverable, if exchange of chemicals between them were allowed, and controlled, while bringing the two subsystems to chemical equilibrium.
    - Moreover, if 1 and 2 were each, alone, at chemical equilibrium but not at chemical equilibrium with an accessible medium, there would be additional available energy.
    - Additionally, if the left-hand piston in Figure 2 were controllable (in essence, making both $V_1$ and $V_2$ constraints that could be manipulated) spontaneous change of composition within 1 and 2 could be controlled, reducing (and in theory eliminating) associated entropy production.
  - This simple example, chemical, is only an example. The important point is that it would be significant if new constraints can be found, to unlock heretofore unavailable energy. (Relatedly, there may exist available energy that is more or less ‘hidden’, within the context of today’s science – like nuclear disequilibrium was hidden 200 years ago).
- If a medium is accessible with a lower temperature and/or with a lower pressure, and/or lower chemical potentials (or lower potentials associated with any new controlling constraint), the delivery can be increased.

5. Closure

Traditionally, the development of exergy has assumed the existence of a ‘surrounding environment’. Necessarily then, in practice exergies are evaluated relative to a reference

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7By the way, on Figure 5, the vertical lines ending on the straight lines correspond to exergies of the object. The mediums have no exergy.
8Earlier it was stated, for conceptual simplicity, that Subsystems 1 and 2 were identical. That assumption was unnecessary for the discussions that ensued, as long as 1 and 2 were constrained from exchanging chemicals.
9A theoretical scheme whereby chemical conversion of a fuel could be accomplished without entropy generation was proposed by Keenan ([10], p. 279). The method is also presented in [11], Article 3-19.
environment, which must be selected by the evaluator. Several alternative ‘standard’ reference environments have been proposed, and commonly the evaluator will choose one of them. In any case, the engineering ‘dead state’ is dictated by the selected reference environment. And it is commonly held that, in theory at least, the dead state should be the same for all of the contents of, and the flow streams between, the subsystems of the facility being analyzed.

These habitual practices have shortcomings. By and large the shortcomings can be circumvented by referring back to the more fundamental concept underlying exergy, namely available energy.

As shown above, if an overall system is given, then (at any moment) the overall dead state and the dead states of all subsystem and their materials is unique. No reference environment is necessary. If, as usual, one of the subsystems is a large surrounding medium, in a sense it is ‘just one more subsystem’. Nevertheless, it may have a dominant (if not total) effect upon the dead state of the other subsystems. However, those subsystem dead states will not all be in complete equilibrium with the surrounding medium. Generally, subsystems will be in constrained equilibrium with the surroundings (For example, as referred to earlier, at its dead state the refrigerant in a vapor-compression system will be in thermal equilibrium with the system’s surroundings, but not in pressure or chemical equilibrium.)

The preceding paragraph began with “. . . if an overall system is given . . . the overall dead state . . . is unique.” That statement is subject to several, related stipulations:

- The modes of interaction between subsystems must be specified.
- The constraints on subsystems must be specified.

That is, defining an overall system (making it ‘given’) requires not only identification of its parts, but also how they will be allowed to interact and what constraints are imposed upon the parts and the interactions.

5.1 Defining an Overall System

It is imperative that, whenever the results of an exergy analysis or exergy evaluation of resources is presented, it should be clear to the reader what the underlying “overall system” is – its make-up and the assumed interactions and constraints. In theory, this clarification should be made by the authors. If it has not been made explicitly, a careful reader will seek to determine what overall system has been assumed. If an answer cannot be found or assumed judiciously, the reader should question (if not be skeptical, or even dismiss) the conclusions that have been drawn.

5.2 Engineering Systems

In the case of exergy analyses of engineering systems, it is generally straightforward for the reader to ascertain the overall system, as long as a reference environment has been clearly stated. The reader will naturally assume that the subsystems shown on the flowsheet, are ‘standard’ – current technology. If some are not standard the authors hopefully will have made that known.

5.3 Resource and Ecologic Assessment

Many laudable applications of exergy to ecology and sustainability have been carried out. These studies refer to the future and often project into the future – making predictions (often dire) about the future – and then make recommendations. Care needs to be exercised when considering some

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10 Some might think that it doesn’t matter what the dead state is, because when one calculates exergy differences between points in a cycle, the dead state values cancel. That thinking is flawed; it is important to know the correct, total values at every point. Otherwise significant mistakes can occur in evaluating subsystem efficiencies and especially unit costs [9].
of the conclusions drawn (especially when the conclusions and recommendations are presented ardently).

It seems that there generally are assumptions that go unrecognized or are taken for granted by both authors and readers. So the following kinds of questions arise:

- What is the overall system? Generally, it is evident that the overall system has been limited to the earth and its resources. Is that a reasonable limitation when predicting the future?
  - Are there resources outside our ‘sphere’ that will become accessible? Literal energy resources? Or subsystems that can be invoked?
  - In some remote places, the night sky is used as a source of exergy today. The background temperature of the universe is about 3K; could it be used as a ‘medium’?
  - Consider the two straight lines on Figure 5.
  - What’s the point of ‘all this’? Only that the reader of the assessments should realize that the assumed scope of the overall system has a very big effect on the results and conclusions.

- What is the overall system? (Same question!) For available energy and exergy to be meaningful, there must be a complete overall system; that is, besides the resources there must be means – theoretical and practical – for harvesting and converting them that are assumed.
  - What science and technologies have been assumed for the harvesting and converting? Presumably today’s, with their ‘control constraints’? If so, that dismisses prospective, relevant developments in science and technology.
  - Scientific advances can lead not only to new technologies but also to new resources (like fission and fusion have ‘made’ new resources – even if only theoretical so far, in the case of fusion).
  - A conjecture: Can means be found for controlling nuclear reactions, analogous say to fuel cells controlling chemical reactions, to eliminate ‘heat generation’ (entropy production) as the means for extracting the available energy? Why not?

- What are the ‘controlling constraints’?
  - Is it implicit that the control variables are classical? Electrical, mechanical, chemical and perhaps nuclear? – such that the perceived resource conversion is subject to the laws of ‘classical’ science (e.g. today’s chemical thermodynamics, with its assumed variables).
  - Again, the reader of assessments should realize that there is an implicit science and technology being assumed. Quite conceivably, future developments likely will introduce unforeseen variables, employable to control/constrain phenomena relevant to resource conversion.

5.4 Viewpoints

All ‘energy resources’ have usefulness because there exists an associated disequilibrium with our environment. It is typical of resources that the disequilibrium is constrained (thankfully) such that there is a metastable equilibrium. Their usefulness depends upon ‘breaking’ the metastable equilibrium via one constraint or another. The better the control of the ensuing equilibration, using constraints, the more efficient is the use of the resource.

Particularly regarding resources, history is filled with dreadful forecasts which have arisen in the face of challenging circumstances. Invariably, the forecasts have been made under the (inherently pessimistic) assumption that the then-current science and technology was definitive. However, humankind has not only overcome the challenges but in dealing with them has advanced – has discovered ‘new’ resources, unlocked them with new science and new technologies, improved the efficiency of usage, . . . and as a consequence has improved our subsistence.

One could say that the advances resulted, at least in part, as consequence of the challenges. So assessments of the type referred to above should be appreciated – as challenges.

Nevertheless, there is a great amount of disequilibrium, particularly metastable equilibrium in our universe. Our future technology is not earthbound. Moreover, it can be hoped (and from a historical perspective, expected) that – spurred on by challenges – future science and technology
will unlock not only remote resources but ‘hidden’ or currently ‘unreachable’ earthly resources as well. Some would say, “That’s overly optimistic. Careless. We should ‘play it safe!’” The readers will have a variety of viewpoints (worth discussing!).

In any case, let the readers of ‘assessment’ papers that refer to the future understand that there are implicit assumptions that are very important, and will prove to have been very important.

Acknowledgments

I would like to acknowledge and thank the following ‘schools of thermo’ that I have learned from: Obert, Hirschfelder-Curtiss-Bird, Hatsopoulos-Keenan-Gyftopoulos, Tribus-Evans-ElSayed. I have benefitted from many others of course, and I appreciate and thank all of you.

Appendix

The concept of entropy has been taken for granted in this presentation. The author [12] prefers to take the existence of entropy axiomatically, rather than derive it in manners such as the common $dS = dQ_{rev}/T$ or methods similar to the $dS = C d[E-\Omega]$ of [4], where $\Omega$ is the ‘available work’. To the extent of the author’s awareness, Obert [13] was the first to postulate the existence of entropy, and then Callen [14]; these authors defined entropy only for equilibrium states.

Using the likes of $dS = C d[E-\Omega]$, Hatsopoulos and Gyftopoulos [15] proved the existence of entropy for non-equilibrium states, too (or, see Gyftopoulos and Beretta [16]). If it is accepted that entropy exists for nonequilibrium states then there can be logical objection to postulating that it exists for these states as well as equilibrium states, as long as it can be proved that $dS = C d[E-\Omega]$ is then a result. Whether to ‘begin’ with $dS = C d[E-\Omega]$ or with the postulation of entropy’s existence is then a matter of preference. The author contends that postulation is preferable, because then all of useful thermodynamic relations can be derived in a much more streamlined manner [12]. Many concepts that students struggle with and/or find ‘superfluous’ are eliminated. For examples, the concepts of reservoir or, even, reversibility are not needed. Unlike available work or adiabatic availability, available energy is deliverable by any mode – mechanical, with Force or Torque (momentum currents); electrical, with charge current; . . . ; thermal, with entropy current). By the way, available energy (and exergy) delivered with any one current is as good as that delivered with any other. With the postulation of entropy, maintaining strict logic doesn’t require ponderous definitions of work and/or heat. As a matter of experience, students find the concept of entropy and, in turn, all of thermodynamics easier to comprehend when entropy is postulated. Developing and then putting ‘heat’ – a transport not an additive property – ahead of entropy is in the author’s opinion, putting the cart ahead of the horse, and very difficult to ‘operate’.  

\[\text{\textsuperscript{11}}\text{There is an old saying, “Don’t let a crisis go by without taking advantage of the opportunity.” It should not be assumed that to ‘play it safe’ is without ‘cost’.}

\[\text{\textsuperscript{12}}\text{It is a matter of convenience and ‘standard practice’ that the assignment of units to energy is via mechanical work. Keenan and Shapiro [17] proposed a thermal method for stating the 1\textsuperscript{st} Law and assigning units to energy. That possibility supports, implicitly, the rationality of postulating the existence of entropy.}

\[\text{\textsuperscript{13}}\text{It should have been mentioned that, following Shannon and Jaynes, Tribus [18] postulates an entropy (call it } \eta \text{ here) to be a certain probability-measure of uncertainty, namely } \eta = - k \Sigma [p_i \ln(p_i)] \text{ where } p_i \text{ is the probability of the } i\text{th quantum state of the material. With that postulate certain ‘general’ and useful relationships of Statistical Thermostatics (the ‘Boltzmann distribution’ and the associated ‘partition function’) follow straightforwardly. To relate that entropy to the entropy of thermodynamics, a resulting equation for ‘reversible’ processes, } d \langle e \rangle = [1/\beta] d \eta - p \, dv \text{ is compared to } de = T \, ds - p \, dv. \text{ Assuming that } \eta \text{ and } s \text{ are the same thing, and that the probable energy } \langle e \rangle \text{ is what } e \text{ is, then it is rational to conclude that } \beta = 1/T. \text{ The deduction is applicable only for equilibrium states.}

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REFERENCES


THE MAGNETOCALORIC ENERGY CONVERSION

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Abstract:
The article presents a review on research and developments of the magnetocaloric energy conversion. This promising alternative technology has a large potential in domains of refrigeration and heat pumping. Moreover, it represents a potential alternative for the power generation by the application of low temperature energy sources. High energy efficiency and application of environmentally friendly refrigerants make this technology as a serious alternative to phase out vapour-compression. Substantially increased international research activities in the last two decades led to development of about 45 prototype devices. Despite strong research efforts are still required, the technology is ready to be developed for certain special market niches. This article shows some basic information on physics of the magnetocaloric energy conversion. It presents most important research activities and achievements. Temporary limits that researchers are facing at the moment are described in the article. Perspectives of the technology are presented and the guidelines for the future research and developments are given.

Keywords:
Magnetocaloric, Energy conversion, Energy efficiency, Magnetic refrigeration

1. Brief history of research and developments

The magnetocaloric energy conversion is a technology which applies the magnetocaloric effect (MCE). The technology applies solid refrigerants (magnetocaloric materials) which have global warming potential (GWP) and ozone depletion potential (ODP) equal to zero. The MCE of many of existing magnetocaloric materials represent a reversible process. Already the earliest prototypes have demonstrated exergy efficiency higher than that of existing compressor-based technologies. The magnetocaloric energy conversion has a potential of running machines with the very high exergy efficiency. A silent operation without vibrations makes this technology attractive for large number of applications. The magnetocaloric energy conversion regards the magnetic power generation, magnetic heat pumping, and the magnetic refrigeration.

The magnetocaloric effect (MCE) was first discovered by Warburg [1], who in 1881 observed an increase of temperature when he had brought an iron sample into a magnetic field and a decrease when the sample was removed out of it. Soon after this discovery, approximately in 1890, Tesla [2] and Edison [3] independently and unsuccessfully tried to benefit from this effect by running heat engines for “power production”. In 1918 Weiss and Piccard [4] explained the magnetocaloric effect. Later Debye [5] and Giauque [6] proposed a method of magnetic refrigeration for low temperature physics in order to obtain sub-Kelvin temperatures. In 1933 Giauque and MacDougall [7]
successfully verified the method by experiment. Since the 1930’s magnetic refrigeration is a standard technique in low temperature physics.

In the magnetic power generation, there were not much research and development activities performed until the 1950’s, when a large interest of scientists was created by the idea of performing magnetic power generators by applying magnetocaloric suspensions as working fluids. Most of this pioneering work was performed by Resler and Rosensweig [8,9]. However, some single earlier publications than those may be found in [10-13]. There is no evidence that any of these early ideas were transformed to real working prototypes. Thirty years later most of the publications were related to studies of magnetocaloric power generators with solid working materials [14-16]. In the last few years activities on the magnetic power generation can be found in the following references [17-23].

In 1976 Brown [24, 25] designed the first magnetic refrigerator working at room temperature. After that a number of patents were announced, which describe such refrigerators. This may be noted to be the time of the first generation of magnetic refrigerators. With the discovery of the “giant magnetocaloric effect“ [26], the development of magnetic refrigeration gained increased momentum. Since then, the number of papers published in international journals has grown exponentially. The number of patents in this area is also increasing. The first “room temperature” magnetic refrigerator – containing permanent magnets – was designed and built in 2001 [27]. Then the start of the development of a new second generation family of magnetic refrigerators began.

Approximately forty five prototype magnetic refrigerators and heat pumps have been built in different parts of the world [28]. The research in magnetic refrigeration is nowadays focused on improvements on magnetocaloric materials, magnets and their materials, thermodynamics and fluid dynamics and an optimal design and building of devices. Large number of studies on the simulation and optimization of magnetocaloric regenerators have been performed [29], while other studies deal with the design and optimization of the permanent-magnet assemblies that are normally used in prototypes [30-35]. Large number of studies has been focused on the magnetocaloric materials [36-40], and few newer publications are related also to the economics of magnetic refrigeration [41-45].

2. Thermodynamics

The first law of thermodynamics for a closed thermodynamic-magnetocaloric system can be written as:

\[ du = \delta q + \mu_e H \, dM \]  

(1)

where \( H \) represents the magnetic field intensity in the material and \( M \) represents the magnetization within the magnetocaloric material. For a reversible process it is permissible to rewrite the Eq.(1) into the following relation:

\[ du = T \, ds + \mu_e H \, dM \]  

(2)

where \( s \) represents the total specific entropy of the magnetocaloric material. Its derivative for constant pressure and volume may be defined as:

\[ ds(T,H) = \left( \frac{\partial s}{\partial T} \right)_H \, dT + \left( \frac{\partial s}{\partial H} \right)_T \, dH \, . \]  

(3)
One of the most important thermodynamic potentials applied in engineering is enthalpy. It presents the potential to describe the behaviour of an open thermodynamic system with the work performed over its boundary.

\[ h = u - \mu_0 H M \]  

The derivative of this potential is:

\[ dh = du - \mu_0 H \, dM - \mu_0 McdH \]  

Inserting (3) it follows that:

\[ dh(s, H) = \left( \frac{\partial h}{\partial s} \right)_H \, ds + \left( \frac{\partial h}{\partial H} \right)_s \, dH = T \, ds - \mu_0 McdH \]  

In the closed thermodynamic system, no magnetocaloric material is transferred in or out of the system boundaries. In an open magnetic thermodynamic system, the magnetocaloric material “flows” as the continuum in and out of the system boundaries. The first law of thermodynamics for such systems states that the increase in the internal energy of the system equals the amount of energy added to the system by the “flow” (e.g., rotation) of the magnetocaloric material into the system’s boundary and by heating, reduced by the amount of energy lost by the “flow” of the magnetocaloric material out of system’s boundaries and reduced by the work done by the system. The specific technical work may be defined as:

\[ dw = dq - dh = \mu_0 M \, dH \]  

The heat alternation in the magnetocaloric material in its specific form may be defined as:

\[ dq = c_H(T, H) \, dT + c_T(T, H) \, dH \]  

where \( c_H \) denotes the specific heat capacity at a constant internal magnetic field \( H \). The second specific heat \( c_T \) denotes the specific heat capacity at a constant temperature. The specific heat may also be expressed using Maxwell’s relations:

\[ c_H = \left( \frac{\partial q}{\partial T} \right)_H = T \left( \frac{\partial s}{\partial T} \right)_H \]  

and

\[ c_T = \left( \frac{\partial q}{\partial H} \right)_T = T \left( \frac{\partial s}{\partial H} \right)_T = \mu_0 T \left( \frac{\partial M}{\partial T} \right)_H \]  

Magnetic refrigeration process can be based on different thermodynamic cycles, i.e. like Brayton, Ericsson, Carnot, etc. Those potential cycles are in general based on three processes, which will further be explained in detail.

The Isothermal (de)magnetization process occurs in the Carnot, Ericsson and Stirling magnetic cycles. Isothermal magnetization requires simultaneous magnetization and heat transfer within the magnetocaloric material in such a way that during the alternation of the volumetric magnetic flux the temperature does not change. Heat alternation in this particular case leads to:

\[ dq = c_T(T, H) \, dH = T \left( \frac{\partial s}{\partial H} \right)_T \, dH = \mu_0 T \left( \frac{\partial M}{\partial T} \right)_H \, dH \]  

The derivative of the specific enthalpy is then:
The total specific entropy change is calculated by applying Eq. (3):

\[ ds(T, H) = \left( \frac{\partial s}{\partial H} \right)_T dH. \]  

(13)

Or by an integration between two magnetic fields:

\[ \Delta s = s_2 - s_1 = \int_{H_1}^{H_2} \left( \frac{\partial s}{\partial H} \right)_T dH = \int_{H_1}^{H_2} \mu_0 \left( \frac{\partial M}{\partial T} \right)_H dH = \int_{H_1}^{H_2} \frac{c_T}{T} dH, \]  

(14)

where \( s_1 \) is the specific entropy at the field \( H_1 \) and \( s_2 \) at \( H_2 \).

The **isofield heating** (cooling) processes of heating and cooling of the magnetocaloric material in a constant magnetic field correspond to the Brayton, Ericsson, and Stirling magnetic cycles. The heat transfer is mostly provided by the flow of the working fluid through the porous structure of the magnetocaloric material. Heat alternation in this particular case leads to the following expression:

\[ dq = c_H dT = T \left( \frac{\partial s}{\partial T} \right)_H dT \]  

(15)

Furthermore, the specific enthalpy derivative takes the following form:

\[ dh = dq \]  

(16)

Eq. (16) shows that the enthalpy difference may be defined for the isofield in a similar way as in conventional gas thermodynamics for the isobaric process where:

\[ c_H = \left( \frac{\partial h}{\partial T} \right)_H \]  

(17)

The **Adiabatic (de)magnetization** process occurs in the Brayton and Carnot cycles. In the ideal case the adiabatic magnetization can be considered as an isentropic process. Since the alternation of the heat equals zero, then Eq.(8) takes the following form:

\[ c_H(T, H) dT = -c_T(T, H) dH = -\mu_0 \left( \frac{\partial M}{\partial T} \right)_H. \]  

(18)

The differential of the specific enthalpy equals:

\[ dh = -\mu_0 M dH = -dw, \]  

(19)

Eq.(19) denotes that for isentropic magnetization or demagnetization, the derivative of the enthalpy is equal to the technical work. The same may be obtained in conventional thermodynamics for isentropic gas compression or expansion, where \( dw = -vdP \). In an adiabatic process the total specific entropy does not alter \((ds=0)\). It follows that:

\[ \left( \frac{\partial s}{\partial T} \right)_H dT = -\left( \frac{\partial s}{\partial H} \right)_T dH. \]  

(20)

Rearranging the Eq.(18), a further relation is obtained:

\[ dT = -\frac{c_T}{c_H} dH. \]  

(21)
It follows:

\[
\frac{dT}{T} = -\frac{\mu_0}{c_H} \left( \frac{\partial M}{\partial T} \right)_H dH.
\] (22)

With a knowledge of the temperature as a function of the specific entropy for different isofields, it is more convenient to perform the following integration:

\[
\Delta T = \int_{T_1}^{T_2} dT = T_2(s, H_2) - T_1(s, H_1),
\] (23)

where \(T_2(s, H_2)\) is the temperature of the magnetocaloric material at the higher magnetic field \(H_2\) and \(T_1(s, H_1)\) at the lower magnetic field intensity, both evaluated at the same specific entropy.

Figure 1: Left: The analogy with the vapour compression (I. magnetization vs compression, II: heat flow to heat sink vs condensation, III. Demagnetization vs expansion, IV. Heat flow from the heat source vs evaporation), Right: Calculated adiabatic temperature change and isothermal entropy change for the reference magnetocaloric material Gadolinium

3. Magnetocaloric devices and their characteristics

The existing magnetocaloric materials in magnetic fields accessible by permanent magnets do not exhibit a sufficiently large magnetocaloric effect that would enable its direct application in a refrigeration device. This is especially true for systems based on rather small magnetic field changes; for instance, applications with permanent magnets. Therefore, most of magnetic refrigerators perform a regenerative process in order to increase the temperature span. The regenerator in magnetic refrigeration represents a device that serves for the heat transfer between different phases of a thermodynamic process and thus enables an increase of the temperature span. There are two basic types of regenerators, the passive and the active magnetic regenerator (AMR)
respectively. The passive regenerator may store and/or transfer heat during different processes of the thermodynamic cycle. It applies the working fluid for the heat transfer. In the domain of magnetic refrigeration, such regenerators are applied mostly in applications in low-temperature physics. At or near the room temperature, all the current prototypes of magnetic refrigerators are based on the AMR principle (Yu et.al [28]). A review of numerical models for the AMR was given by Nielsen et al. [29]. Following the early work of Brown [25], the concept of the active magnetic regenerator (AMR) refrigeration was introduced by Steyert [46] and developed by Barclay [47, 48]. After Barclay the research on the active magnetic regeneration led to several publications in the 1980s and 1990s (see, e.g., [14-15, 49-51]). Some examples of newer publications can be found in e.g. [29, 52, 53].

The active magnetic regeneration (AMR) is a process, when the magnetocaloric material itself acts as a regenerator, and as the source/sink of the heat induced by the magnetocaloric effect. In active regeneration (AMR) systems there is no overlapping of the “cycles”, as is usually the case in a cascade system. As explained by Hall et al. [55] and Tishin and Spichkin [36], each particle of the AMR does not directly pump heat to the next-neighbour particle, but all particles accept or reject heat to the heat-transfer fluid at the same time and are coupled indirectly through the fluid. Because of the “counter current” fluid flow, particles and their internal (local) cycles interact with the neighbouring ones by the heat transfer of the fluid, thus performing the regenerative process. AMR therefore performs a unique thermodynamic process, where each infinitesimally small particle of the magnetocaloric material performs its own thermodynamic cycle. Almost all the existing analyses of the AMR are based on the Brayton-like thermodynamic cycle. However, there is a possibility to perform a number of different thermodynamic cycles in combination with the AMR process.

3.1. Types of magnetocaloric devices

The magnetic field sources, which can be applied in magnetocaloric devices, are: permanent magnets, superconducting magnets, electromagnets. Below are given certain most common features of magnetic refrigerators. Those, who have not been developed yet in practice, are underlined. Machines with moving parts are:

- rotary (rotation of magnetocaloric material or rotation of magnetic field source),
- linear (linear motion of magnetocaloric material or linear movement of the magnetic field source).

Without moving parts:

- magnetocaloric suspensions or, nanofluids,
- »on-off« magnetic field.

Rotary magnetic refrigerators

Rotary magnetic refrigerators present (at the moment) the most efficient way to perform magnetic refrigeration. Most of the prototypes apply rotation of the magnetocaloric material through the static magnetic field, performed by the permanent magnet assembly. Magnetocaloric material forms or it is embodied in the structure which has a form of a disc, torus or a cylinder. Rotary magnetic cooling devices can be realized in order to perform various thermodynamic cycles. Figure 2 shows a schematic example of the rotary type of magnetic refrigerator (heat pump), where the magnetocaloric material is contained in the ring, which rotates through static magnetic field (in the figure this is shown by grey region). The fluid flow in the case of the Figure 2 is such, that the magnetocaloric regenerator performs active magnetic regeneration. Since magnetocaloric materials have restricted
temperature range of their efficient operation, the regenerator must consist of different magnetocaloric materials, which are layered in a direction of a temperature gradient. If the operation of the magnetic refrigeration cycle is such that it operates between two constant magnetic fields (isofields, analogue to isobars in conventional refrigeration), and two isentropic processes (fast reversible adiabatic magnetization or demagnetization, e.g states 2-3 and 4-1 respectively), then such process is Brayton AMR process. By the simultaneous variation of the magnetic field intensity and the heat transfer it is possible to create also other types of magnetocaloric thermodynamic cycles. Such an example is shown in the Figure 5, where an Ericsson AMR magnetic refrigeration (heat pump) cycle is shown.

Figure 2: Left: An example of the “Brayton” type of magnetic refrigerator with the rotary motion of the magnetocaloric material Right: The T-s diagram of the Brayton AMR regenerative magnetic refrigeration cycle

Figure 3: Left: The first rotary magnetic refrigerator built at the University of Ljubljana. In the middle, the coaxial ring is shown with 34 magnetocaloric regenerators[54]. Right: second rotary magnetic refrigerator built at the University of Ljubljana.
Linear magnetic refrigerators

This kind of devices may be considered as experimental devices or demonstrators, rather than prototypes for potential market applications. The operation of such devices is based on the linear motion of magnet or magnetocaloric material through a magnetic field. All types of magnets have already been applied in such prototypes. Magnetocaloric material is usually in a form of a cylinder or a block. The last may be filled with the magnetocaloric material in a shape of rods, spheres, grains, plates, etc. The construction and design of such a device is simpler than for the rotary one. However, in order to perform a continuous operation, such have the rotary magnetic refrigerators, the device has to be consisted of two coupled devices, unless certain reservoirs are used. The frequency of the operation and related cooling power cannot be compared with the rotary device. Furthermore, the linear device has lower efficiency due to the acceleration and deceleration.

Figure 6: Left: An example of the “Brayton” type of magnetic refrigerator with linear motion of the magnetocaloric material or motion of the magnetic field source, Right: The T-s diagram of the Brayton AMR regenerative magnetic refrigeration cycle
Figure 7: A photography of the linear magnetic refrigeration experimental device and the permanent magnet assembly developed at the University of Ljubljana

3.2. Magnetic field source and magnetocaloric materials

Magnetic field is a driving force of the magnetocaloric effect and consequently of the magnetic refrigerator. The magnetic field can be produced with electromagnets, superconducting magnets or permanent magnets. Electric magnets require additional power, and the electric resistance of conductors partly converts electricity into joule heating. Superconducting magnets are more interesting; however their price limits their use only to large scale applications. These are reasons why permanent magnets are applied in most of prototypes. Currently, the strongest permanent magnets are based on neodymium-iron-boron (Nd-Fe-B) due to the highest maximum energy product (BH$_{\text{max}}$), which is one of crucial parameters for the selection of a permanent magnet. In magnetic refrigeration (heat pumping) at room temperature, the magnetic fields applied in devices are in the range between 0.7 to 2.4 Tesla. The tendency is to reduce the magnetic field, since this is coupled with the third order with the mass of magnets, which are rather expensive.

A large number of different magnetocaloric materials can be applied in magnetocaloric energy conversion. From the periodic system, the rare earth metal gadolinium may be regarded to be the ideal substance of magnetic refrigeration, just as the ideal gas is for conventional refrigeration. However, the magnetocaloric effect of gadolinium is not so large as this is the case for some other magnetocaloric materials. Furthermore, each magnetocaloric material can operate in a limited temperature span. At present, most interesting materials are for example La(Fe,Si,H), La(Fe,Co,Si), or La(Fe,Co,Mn,Si), or Mn(Fe,Si,P). More information on magnetocaloric materials may be found in [36-40, 56, 57].

4. CONCLUSION

Magnetocaloric energy conversion did not reach yet market applications. The major obstacle of this green technology is the cost of device, which is strongly related to materials (mostly permanent magnet materials, partly magnetocaloric materials). Most of existing prototype devices operate with the low frequency of the operation (small number of thermodynamic cycles per unit of time, what leads to low power density). The reasons, not only for the low power density, but also for the low efficiency of existing prototype machines are related to low manufacturability of magnetocaloric
materials, high heat transfer irreversible losses, losses related to flow dividers, and losses related to fluid switching valves with internal leakage of the fluid. In certain cases high viscous losses are present, and some machines operate with high mechanical friction losses.

![Yearly published papers](image)

**Figure 8: Yearly published papers (by keyword: “magnetocaloric” in ScienceDirect search engine)**

Researchers are trying to solve each of the above issues by innovation of the new solutions. Improvements regard: optimization of magnet assemblies, application of new working liquids, better processing of magnetocaloric materials, new magnetocaloric materials, introduction of new thermodynamic cycles, introduction of new heat transfer mechanisms, new machine concepts, etc. And there still exists a large room for improvements, as it was proposed by Kitanovski and Egolf [58]. Such solutions may lead to an increase of the existing maximal frequency of the operation of 5 Hz up to an order higher, what will substantially influence the future of magnetocaloric devices and their market applications. Following the existing achievements, the magnetocaloric energy conversion, despite it was up to present mostly focused in the refrigeration domain, offers the possibility of market penetration in several different domains, especially for devices with rather smaller power of up to few kW.

### 5. Nomenclature

#### Standard

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
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<tbody>
<tr>
<td>c</td>
<td>Specific heat capacity</td>
<td>J m⁻³ K⁻¹</td>
</tr>
<tr>
<td>COP</td>
<td>Coefficient of performance</td>
<td>/</td>
</tr>
<tr>
<td>h</td>
<td>Specific enthalpy</td>
<td>J m⁻³</td>
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<td>A m⁻¹</td>
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<tr>
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#### Greek

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<td>φ</td>
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<tr>
<td>µ</td>
<td>Permeability of vacuum</td>
<td>VsA⁻¹ m⁻¹</td>
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#### Subscripts

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<td>vacuum</td>
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U Internal energy J
U Specific internal energy J m⁻³
W Work J
W Specific work J m⁻³

References

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