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Exergy analysis in ProSimPlus[®] simulation software: A focus on exergy efficiency evaluation

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A B S T R A C T

On industrial sites, the promotion of best practices to enable an efficient utilization of energy has emerged as one of the major point of focus. Among the different approaches existing to improve industrial processes, the exergy analysis, although limited to the academic world, has been shown to be a powerful tool for improving energy efficiency of thermal and chemical systems. The purpose of this paper is then to present the use of the ProSimPlus[®] modelling and simulation environment as an exergy analysis computer-aided tool. Expressions implemented in the simulator for computing exergies in its various forms are presented. The adopted approach for calculating exergy efficiency in a systematic way is also exposed; it combines the fuel-product concepts to the transit exergy concept. ProsimPlus[®] exergy module's capabilities are illustrated through the example of an ammonia production plant.

1. Introduction

The industrial sector accounts for one third of the worldwide energy consumption. High volatility of energy prices and the more and more stringent environmental regulations have stimulated the search for further improvements to cut the energy consumption down and reduce GHG emissions. A short term solution consists in improving energy efficiency of industrial processes. As attested by the numerous publications (Luis, 2013), exergy analysis has been shown to be a powerful tool for assessing and improving energy efficiency of thermal and chemical processes. Such a kind of analysis is based on the so-called exergy concept. The latter results from the combination of the first and second principles of the thermodynamics. Several authors (Kotas, 1985; Sciubba and Wall, 2007; Szargut et al., 1988) defined exergy as the maximum theoretical useful work obtained if a system is brought from its actual state (T, P, z) to a thermodynamic equilibrium with an exergy reference environment (T^{00}, p^{00}, z^{00}) by means of reversible processes.

Since the 2000s, case studies have encouraged the development of dedicated exergy calculation tools (Abdollahi-Demneh et al.,

2011; Modarresi et al., 2012; Montelongo-Luna et al., 2007). Yet although such tools enable to obtain satisfactory results for the considered case study, they have not provided a generic tool which can be applied in other case studies. ExerCom is a plug-in software routine to calculate exergy of material stream in Aspen and Pro/II (CCS Energie Advies, 2014) using formulations described by Hinderink et al. (1996). However this tool does not allow for the calculation of exergy destruction and exergy efficiency (CCS Energie Advies, 2014).

The difficulty to handle exergy concept and the lack of exergy analysis methodology in process simulators make this kind of analysis more or less limited to the academic world. One solution to promote such an analysis and to provide engineers with a computer aided and dedicated tool would be to implement it in a process simulation software which would automatically compute exergy balance so as easily as for mass and enthalpy balances.

This work is part of the ANR-COOPERE project (French National Research Agency – Combiner Optimisation des Procédés, Récupération énergétique et analyse Exergétique – Combining Process optimisation, Energy Recovery and Exergy analysis) involving several partners (Veolia Environnement Recherche et Innovation, AgroParisTech, ProSim S.A and Laboratoire de Génie Chimique) and aimed at implementing a complete methodology of exergy analysis for process retrofitting in the process simulation software ProSimPlus[®].

Nomenclature

General symbols

B	exergy flow (kW)
b	molar exergy (kJ/mol)
H	enthalpy flow (kW)
h	molar enthalpy (kJ/mol)
s	molar entropy (kJ/(mol K))
z	global molar composition of material stream (–)
x	liquid molar fraction (–)
y	vapor molar fraction (–)
f	fugacity
T	absolute temperature (K)
P	absolute pressure (atm)
N_c	number of components (–)
R	universal gas constant (kJ/(mol K))
W	power (kW)
I	irreversibility or internal losses (kW)
C_p	specific heat capacity (kJ/(mol K))
Q	amount of exchanged energy (kW)
a	molar activity (–)
n	molar flow rate (kmol/h)
\bar{T}	thermodynamic average temperature (K)

Greek symbols

η	exergy efficiency
ϕ	fugacity coefficient
ω	vaporization rate

Subscripts

in	input stream
out	output stream
rat	rational efficiency
int	intrinsic efficiency

Superscripts

ch	chemical
ph	physical
l	liquid phase
v	vapor phase
E	relative to the free excess enthalpy or entropy
φ	physical phase
*	relative to perfect gas
ΔP	mechanical component of physical exergy
ΔT	thermal component of physical exergy
0	standard state (pure-component, ideal gas, $T^0 = 298.15$ K, $P^0 = 1$ atm)
00	environmental state
W	related to work stream
Q	related to heat stream
<i>consumed</i>	related to consumed exergy
<i>produced</i>	related to produced exergy
<i>utilized</i>	utilized stream
<i>waste</i>	waste stream

In the previous work, Ghannadzadeh (2012) and Ghannadzadeh et al. (2011, 2012) introduced the use of ProSimPlus® simulator for exergy analysis of processes and especially the use of rational exergy efficiency as an optimization criterion. Yet, although it appeared to be a very promising performance criterion, the definition of this parameter usually requires the intervention of the user which is quite incompatible with the implementation in a process simulator. This paper presents another exergy efficiency criteria, the intrinsic exergy efficiency introduced by Brodyansky et al. (1994), which has finally been retained as the exergy performance criteria in ProSimPlus®. Although the literature (Brodyansky et al., 1994) highlights the benefits of this criterion, its generic formulation in view of its implementation in a process simulator has not been developed. Moreover, an original graphical tool is also introduced to help the engineer in the exergy analysis and guide him towards the proposal of improvement solutions.

In a first part of the paper, an exhaustive presentation of all the formulations implemented in Simulis Thermodynamics® and ProSimPlus® for the calculation of exergy of material streams regardless of how the thermodynamic model is described. Then, the emphasis is put on the good practices for the modelling of processes dedicated to the exergy analysis and the automatic computation of the intrinsic exergy efficiency in the simulator is largely detailed. Finally, a representative case study is developed in order to highlight the significant contribution of simulation for the exergy analysis and the improvement of the exergy efficiency of industrial processes.

2. Exergy calculations

For the purpose of exergy balance, all types of exergy associated with material, heat and work streams involved in a process have to be calculated. In this section, generic formulations for computing exergy in the process simulation software are discussed. In order to outline the developments performed in the simulator, an exhaustive presentation of the formulation dedicated to the computing of exergy is given in the following section.

2.1. Exergy of material stream

2.1.1. General formulations

Analogously to energy, and neglecting kinetic and potential terms, the total exergy of a material stream is expressed as the sum of chemical exergy and physical exergy (Szargut et al., 1988).

Physical exergy, given by Eq. (1), can be further decomposed into thermal and mechanical exergies (Tsatsaronis, 2007). Thermal exergy is related to temperature and is given by Eq. (2) while mechanical exergy is associated to pressure and can be calculated from Eq. (3). As explained above, the exergy concept results from the combination of the first and second laws of thermodynamics.

$$b^{ph} = (h(T, P, z) - h(T^{00}, P^{00}, z)) - T^{00} \cdot (s(T, P, z) - s(T^{00}, P^{00}, z)) \quad (1)$$

$$b^{\Delta T} = (h(T, P, z) - h(T^{00}, P, z)) - T^{00} \cdot (s(T, P, z) - s(T^{00}, P, z)) \quad (2)$$

$$b^{\Delta P} = (h(T^{00}, P, z) - h(T^{00}, P^{00}, z)) - T^{00} \cdot (s(T^{00}, P, z) - s(T^{00}, P^{00}, z)) \quad (3)$$

Chemical exergy which is related to the chemical composition of a material stream is given by Eq. (4) (Ghannadzadeh et al., 2012).

ProSimPlus® is a process engineering software that performs rigorous steady-state mass and energy balances for a wide range of industrial processing plants (ProSim S.A., 2014). Simulis Thermodynamics®, ProSim's acclaimed thermodynamic server, is embedded in ProSimPlus®. This allows seamless access to all kinds of physical properties calculations and in-depth analysis on the pure components or mixtures involved (ProSim S.A., 2014).

This paper comes as a follow-up to previous work carried out by Ghannadzadeh (2012), Ghannadzadeh et al. (2011, 2012).

$$b^{ch} = (h(T^{00}, p^{00}, z) - T^{00} \cdot s(T^{00}, p^{00}, z)) - \sum_{i=1}^{N_c} z_i \cdot \left[\sum_{j=1}^{N_{ref}} v_{i,j} \cdot [h_j(T^{00}, p^{00}, z^{00}) - T^{00} \cdot s_j(T^{00}, p^{00}, z^{00})] \right] \quad (4)$$

where $v_{i,j}$ is the number of moles of the reference substance j generated by one mole of substance i . N_{ref} is the number of reference substances in the reference environment. Moreover, according to Eq. (4), the calculation of chemical exergy requires to be able to compute the enthalpy h_j and entropy s_j of the reference substances in the reference environment. These calculations have already been made by [Rivero and Garfias \(2006\)](#) and introduced in the concept of standard chemical exergy proposed by [Szargut et al. \(1988\)](#). Furthermore, in analogy to partial molar quantities of thermodynamic functions, the partial molar chemical exergy of the j component, $b^{ch,j}$, can be defined as shown in Eq. (5) ([Szargut et al., 1988](#)).

$$b^{ch,j} = \left(\frac{\partial B^{ch}}{\partial n_j} \right)_{T^{00}, p^{00}} \quad (5)$$

Involving thermodynamic calculations, formulations to compute exergies of material stream have been implemented in the ProSimPlus' thermodynamic server Simulis Thermodynamics®.

2.1.2. Implementation in Simulis Thermodynamics®

It should be mentioned that while physical, thermal and mechanical exergy (Eqs. (1)–(3)) can be immediately implemented and computed by using available functions from Simulis Thermodynamics®, the formulation used for computing chemical exergy in the ProSim's thermodynamic server depends on the thermodynamic approach, i.e. homogeneous or heterogeneous thermodynamic approach. Note that both approaches presuppose the presence of several physical phases.

In this section a homogeneous approach consists in a computation of thermodynamic values by means of an equation of state (Soave–Redlich–Kwong, Peng–Robinson, Lee–Kesler, etc.) whatever the physical state is. On the contrary, a heterogeneous approach applies to each physical phase different models. For liquid mixtures, fugacities are calculated from a reference state, which is characterized by the pure component in the same conditions of physical state, temperature and pressure, the laws of the ideal solutions being corrected by using a model of free excess enthalpy, so-called activity coefficient model (NRTL, UNIQUAC, UNIFAC, etc.). Gaseous mixtures fugacities are calculated using an equation of state ([ProSim S.A., 2014](#)).

Given this distinction, we provide expressions for computing chemical exergy for each physical phase with either a homogeneous approach or a heterogeneous approach.

2.1.2.1. Chemical exergy calculations for each physical phase at T^{00} and p^{00} .

2.1.2.1.1. Chemical exergy calculations using a homogeneous approach.

The expressions for computing enthalpy and entropy for a liquid or a vapor mixture are unique and are given by Eqs. (6) and (7), respectively.

$$h^\varphi(T, P, z) = \sum_{i=1}^{N_c} z_i \cdot h_i^{0,*}(T, P) + (h^\varphi - h^*)_{T,P} \quad (6)$$

$$s^\varphi(T, P, z) = \sum_{i=1}^{N_c} z_i \cdot [s_i^{0,*}(T, P) - R \cdot \ln(z_i)] + (s^\varphi - s^*)_{T,P} \quad (7)$$

where $h_i^{0,*}$ and $s_i^{0,*}$ are the enthalpy and the entropy of the i component in the ideal gas state and the second terms in Eqs. (6) and

(7) are the mixture enthalpy departure $(h^\varphi - h^*)_{T,P}$ and the mixture entropy departure $(s^\varphi - s^*)_{T,P}$, respectively. These terms can be calculated from the chosen equation of state.

Moreover, in order to simplify the chemical exergy calculations, [Szargut et al. \(1988\)](#) introduced the gaseous standard chemical exergy $b_i^{0,*}$ that can be expressed by Eq. (8)

$$b_i^{0,*} = (h_i^{0,*}(T^{00}, p^{00}) - T^{00} \cdot s_i^{0,*}(T^{00}, p^{00})) - \left[\sum_{j=1}^{N_{ref}} v_{i,j} \cdot [h_j(T^{00}, p^{00}, z^{00}) - T^{00} \cdot s_j(T^{00}, p^{00}, z^{00})] \right] \quad (8)$$

By substituting Eqs. (6)–(8) into Eq. (4), one may obtain the following equation:

$$b^{ch,\varphi} = \sum_{i=1}^{N_c} z_i^\varphi \cdot [b_i^{0,*} + T^{00} \cdot R \cdot \ln(z_i^\varphi)] + (g^\varphi - g^*)_{T^{00}, p^{00}, z} = \sum_{i=1}^{N_c} z_i^\varphi \cdot [b_i^{0,*} + T^{00} \cdot R \cdot \ln(z_i^\varphi \cdot \phi_i^\varphi)] \quad (9)$$

where ϕ_i^φ is the fugacity coefficient of the i component in the φ phase calculated from the equation of state. As explained before, Eq. (9) can be used for both liquid and vapor phases. The computation of $b_i^{0,*}$ from chemical exergy of elements has already been explained in ([Rivero and Garfias, 2006](#)).

2.1.2.1.2. Chemical exergy calculations using a heterogeneous approach.

A heterogeneous approach applies different models to each different physical phase. Concerning the gaseous phase, chemical exergy of the mixture can be calculated thanks to the Eq. (9). Expression for computing chemical exergy of a liquid mixture is however somewhat different.

General expressions for computing enthalpy and entropy of a liquid mixture with a heterogeneous approach are given in Eqs. (10) and (11)

$$h^L(T, P, x) = \sum_{i=1}^{N_c} x \cdot h_i^{0,L}(T, P) + h^E(T, P, x) \quad (10)$$

$$s^L(T, P, x) = \sum_{i=1}^{N_c} z_i \cdot [s_i^{0,L}(T, P) - R \cdot \ln(x_i)] + s^E(T, P, x) \quad (11)$$

In addition, like the gaseous standard chemical exergy, [Szargut et al. \(1988\)](#) defined the liquid standard chemical exergy $b_i^{0,L}$ by the Eq. (12).

$$b_i^{0,L} = (h_i^{0,L}(T^{00}, p^{00}) - T^{00} \cdot s_i^{0,L}(T^{00}, p^{00})) - \left[\sum_{j=1}^{N_{ref}} v_{i,j} \cdot [h_j(T^{00}, p^{00}, z^{00}) - T^{00} \cdot s_j(T^{00}, p^{00}, z^{00})] \right] \quad (12)$$

The liquid standard chemical exergy $b_i^{0,L}$ can also be computed according to Eq. (13) where $f_i^{0,L}(T^{00}, p^{00})$ is the standard liquid fugacity of the i component at T^{00} and p^{00} .

$$b_i^{0,L} = b_i^{0,*} + R \cdot T^{00} \ln \left(\frac{f_i^{0,L}(T^{00}, p^{00})}{p^{00}} \right) \quad (13)$$

It results from Eqs. (4), (10), (11) and (12) that the chemical exergy of a liquid mixture using a heterogeneous approach can be

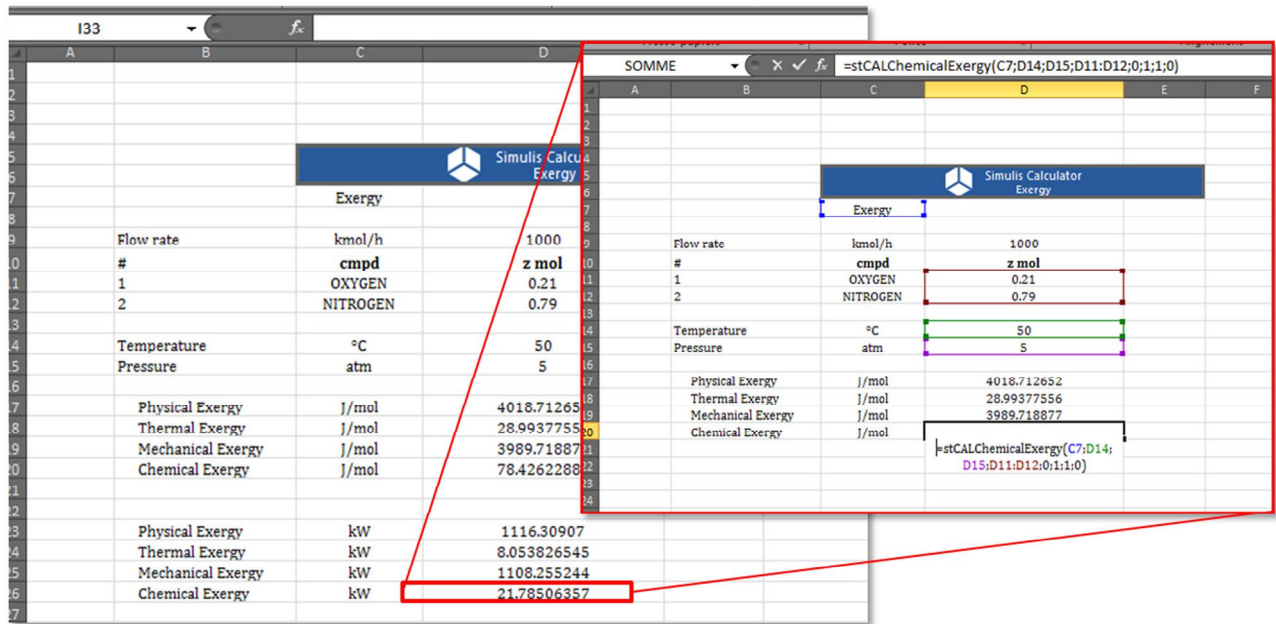


Fig. 1. Screenshot – use of exergy functions available from Simulis Thermodynamics® in Excel®.

calculated from Eq. (14).

$$b^{ch,L} = \sum_{i=1}^{N_c} x_i \cdot [b_i^{0,L} + T^{00} \cdot R \cdot \ln(x_i)] + g^E(T^{00}, p^{00}, z)$$

$$= \sum_{i=1}^{N_c} x_i \cdot [b_i^{0,L} + T^{00} \cdot R \cdot \ln(x_i \cdot \gamma_i)] \quad (14)$$

2.1.2.2. Chemical exergy of a multiphase stream at T^{00} and p^{00} .

Concerning a multiphase stream, the exergy of the mixture can be computed according to Eq. (15)

$$b^{ch} = \sum_{k=1}^{N_\phi} \omega_k(T^{00}, p^{00}, z) \cdot b^{ch,k}(T^{00}, p^{00}, z^k) \quad (15)$$

where $\omega_k(T^{00}, p^{00}, z)$ is the ratio of the k phase in the mixture, z^k is the chemical composition of the k phase, $b^{ch,k}(T^{00}, p^{00}, z^k)$ is the chemical exergy the k phase and can be calculated from equations presented above.

2.1.2.3. Conclusion on the implementation in Simulis Thermodynamics®.

Equation for computing chemical exergy provided in Szargut et al. (1988) has been revised for a complete integration in ProSimPlus' thermodynamic server Simulis Thermodynamics®.

Fig. 1 illustrates the use of exergy functions available from Simulis Thermodynamics® for the computation of exergies of an oxygen-nitrogen mixture at 50 °C and 5 atm.

2.2. Calculation and implementation of exergy of work and heat stream

Exergy associated with work streams can be calculated thanks to Eq. (16) (Dincer and Rosen, 2007) while exergy of heat streams is usually given by Eq. (17) where Q represents the amount of exchanged heat and \bar{T} the temperature of the heat source.

$$B^W = W \quad (16)$$

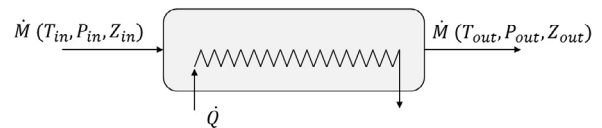


Fig. 2. Evaluation of the thermodynamic average temperature.

$$B^Q = Q \cdot \left(1 - \frac{T^{00}}{\bar{T}}\right) \quad (17)$$

Note that there is a direct equivalence between a heat stream and a material stream when the temperature \bar{T} of the heat stream is equal to the thermodynamic average temperature \bar{T} of the material stream. This temperature as expressed in Eq. (18) corresponds to the temperature of the utility, assuming a reversible heat exchange with the process stream and can be obtained by combining the first and second laws of thermodynamics (see Fig. 2) (Tsatsaronis, 1993).

$$\bar{T} = \frac{H_{out} - H_{in}}{S_{out} - S_{in}} \quad (18)$$

Contrary to material streams, formulations for computing exergy of heat and work streams have been directly implemented in ProSimPlus® as it does not necessitate thermodynamic calculations.

2.3. Conclusion

Exergy formulations have been implemented directly in ProSimPlus® when it does not necessitate thermodynamic calculations and in Simulis Thermodynamics® for material streams. It should be recalled that Simulis Thermodynamics® is embedded in ProSimPlus®.

Given the formulations for computing exergy in its several forms implemented in ProSimPlus® modelling and simulation environment, it is now possible to carry out exergy balances and exergy efficiency calculations.

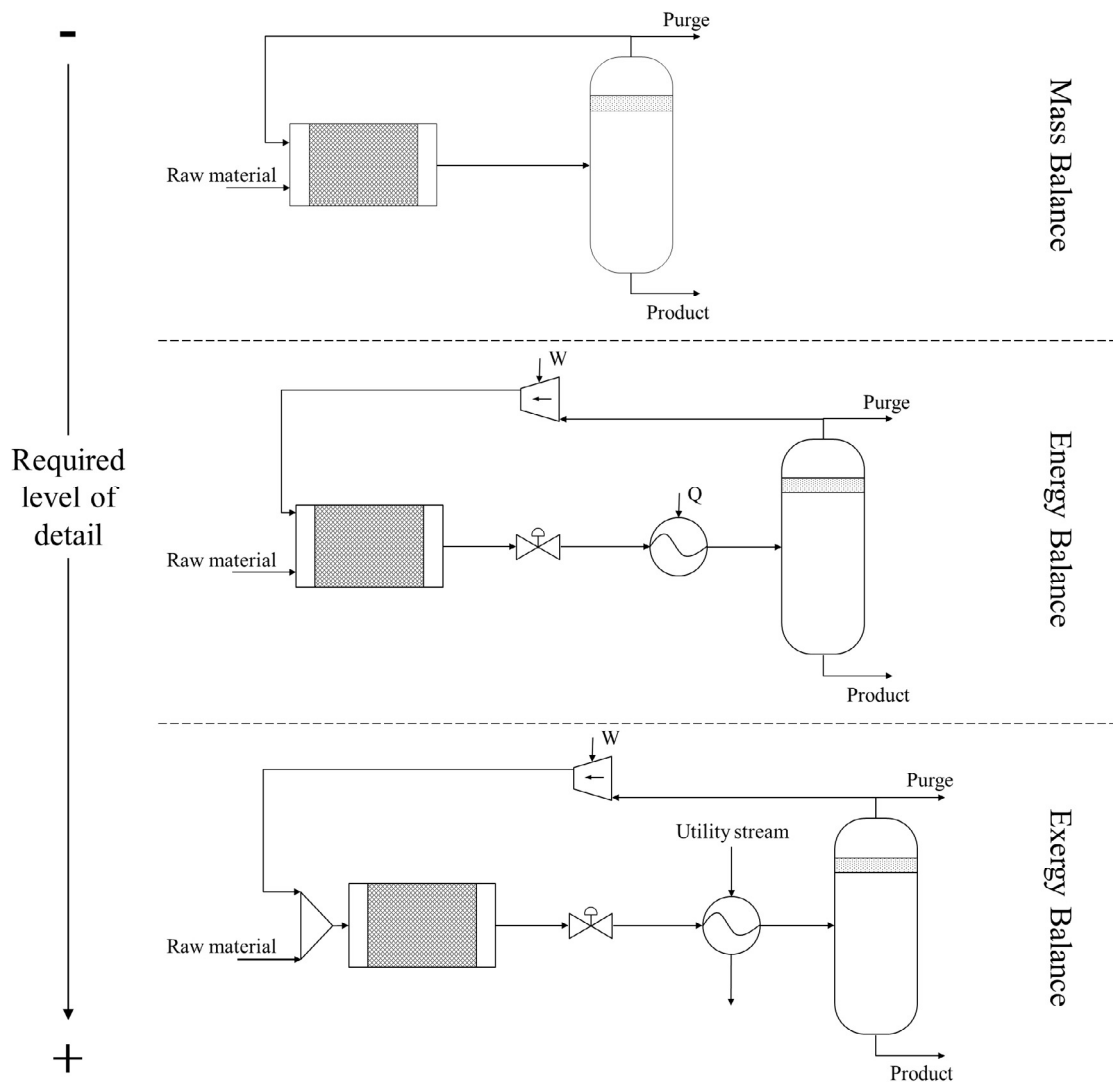


Fig. 3. Level of detail in modelling of a process according to the objective.

3. Exergy analysis in a process simulation software

The main purpose of an exergy analysis is to pinpoint sources and quantify its degree of thermodynamic imperfection of a process. These can be achieved by computing the exergy balance on one hand, and estimating the exergetic efficiency of operations on the other hand. This section relies on the ProSimPlus' ability to calculate exergy of any stream involved in a process model in a systematic way. To do so, the process needs first to be modelled in the process simulator.

3.1. Modelling of a process dedicated to exergy analysis

Levels of abstraction and detail to provide for modelling and simulating a process in a simulator highly depend on the purpose of the modelling. The level of detail needed to compute the mass balance of a process cannot be compared to that which would be appropriate to undertake an energy analysis and thus an exergy analysis.

For instance, Fig. 3 illustrates a multi-level representation of a same process producing a product from a raw material by means of a chemical reaction and a separation step. In the "mass balance" level, all pressure and temperature changes are specified in the chemical reactor and diphasic separation step. Such a modelling

approach does not provide accurate information about the energy consumption. To get such an information, the user needs to introduce in the model unit operations like pump, compressor, expander, heat exchanger, etc. that perform temperature or pressure changes. To go further, a computer-aided exergy analysis requires a modelling as close to reality as possible. This implies, for instance, an exact representation of heat utility stream. The best way to satisfy this requirement would be to represent the utility stream as a material stream instead of a heat stream. Moreover, operations should be split into several unit operations so as to distinguish the thermodynamic imperfection associated with each thermodynamic transformation. For instance, the reactor is subdivided into a mixer and a reactor.

3.2. Exergy analysis

Before presenting the exergy module implemented in ProSimPlus®, it seems appropriate to present equations used for its implementation.

3.2.1. Exergy balance in a process simulator

The evaluation of internal losses, also known as irreversibilities or exergy destructions (Tsatsaronis, 2007) can be performed using Eq. (19). Moreover, as shown in Fig. 4, output streams can also be

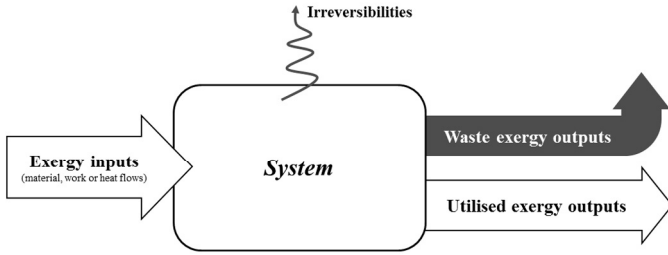


Fig. 4. Exergy balance of a system.

split into waste and utilized ones (Wall and Gong, 2001) where the waste streams represent the streams that are directly released to the environment.

$$B_{in} = B_{out}^{utilised} + B_{out}^{waste} + I \quad (19)$$

Once the exergy balance region is defined and provided that the output stream are typed (utilized or waste), Eq. (19) can be easily calculated by the process simulator ProSimPlus[®] to evaluate internal and external exergy losses.

3.2.2. Choice of exergy efficiency formulation

To perform an exergy analysis, indicators measuring the thermodynamic performance of a process are required. In our previous work (Ghannadzadeh et al., 2012), the rational efficiency (Kotas, 1985) has been chosen. However, although this formulation is a very consistent criterion, it requires the intervention of the engineer and thus cannot be automatically calculated. Of course, the opportunity to get the exergy efficiency value through automatic calculations is an essential choice criterion. Moreover, to be used in chemical engineering field, the exergy efficiency formulation should be applicable on unit operations that perform chemical transformation and not only on thermal systems. Eventually, one should observe significant variation of the exergy efficiency values when modifying process parameters. In this section, a comparative analysis of the various exergy-based efficiency formulations existing in the literature is presented.

Lior and Zhang (2007), Marmolejo-Correa and Gundersen (2012) and then Nguyen et al. (2014) suggested classifying proposed exergy efficiencies into two groups: input–output efficiencies and produced–consumed efficiencies. Table 1 summarizes some of the main exergetic efficiency formulations proposed in the literature by providing names and actual definitions given by referenced authors.

Marmolejo-Correa and Gundersen (2012) also compared the different formulations and showed that most of the produced–consumed efficiencies provide the same value of efficiency for simple unit operation.

In order to find the most suitable definition to be implemented in the simulator, we proceed to an exemplified comparison of three of the main definition: the simple efficiency considering waste exergy, the fuel-product excluding unavoidable exergy destruction and the intrinsic efficiency. This comparison based upon four representative chemical engineering unit operations (a cross-ambient turbine for representing unit operation involving work stream, heat-exchangers operating below or above ambient temperature to illustrate unit operations with heat transfers and a chemical reactor which represents unit operations involving chemical transformations) is available in Appendix A.

It results from this comparison that the simple efficiency, which is defined as the ratio of all exergy output to all exergy inputs, is the easiest formulation to implement in a process simulator. However as stated in the comparison and mentioned in numerous references (Cornelissen, 1997; Marmolejo-Correa and Gundersen, 2012; Szargut et al., 1988; Tsatsaronis, 1993), such a formulation

may provide misleading results for some unit operation. Indeed, the sensitivity of the simple efficiency reduces with increasing quantities of untransformed components, which makes this kind of efficiency unsuitable for accurate exergy analysis. Nevertheless, as stated by Tsatsaronis (1993), this approach can be successfully applied when the studied process consists of a large number of unit operations.

In order to provide the user with a more meaningful efficiency in the simulator, a produced–consumed exergy efficiency has also been developed. The fuel–product efficiency is defined as the ratio of desired exergy increases to the sum of exergy decrease minus undesired exergy increases. Although the fuel product–efficiency (Lazzaretto and Tsatsaronis, 2006; Tsatsaronis, 1993) seems to be most proper way to define the exergy efficiency, this efficiency definition needs the engineers to previously make a decision about the purpose of the system (Lazzaretto and Tsatsaronis, 2006). This need for decision-making makes this efficiency difficult to automate and thus not as easy as claimed by authors to be implemented in a process simulator.

The intrinsic efficiency (Brodyansky et al., 1994), although cumbersome, seems to be a good alternative to the fuel–product efficiency. Contrary to the fuel–product efficiency, however, the intrinsic efficiency does not make any distinction between desired and undesired exergy increases. Based upon the concept of transit exergy, this formulation represents the amount of entering exergy which simply goes through the system without undergoing any transformation (Kostenko, 1983). The algorithm for its computation proposed by Brodyansky et al. (1994) does not depend on user’s decision. The transit exergy concept is then particularly adequate to an implementation in the ProSimPlus[®] modelling and simulation environment.

To conclude, both the simple efficiency and a modified intrinsic efficiency have been integrated in ProSimPlus[®]. Note that the intrinsic efficiency is limited to a single unit operation whereas the simple efficiency can be applied to both a single unit operation and a large number of unit operations.

3.2.3. Intrinsic efficiency calculation

Like the intrinsic efficiency, the implemented efficiency is based on the concept of transit exergy B^{tr} developed by Brodyansky et al. (1994). However in order to be implemented in the simulator, formulations for calculating transit exergy supplied in Brodyansky et al. (1994) and Sorin et al. (1998) have been revised. While Brodyansky et al. (1994) considered only a transit physical exergy term, the implemented approach subdivided the physical exergy into thermal and mechanical exergies, thus generating a transit term for both exergy contributions. Moreover, the concept of substreams proposed by Brodyansky et al. (1994) has been replaced by the concept of materially connected streams presented in Appendix B. To refine the exergy efficiency, as proposed with the fuel–product efficiency (Feng et al., 1996; Tsatsaronis and Park, 2002) the unavoidable exergy destruction is also included.

Exergy efficiency calculated in ProSimPlus simulator results from the combination of fuel–product efficiency and intrinsic efficiency and is given by Eq. (20)

$$\begin{aligned} \eta_e &= \frac{\text{Useful Exergy increase}}{\text{Exergy decrease} - \text{Unavoidable Ex. Destruction}} \\ &= \frac{B_{out}^{useful} - B^{tr}}{B_{in} - B^{tr} - I_{INE}} \end{aligned} \quad (20)$$

Algorithms for computing transit exergy in the simulator are presented in the next paragraph.

Table 1
Summary of exergy efficiency formulations proposed in literature.

Group	Name	Definition	Authors/References
Input–output efficiencies	Degree of perfection (Szargut et al., 1988), Simple efficiency (Cornelissen, 1997), Grassmann efficiency (Labidi et al., 2000)	$\eta_e = \frac{\sum \text{Exergy output}}{\sum \text{Exergy input}} = \frac{B_{out}}{B_{in}} = 1 - \frac{I}{B_{in}}$	Szargut et al. (1988), Cornelissen (1997), Labidi et al. (2000)
	–	$\eta_e = \frac{B_{useful}}{B_{in}} = 1 - \frac{I + B_{waste}}{B_{in}}$	Wall and Gong (2001)
	–	$\eta_e = \frac{\text{useful exergy output}}{\text{useful exergy input}}$	Grassmann (1950)
	–	$\eta_e = \frac{\text{exergy increases}}{\text{exergy decreases}}$	Baehr (1968)
	Rational efficiency (Kotas, 1985)	$\eta_e = \frac{\text{desired output}}{\text{necessary input}}$	Kotas (1985), Horlock (1992), Cornelissen and Hirs (1998)
Produced–consumed efficiencies	Exergetic efficiency (Szargut et al., 1988)	$\eta_e = \frac{\text{useful exergy effect}}{\text{driving exergy}}$	Szargut et al. (1988)
	Fuel–product efficiency (Tsatsaronis, 1993)	$\eta_e = \frac{\text{product exergy}}{\text{fuel exergy}}$	Tsatsaronis (1993), Lazzaretto and Tsatsaronis (2006)
	–	$\eta_e = \frac{\text{product exergy}}{\text{fuel exergy} - \text{unavoidable irreversibility}}$	Feng et al. (1996), Tsatsaronis and Park (2002)
	Intrinsic efficiency (Brodyansky et al., 1994)	$\eta_e = \frac{\text{exergy output} - \text{transit exergy}}{\text{exergy input} - \text{transit exergy}}$	Brodyansky et al. (1994) Sorin and Brodyansky (1992)
	Sink–Source efficiency (Marmolejo-Correa and Gundersen, In Press)	$\eta_e = \frac{\text{exergy sink}}{\text{exergy source}}$	Marmolejo-Correa and Gundersen (In Press)

3.2.3.1. Transit exergy calculation.

As explained earlier, the transit exergy which can be defined as the exergy that simply goes through the system without undergoing any transformation enables us to automatically define the total amount of exergy produced and consumed in unit operations.

Before starting anything new about the computation of transit exergy, let us remark that in this study, a unit operation is assumed to be an elementary and indivisible system. Under this assumption a distillation column is not a unit operation but a set of unit operations composed of a set of theoretical stages, including the reboiler and the condenser.

In the following equations, the following notations have been chosen: i represents an input stream, o an output stream, and j a chemical compound. NC, NIS and NOS define the number of components, the number of input streams and the number of output streams, respectively. n_k is the molar flow rate of the k th stream. $n_{j,k}$ is the partial molar flow rate of the j th component in the k th stream.

To start with, let us consider a ‘SISO’ unit operation shown in Fig. 5, such as a compressor or a turbine, composed of only one input stream and one output stream. Contrary to Brodyansky who only consider a physical transit exergy and a chemical transit exergy (Brodyansky et al., 1994), the suggested approach relies on the thermal, mechanical and chemical decomposition of exergy proposed in the fuel–product approach (Tsatsaronis and Winhold, 1985).

For such a system, the proposed formula to calculating transit exergy is given by Eq. (21). This latter can be subdivided into thermal transit exergy $B_{i,o}^{tr,\Delta T}$, mechanical transit exergy $B_{i,o}^{tr,\Delta P}$, and chemical transit exergy $B_{i,o}^{tr,ch}$.

$$B_{i,o}^{tr} = B_{i,o}^{tr,\Delta T} + B_{i,o}^{tr,\Delta P} + B_{i,o}^{tr,ch} \quad (21)$$

The two latter terms may be computed using Eqs. (22) and (23).

$$B_{i,o}^{tr,\Delta P} = \min(n_i; n_o) \cdot \min(b_i^{\Delta P}; b_o^{\Delta P}) \quad (22)$$



Fig. 5. Simple unit operation (1 input–1 output) (‘SISO’ system).

$$B_{i,o}^{tr,ch} = \sum_{j=1}^{NC} \min(n_{i,j}; n_{o,j}) \cdot \min(b_i^{ch,j}; b_o^{ch,j}) \quad (23)$$

In the case of the thermal transit exergy $B_{i,o}^{tr,\Delta T}$, temperature conditions need to be first analyzed. Indeed, as shown in Fig. 6 the thermal exergy reaches a minimum at the ambient temperature T^{00} .

While the operation is running below or above the ambient temperature T^{00} , thermal transit exergy may be computed thanks to Eq. (24). However, for cross-ambient cases, no thermal transit exergy is going through the system – Eq. (25), as the temperature inside the unit operation goes through T^{00} where $B^{\Delta T}$ is equal to 0.

$$B_{i,o}^{tr,\Delta T} = \min(n_i; n_o) \cdot \min(b_i^{\Delta T}; b_o^{\Delta T}) \quad \text{when } T_i \text{ and } T_o > T^{00} \text{ or } T_i \text{ and } T_o < T^{00} \quad (24)$$

$$B_{i,o}^{tr,\Delta T} = 0 \text{ when } T_i > T^{00} \text{ and } T_o < T^{00} \text{ or } T_i < T^{00} \text{ and } T_o > T^{00} \quad (25)$$

Let us now assume a ‘MISO’ unit operation represented in Fig. 7 with a single output stream feeds by several input streams, for example a mixer.

In such a case, it is not possible to determine a unique inlet temperature, or an inlet chemical compound concentration before a mixing step. Eqs. (21)–(25) became then unsuitable. To overcome

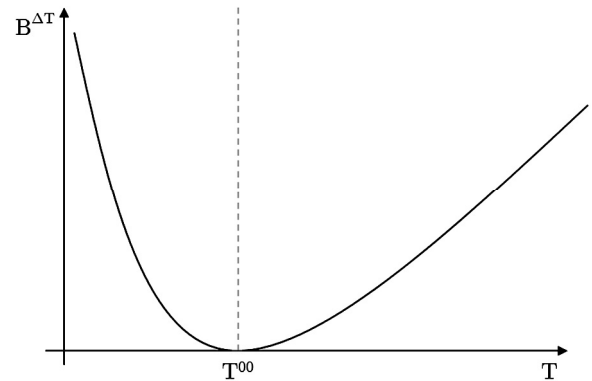
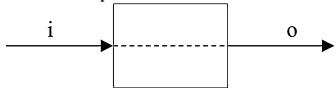
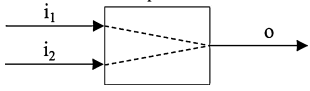


Fig. 6. Influence of temperature on thermal exergy.

Table 2
Formulas for calculating transit exergy.

Transit exergy ending in a single output stream		
	Case 1: 1 input stream	Case 2: Several input streams
		
Thermal exergy	<ul style="list-style-type: none"> • $T_{in} > T^{00}$ and $T_{out} > T^{00}$ $B_{i,o}^{tr,\Delta T} = \min(n_i; n_o) \cdot \min(b_i^{\Delta T}; b_o^{\Delta T})$ • $T_{in} < T^{00}$ and $T_{out} < T^{00}$ $B_{i,o}^{tr,\Delta T} = \min(n_i; n_o) \cdot \min(b_i^{\Delta T}; b_o^{\Delta T})$ • $T_{in} < T^{00}$ and $T_{out} > T^{00}$ or $T_{in} > T^{00}$ and $T_{out} < T^{00}$ $B_{i,o}^{tr,\Delta T} = 0$ 	$B_{in,o}^{tr,\Delta T} = \min \left(\sum_{t=1}^{NIS} B_t^{\Delta T}; B_o^{\Delta T} \right)$
Mechanical exergy	$B_{i,o}^{tr,\Delta P} = \min(n_i; n_o) \cdot \min(b_i^{\Delta P}; b_o^{\Delta P})$	$B_{in,o}^{tr,\Delta P} = \min \left(\sum_{t=1}^{NIS} B_t^{\Delta P}; B_o^{\Delta P} \right)$
Chemical exergy	$B_{i,o}^{tr,ch,j} = \min(n_{j,i}; n_{j,o}) \cdot \min(b_i^{ch,j}; b_o^{ch,j})$ $B_{i,o}^{tr,ch} = \sum_{j=1}^{NC} B_{i,o}^{tr,ch,j}$	$B_{in,o}^{tr,ch,j} = \min \left(\sum_{t=1}^{NIS} B_t^{ch,j}; B_o^{ch,j} \right)$ $B_{in,o}^{tr,ch} = \sum_{j=1}^{NC} B_{in,o}^{tr,ch,j}$
Global exergy	$B_{i,o}^{tr} = B_{i,o}^{tr,\Delta T} + B_{i,o}^{tr,\Delta P} + B_{i,o}^{tr,ch}$	$B_{in,o}^{tr,\varphi} = B_{in,o}^{tr,\Delta T} + B_{in,o}^{tr,\Delta P} + B_{in,o}^{tr,ch}$

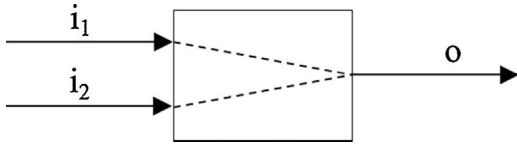


Fig. 7. Simple unit operation with several input streams and a single output stream ('MISO' system).

this problem, Eq. (26) is introduced to enable the computation of transit exergy between a single output stream and several input streams. In this equation, "in" represents a set of input streams. Each term of Eq. (26) can be calculated thanks to Eqs. (27)–(29).

$$B_{in,o}^{tr} = B_{in,o}^{tr,\Delta T} + B_{in,o}^{tr,\Delta P} + B_{in,o}^{tr,ch} \quad (26)$$

$$B_{in,o}^{tr,\Delta T} = \min \left(\sum_{t=1}^{NIS} B_t^{\Delta T}, B_o^{\Delta T} \right) \quad (27)$$

$$B_{in,o}^{tr,\Delta P} = \min \left(\sum_{t=1}^{NIS} B_t^{\Delta P}, B_o^{\Delta P} \right) \quad (28)$$

$$B_{in,o}^{tr,ch} = \sum_{j=1}^{NC} B_{in,o}^{tr,ch,j} = \sum_{j=1}^{NC} \min \left(\sum_{t=1}^{NIS} B_t^{ch,j}, B_o^{ch,j} \right) \quad (29)$$

To summarize, formulas has been reported in Table 2 where the two cases are distinguished.

Note that this concept has been generalized thank to the concept of materially connected streams. Further details about this concept are provided in Appendix B.

Note no transit exergy is granted to work or heat flux. Indeed, the work/heat brought to the system is assumed to be fully consumed.

3.3. ProSimPlus® module for exergy analysis

3.3.1. Exergy module

Now, ProSimPlus® modelling and simulation environment is offering the possibility to perform an exergy analysis in a systematic way. As illustrated on the screenshot in Fig. 8, all of the formulations have been implemented in an exergy analysis module directly

available from the ProSimPlus® interface. This module allows the user to define the exergy balance zone by selecting or not unit operations. It permits to type the output streams (utilized or waste streams). The user can also decide to neglect the chemical exergy of material streams. This option is useful for the analysis of thermal systems excluding chemical transformations such as heat pump, cooling cycle.

Then, this module exploits the mass and heat balances results to generate a report detailing exergy inputs and outputs, irreversibility, and also simple and intrinsic efficiencies for all the selected unit operations. The simple efficiency is also computed for the overall system including all selected unit operations. Note that this module usually computes the exergy balance and exergy efficiency at the end of the simulation from mass and energy balance tables, i.e. in post-processing ('post-run'). It can also compute these calculations during the processing ('on-run') to permit the use of the exergy efficiency as an optimization criterion.

3.3.2. A basic example: exergy analysis of a chemical reactor

This first example illustrates the applicability of exergy analysis in ProSimPlus®. It consists in an adiabatic reactor where the reaction of combustion of methane and air with a conversion rate of 30% occurs. Table 3 provides the exergy balance of this reactor.

The use of the sensitivity analysis tool proposed in ProSimPlus® combined to the exergetic module enables to analyze the impact of conversion rate on exergetic values (see Fig. 9). Fig. 10 shows the influence of conversion on simple and intrinsic efficiency.

The chemical reaction causes unavoidable exergy losses that rise with the conversion rate. This explains the decrease of simple exergy efficiency. However, intrinsic efficiency which is proportional to the ratio produced exergy/consumed exergy increases with the conversion rate. This simple example clearly demonstrates the superiority of the intrinsic efficiency for exergy analysis and optimization of processes (Sorin et al., 1998).

4. Application: analysis of unit operation of an ammonia production plant

To highlight the relevance of a computer-aided exergy analysis for energy optimization of a chemical or thermal process within a process modelling and simulation environment such as

Table 3
Exergy balance of the chemical reactor (perfect gas).

	Flow rate (kmol/h)	Temperature K	Pressure atm	Molar fractions					Chemical exergy kW	Thermal exergy kW	Mechanical exergy kW
				O ₂	CH ₄	CO ₂	H ₂ O	N ₂			
Input 1	0.2	298.15	1.1	0.00	0.90	0.00	0.00	0.10	41.56	0.00	0.01
Input 2	1.8	323.15	1.1	0.20	0.00	0.00	0.00	0.80	0.04	0.01	0.12
Output	2.0	974.56	1.1	0.13	0.06	0.03	0.05	0.73	28.97	6.07	0.13
Irreversibility (kW)	6.58										

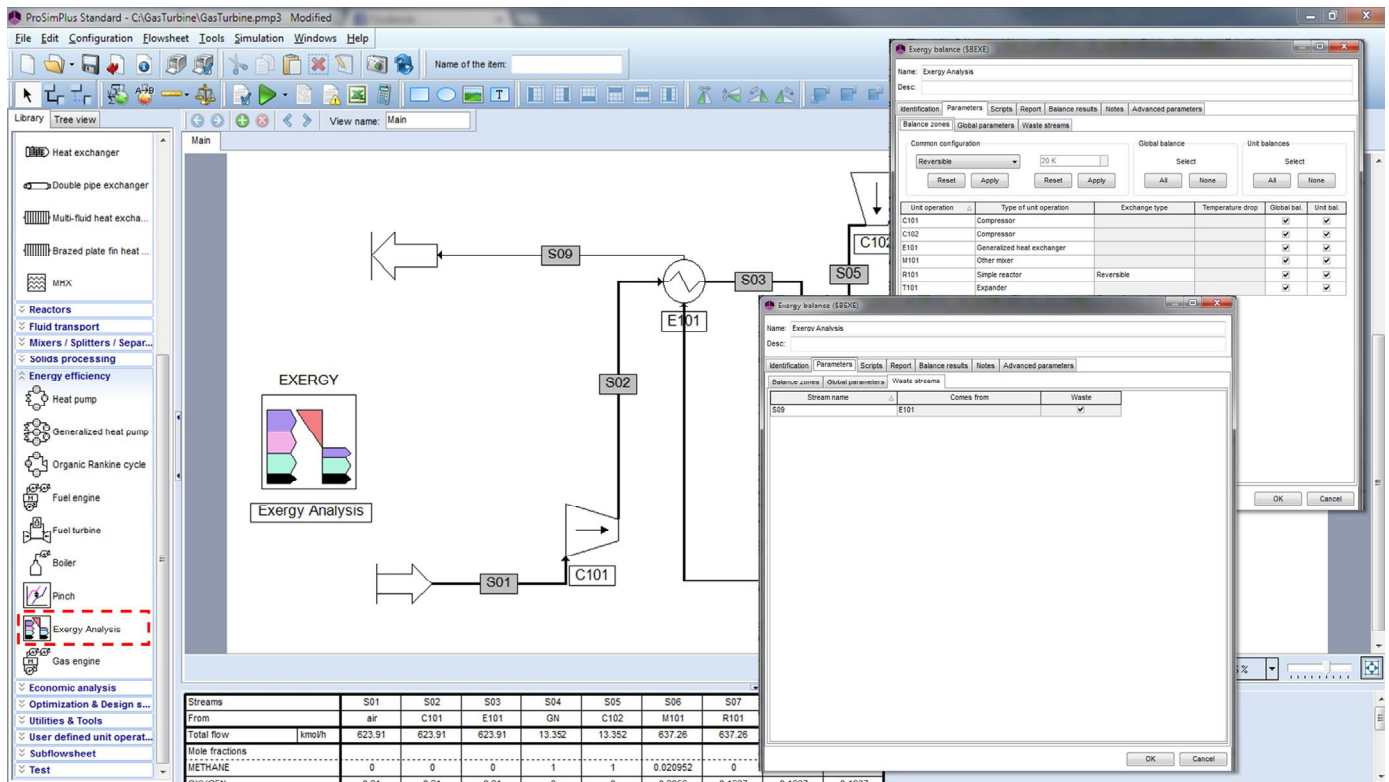


Fig. 8. Screenshot of ProSimPlus® – exergy balance module.

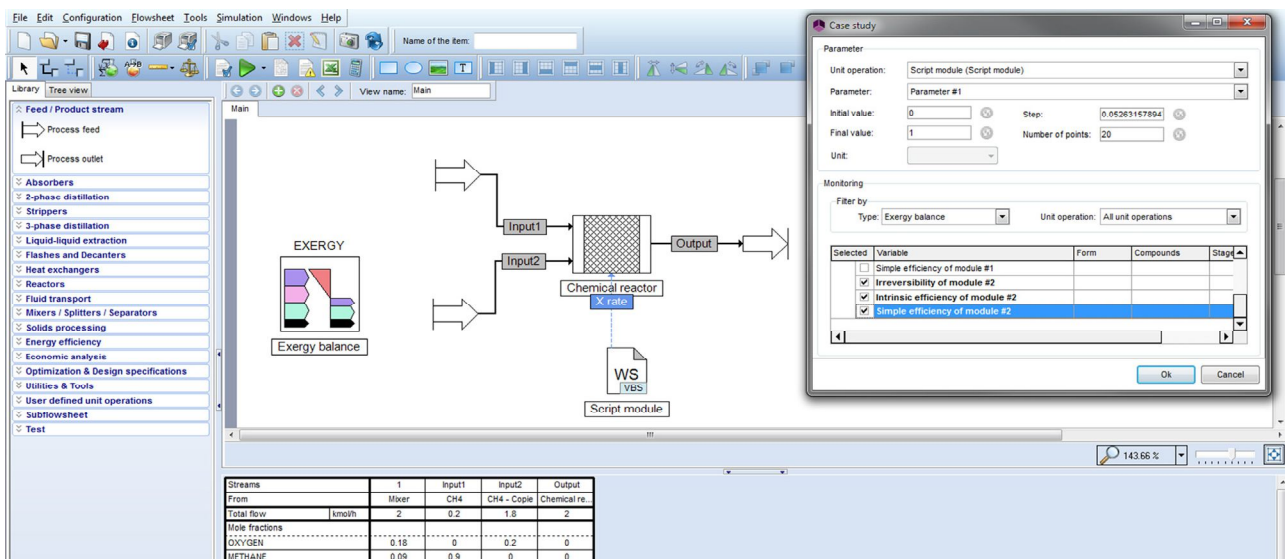


Fig. 9. ProSimPlus® screenshot: sensitivity analysis combined to exergy module.

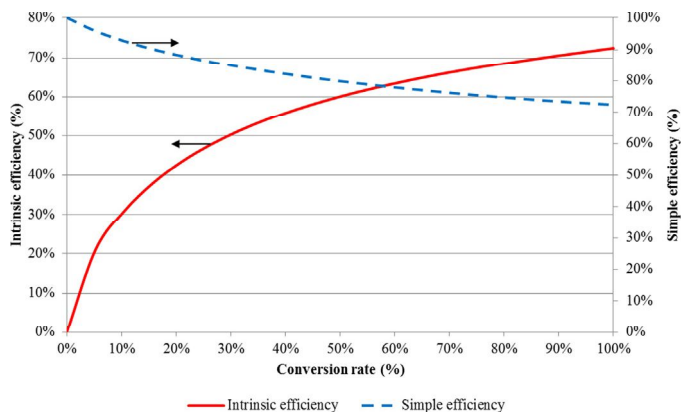


Fig. 10. Influence of conversion rate on exergy efficiencies.

ProSimPlus®, a simplified model of ammonia production plant from the literature (Seider et al., 2003) has been enriched and analyzed as an illustrative case.

4.1. Process description

Fig. 11 represents the ProSimPlus® process flow diagram for ammonia production plant from syngas. Along this process, syngas is compressed up to 150 bar in K-101 and K-102 before entering the production loop. The reacting gas is preheated up to 215 °C (heat exchanger E-101) and sent to convertor R-101. The conversion rate

within the convertor is approximately 30% of nitrogen. The mixture leaving the reactor is cooled down to -10°C and partly liquefied to separate ammonia from unconverted gas in heat exchangers E-102, E-104 and in refrigeration machine HP-101. 70% of the unconverted gas is directly recycled while the rest is shipped to a membrane which aims at recovering 85% of hydrogen. The stream CA-23 exiting the loop at the membrane step is released to the environment (purge). Cold water ($T=20^{\circ}\text{C}$) is used in heat exchangers E-102 and E-105 and in the HP-101 refrigerating machine as cold utility streams.

To summarize, streams “CW-3”, “CW-5”, “CA-15” and “CA-23” (respectively the utility outputs and purges) are considered as waste streams whereas stream “CA-16” is a production one. Isentropic efficiency of compressors is set at 0.8. As the input work of the membrane is unknown, this latter is assumed to be reversible. The flashes chosen as adiabatic and isobar are truly reversible.

Thermodynamic properties are computed thanks to the Soave-Redlich-Kwong (SRK) equation of state. The process is modelled and simulated in ProSimPlus®. Mass and Exergy balances are reported in Table 4. Note that in this case study, heat losses to the environment have been neglected.

4.2. Exergy analysis of the base case process

The first step of the exergy analysis consists in diagnosing the energy performance of the whole process. ProSimPlus® facilitates exergy analysis and optimization of the process by offering the possibility to:

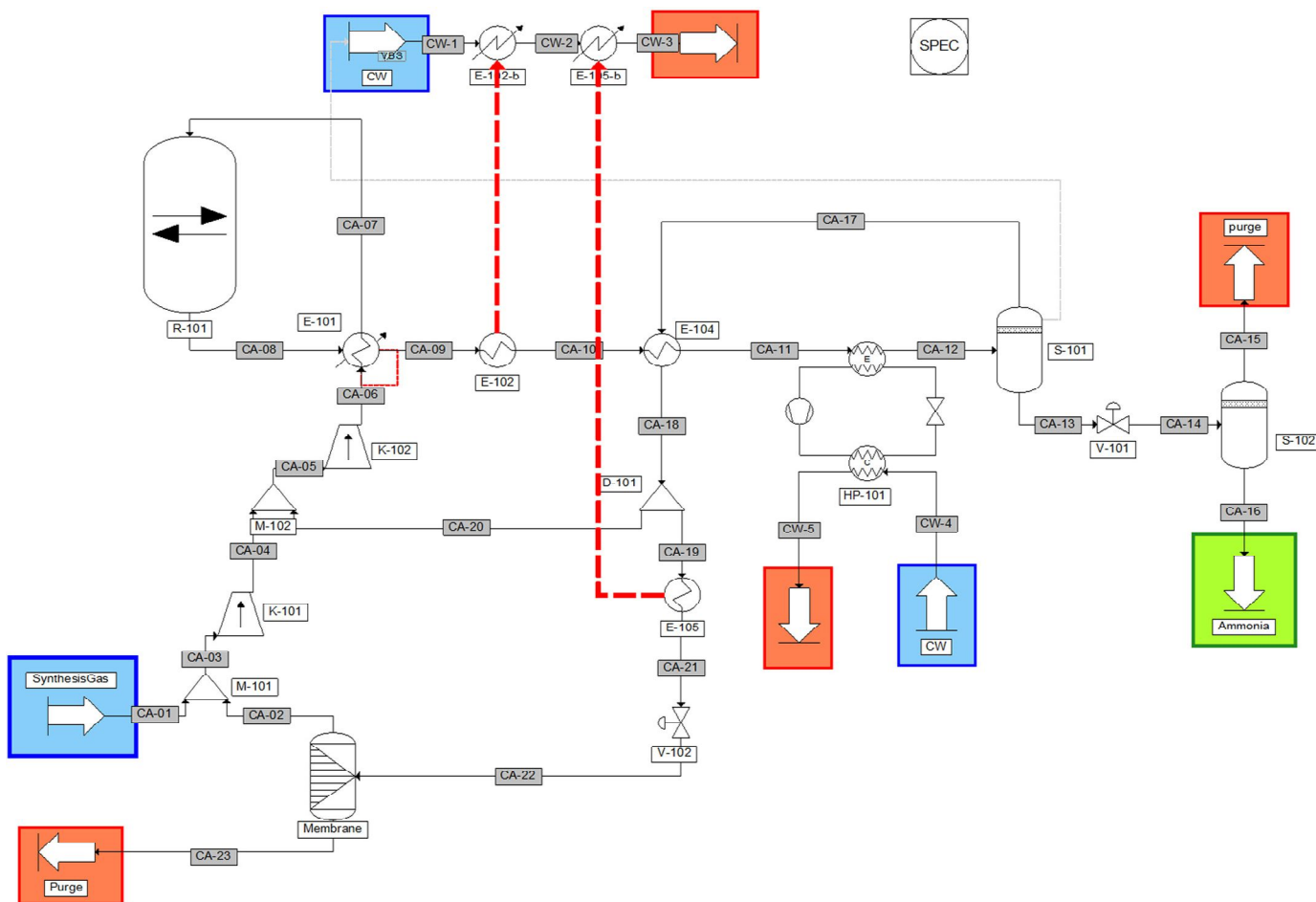


Fig. 11. PFD of an ammonia production plant.

Table 4
Mass and energy balances of process streams.

Streams	CA-01	CA-02	CA-03	CA-04	CA-05	CA-06	CA-07	CA-08	CA-09	CA-10	CA-11	CA-12	CA-13	CA-14
Total flow	114.9	53.8	168.6	168.6	344.3	344.3	344.3	297.9	297.9	297.9	297.9	297.9	46.9	46.9
Molar composition (%)														
H ₂ O	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
H ₂	0.61	0.80	0.67	0.67	0.62	0.62	0.62	0.49	0.49	0.49	0.49	0.49	0.00	0.00
N ₂	0.27	0.15	0.23	0.23	0.22	0.22	0.22	0.18	0.18	0.18	0.18	0.18	0.00	0.00
Ar	0.03	0.00	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.04	0.00	0.00
CH ₄	0.09	0.00	0.06	0.06	0.09	0.09	0.09	0.11	0.11	0.11	0.11	0.11	0.01	0.01
NH ₃	0.00	0.05	0.01	0.01	0.03	0.03	0.03	0.19	0.19	0.19	0.19	0.19	0.98	0.98
Temperature	40.00	35.41	38.50	180.57	86.70	88.39	215.00	439.10	310.80	45.00	40.00	-10.00	-10.00	-11.08
Pressure	50.00	49.00	49.00	148.00	148.00	150.00	149.90	149.90	149.70	149.49	149.29	149.29	149.29	7.00
Chemical Ex.	6840.4	3048.1	9881.4	9881.4	22,154.6	22,154.6	22,154.6	21,920.5	21,920.5	21,920.5	21,920.5	21,920.5	4449.3	4449.3
Physical Ex.	310.4	144.6	453.4	631.7	1213.7	1218.0	1330.8	1476.4	1268.3	1019.3	1017.4	1026.1	83.0	76.3
Thermal Ex.	0.4	0.1	0.4	44.3	17.2	18.1	131.1	462.6	254.8	6.0	4.4	13.2	2.4	15.3
Mechanical Ex.	310.1	144.5	453.0	587.4	1196.4	1199.9	1199.7	1013.8	1013.5	1013.3	1013.0	1013.0	80.6	60.9
Streams	CA-15	CA-16	CA-17	CA-18	CA-19	CA-20	CA-21	CA-22	CA-23	CW-1	CW-2	CW-3	CW-4	CW-5
Total flow	1.6	45.3	250.9	250.9	75.3	175.7	75.3	75.3	21.5	1131.3	1131.3	1131.3	1387.7	1387.7
Molar composition (%)														
H ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00
H ₂	0.11	0.00	0.58	0.58	0.58	0.58	0.58	0.58	0.00	0.00	0.00	0.00	0.00	0.00
N ₂	0.10	0.00	0.21	0.21	0.21	0.21	0.21	0.21	0.38	0.00	0.00	0.00	0.00	0.00
Ar	0.08	0.00	0.04	0.04	0.04	0.04	0.04	0.04	0.16	0.00	0.00	0.00	0.00	0.00
CH ₄	0.31	0.00	0.13	0.13	0.13	0.13	0.13	0.13	0.44	0.00	0.00	0.00	0.00	0.00
NH ₃	0.41	1.00	0.04	0.04	0.04	0.04	0.04	0.04	0.03	0.00	0.00	0.00	0.00	0.00
Temperature	-11.08	-11.08	-10.00	1.99	1.99	1.99	40.00	35.41	35.41	20.00	48.70	47.73	20.00	34.68
Pressure	7.00	7.00	149.29	149.09	149.09	149.09	148.96	50.00	30.40	1.00	1.00	1.00	1.00	1.00
Chemical Ex.	188.2	4263.4	17,537.6	17,537.6	5261.3	12,276.3	5261.3	5261.3	2235.2	49.4	49.4	49.4	60.6	60.6
Physical Ex.	2.2	71.9	876.7	873.4	262.0	611.3	261.6	202.9	50.1	1.2	24.4	22.5	1.4	5.1
Thermal Ex.	0.0	13.1	5.2	2.2	0.7	1.5	0.3	0.1	0.0	1.2	24.4	22.5	1.4	5.1
Mechanical Ex.	2.1	58.8	871.4	871.2	261.3	609.8	261.3	202.8	50.0	0.0	0.0	0.0	0.0	0.0

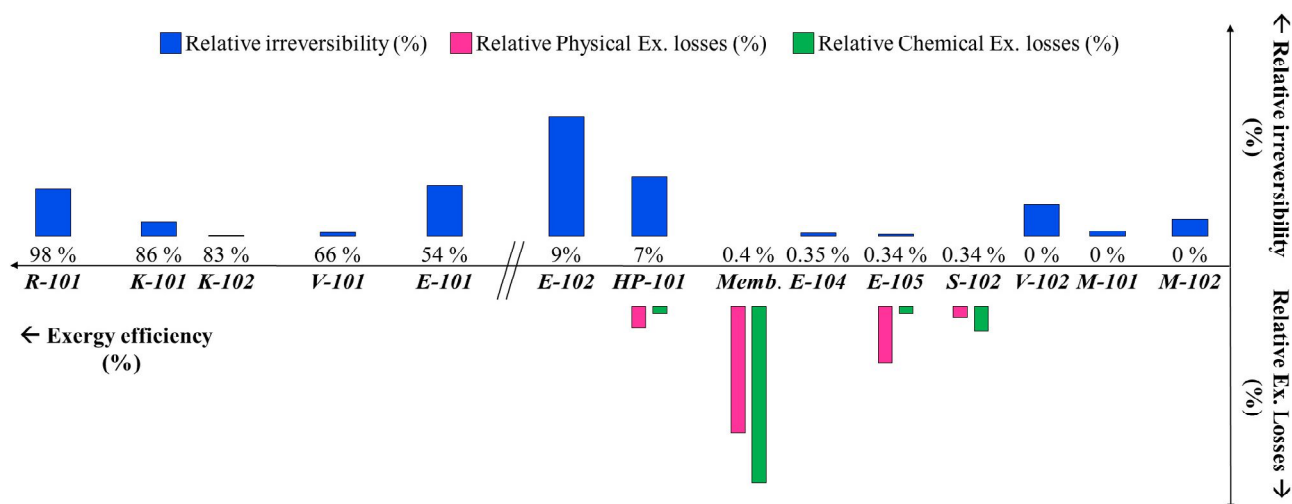


Fig. 12. Base-case "three axis" exergy diagram.

- perform automatic calculations of exergy streams (reported in Table 4),
- evaluate performance indicators detailed in the previous sections (irreversibility, exergy-based efficiencies),
- and to present results of the exergy balance using different kinds of diagrams.

To help the engineer in defining unit operations of a process that should be improved as a priority, it is convenient to draw graphics such as pie graphs, bar charts or even Grassmann diagrams. However, these latter do not enable to represent in the same chart the amount of lost exergy, the amount of destroyed exergy and exergy efficiency for each unit operations.

For that reason, an original diagram has been introduced in ProSimPlus® (see Fig. 12). This new kind of diagram enables to represent on the same graph the exergy efficiency, the exergy destruction and the exergy losses of each unit operations involved in the system. This "three axis" exergy diagram can be read from right to left. Unit operations that should be first analyzed are located at the right. The goal of the engineer when considering this diagram would then to make each unit operation to get closer to the 100% efficiency side (left side) by minimizing exergy destruction and losses.

The base-case process has a total irreversibility of 663.6 kW and a total exergy loss of 2613.3 kW. Those values should be put into perspective, as the global simple efficiency is 56.95%. According to Fig. 12, one may analyze the amount of exergy destroyed on one hand, the external losses in each unit operations from right to left in the other hand.

4.2.1. Analysis of the exergy destruction in each unit operations

4.2.1.1. Mixers M-102 and M-101.

Mixers mainly cause disruption in the thermodynamic equilibrium. This is why mixers are part of the most inefficient unit operations as can be seen in Fig. 12. Whereas the mixer M-101 is almost isothermal and isobar, the amount of exergy destroyed in M-102 can be reduced being mixing streams, to extent possible, as isothermal and isobar as possible.

4.2.1.2. Expander V-102.

V-102 expands a gaseous flow to reduce the pressure before being sent to the membrane. The mixture remains gaseous in the output stream. Exergy destruction occurring in expander V-102 might

be avoided by replacing the expander by a gas turbine. However, contrary to a simple expander, enthalpy of material stream going through the turbine is not constant. A preheating is then necessary to reach the desired output temperature.

4.2.1.3. Cooling devices (E-104, HP-101, E-102 and E-101).

As can be seen in Fig. 12, largest irreversibilities occur in heat exchangers (E-104, E-102 and E-101) and in HP-101 refrigerating machine. These internal losses are mainly due to the large temperature difference between hot and cold streams. Pinch Analysis may be used to improve heat exchange efficiency in the overall process, and then to reduce irreversibilities in heat exchangers.

The base case process, however, is quite well heat integrated. Indeed the actual heat energy consumption is about 782 kW (in E-102) of cold utility and 26 kW of hot utility (in E-105), and the minimum energy requirement computed thanks to a Pinch Analysis is about 756 kW. The other solution consisting in replacing cold utility by hotter utility stream does not appear adequate, in particular as it may raise operating expenditures by increasing energy cost.

It is therefore necessary to look elsewhere to improve the heat exchanger network and to reduce the energy consumptions. By analyzing exergy flows in Table 4, it can be seen that the stream "CA-08" entering the first heat exchanger E-101 (the R-101 gaseous output stream) contains a large amount of mechanical exergy due to the high pressure (150 bars) and a large amount of thermal exergy due to the high temperature. It is then possible to recover a part of these exergies with a turbine directly placed downstream the chemical reactor. By producing shaft-work, the turbine will decrease not only the pressure but also the temperature. Further in the process, the separation step requires a high pressure. The stream is then recompressed up to 150 bars in a compressor coupled to the turbine.

Fig. 13 proposes a retrofit scheme for recovering heat of reaction by integrating a turbine directly downstream the reactor. In the nominal solution, the discharge pressure is fixed to 95 bars. The output of the turbine is then cooled down to 45 °C in E-102 before entering the compressor. The mixture is then cooled from 96 °C down to 40 °C in E-103 before entering the refrigerating machine (not represented in Fig. 13). Cold water is used to cool the process stream down. Water flow rates are fixed in order to get an output temperature of 60 °C to avoid high temperature releases. Output utility streams are assumed to be waste streams.

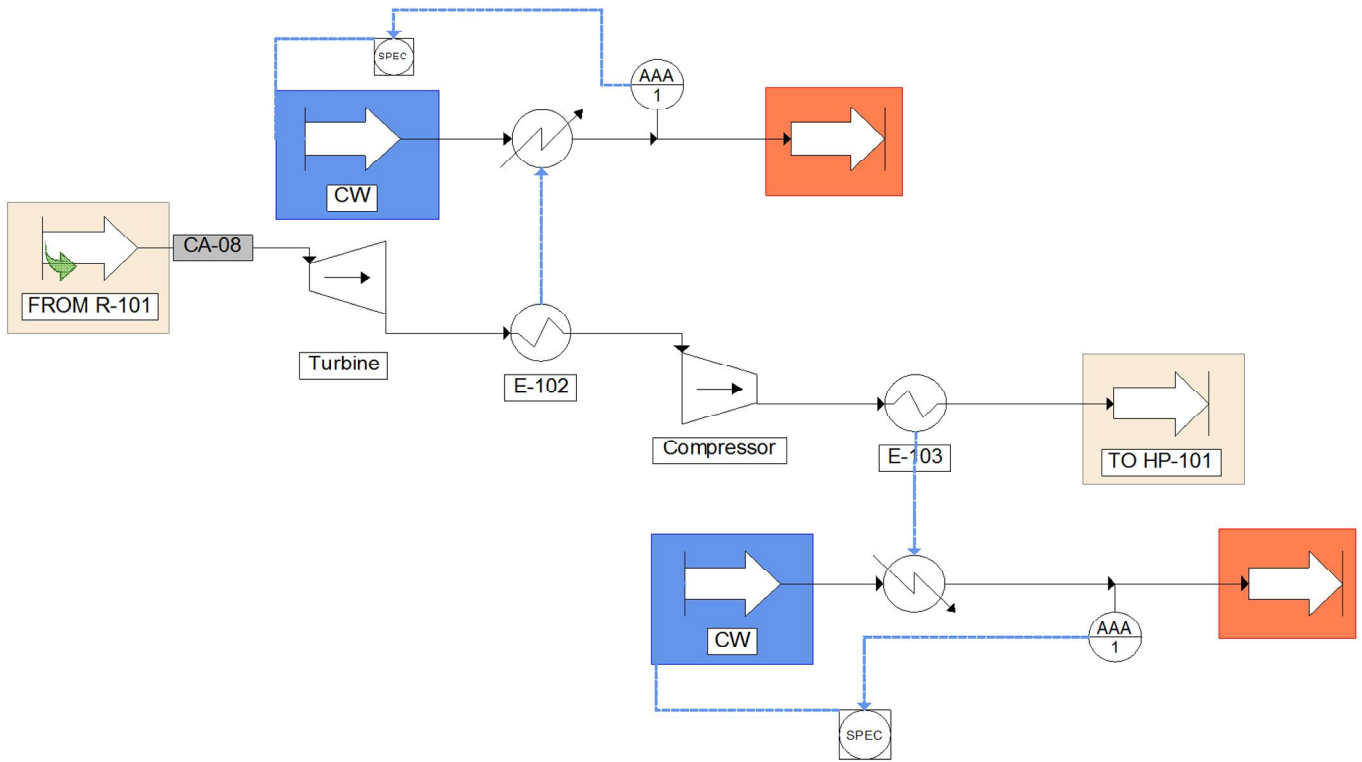


Fig. 13. Proposal for retrofitting the process.

From this proposal, to find the best turbine discharge pressure, a sensitivity analysis is conducted. Results are provided in Fig. 14. Notice that irreversibility curve reaches its minimum at a discharge pressure of 95 bar.

4.2.1.4. Compressors K-102 and K-101.

Concerning the compressors, exergy destroyed in K-102 is negligible compared to the whole process. Exergy destruction in K-101 can be reduced by decreasing input temperature or staging the compression by using an intermediate cooling.

4.2.1.5. Chemical reactor R-101.

According to Fig. 12, the R-101 chemical converter is another major source of exergy destruction. Most of the irreversibility due to chemical conversion is unavoidable (Le Goff, 1979). However, as noticed by Czieszla and co-workers (2006) when considering combustion reactions, preheating input air is one solution to reduce

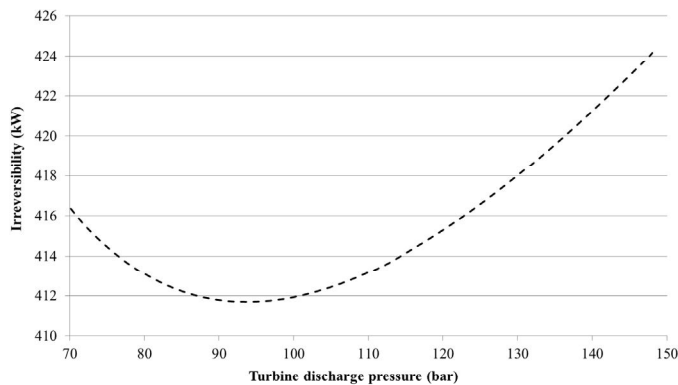


Fig. 14. Influence of discharge pressure on irreversibility and exergy efficiency.

internal losses. Due to the exothermicity of the reaction of ammonia production it would be feasible to adapt this solution and to increase the preheating temperature.

Another sensitivity analysis performed with ProSimPlus® consists in analyzing the influence of input temperature in the thermodynamic efficiency of the reactor (see Fig. 15). From Fig. 15, it can be concluded that the higher the input temperature, the lower the irreversibility. However, due to technical constraints, input temperature of the chemical reactor should not be changed and remain fixed to 215 °C.

4.2.2. Analysis of the exergy losses in each unit operations

Concerning the exergy losses, the main external losses occur in the membrane. Others are negligible.

As the membrane is assumed to be reversible, no accurate data can be extracted from the irreversibility value. However, the large amount of exergy losses, as shown in Fig. 12, indicates that the waste stream CA-23 might be recovered. A further analysis, which is out of this study, should be undertaken to estimate the true potential for recovering this stream.

4.3. Proposal of a retrofitting scheme

Having pinpointed the sources of inefficiencies of the base case process and proposed hints for reducing such inefficiencies, the next step lies in finding out a retrofit scheme based on the analysis.

A proposal of an improved configuration of the process is presented in Fig. 16 and has been simulated within ProSimPlus® modelling and simulation environment (ProSim S.A., 2014). In this process:

- A turbine T-101 and a compressor K-103 have been added in the cooling section. Such an addition enables to produce shaft-work

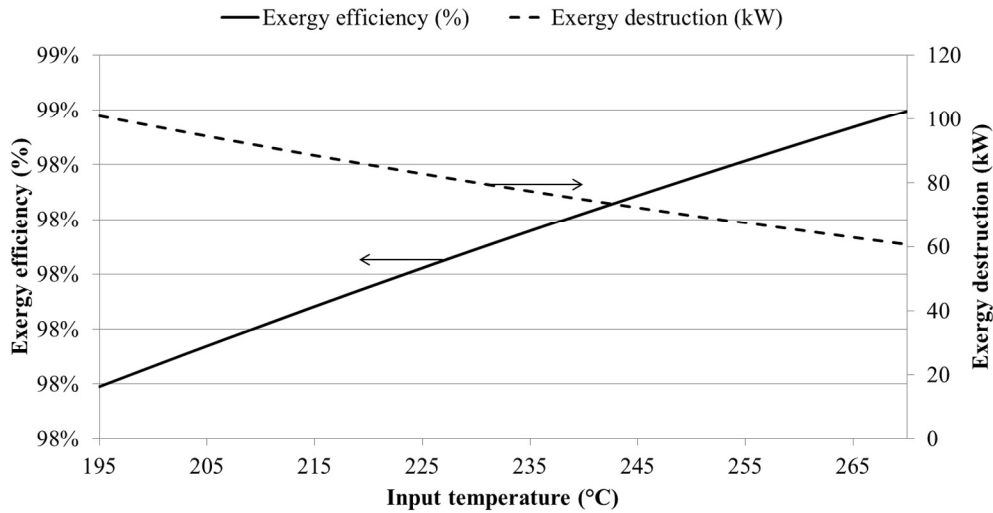


Fig. 15. Influence of input temperature on thermodynamic performance of the reactor.

thanks to the heat of reaction. According to Fig. 14, the T-101 discharge pressure is set at 95 atm.

- The preheating temperature remains unchanged compared to the base case, i.e. 215 °C.
- The T-102 turbine, which replaces the expander V-102, also enables to produce shaft-work. However, the input stream needs to be preheated. The preheating temperature is fixed in order to reach the actual input temperature of the membrane.
- The preheating is done by heat integration between the stream entering the T-102 turbine and the K-101 compressor exiting stream. Such a heat-integration enables to reduce the

temperature difference at the M-101 mixer inlet, and then to reduce the amount of exergy destroyed in M-101.

- Operating conditions of compressors K-101 remain unchanged. The decrease in input temperature of the compressor K-102 enables to reduce the amount of input shaft-work.

Table 5 compares the base case with the retrofitted case. One may notice that proposal for improving the process enables to reduce the amount of exergy destroyed by 15%. The integration of a both turbines T-101 and T-102 enables to reduce the net work consumption by 27%.

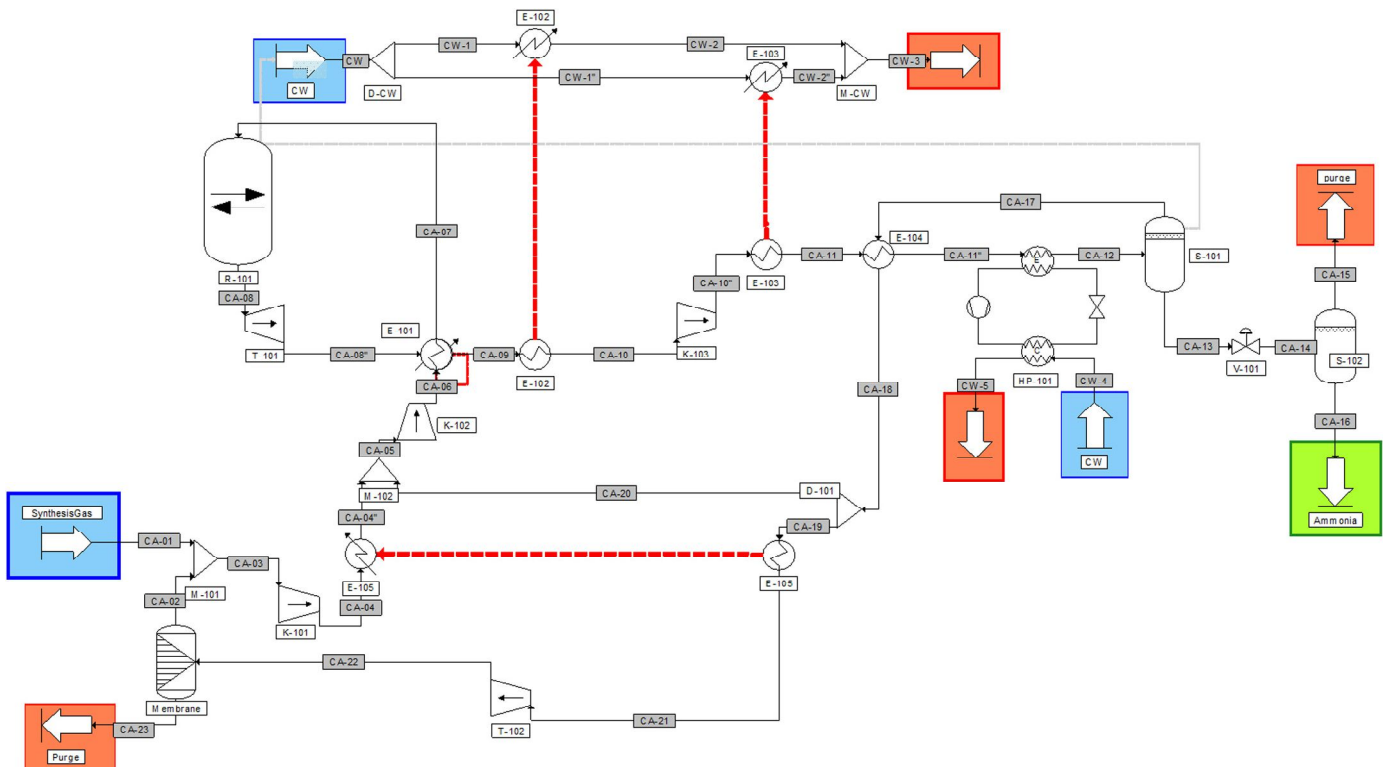


Fig. 16. Retrofitted scheme of the ammonia production plant.

Table 5

Comparison between the base case and the retrofitted case.

	Base case	Retrofitted case	Gain/saving
Overall simple efficiency	57.0	59.0	4%
Total irreversibility (kW)	663.6	562.8	15%
Total exergy losses (kW)	2613.3	2602.7	0.4%
Work consumption (kW)	348.6	480.1	
Work production (kW)	0.0	225.5	
Net consumption (kW)	348.6	254.7	27%
Cold water consumption (t/h)	45.4	38.3	16%

To conclude with the case study, several propositions for improving the process have been implemented. The heat integration in E-105 enables to reduce from 32 kW to 20 kW the irreversibility in mixer M-102. Moreover, this heat integration also enables to produce almost 54 kW of shaft-work in T-102 whereas no work recovering was imagined in the base case process.

The proposition to recover a part of physical exergy at the output of R-101 enables to reduce the cold utility consumption (662 kW for the retrofitted case against 783 kW for the base case). Notice that such a proposition deduced from a systematic exergy analysis is equivalent to the proposition made by [Sahafzadeh et al. \(2013\)](#). Based on the heat recovery solution in methanol synthesis loop presented by [Greiff et al. \(2002\)](#), they suggested to integrate a turbine in the production loop.

Note that the large external exergy loss of the membrane has not been analyzed in this study. Furthermore, the discharge pressure of the membrane has been set according to a sensitivity analysis, without heat integration and economic analysis. A complete thermo-economic analysis should be undertaken to find the best operating conditions.

5. Conclusion

In the present paper, a general presentation of formulations for computing exergies implemented in the process simulator and a methodology for undertaking an exergy analysis within a process simulation software have been presented. After a review of exergy efficiencies found in the literature, a complete description of the generic formulation used for the automatic computation of intrinsic exergy efficiency of unit operations has been developed and an ammonia production case has permitted to illustrate the significant contribution of the simulator as an exergy analysis computer-aided tool.

A relevant exergy analysis highly relies on the engineer's capability to propose alternatives to reduce exergy destruction and losses. To complete the proposed exergy analysis methodology and to assist the engineer in defining alternatives for improving a process, a case-based reasoning methodology ([Negny and Le Lann, 2008](#); [Roldán et al., 2011](#)) is under development. Such a method, which is based on the assumption that similar problems have similar solutions, enables to go further than simple rule-based systems in facilitating the maintenance of an expert system.

Furthermore, as previously noticed the presented intrinsic efficiency only enables to compute exergy efficiency of unit operations. Only the simple efficiency can be applied to multi-operation processes. Although the difference between a simple efficiency and a produced-consumed efficiency on the overall system is paltry in the ammonia case as all the exergy entering the system is mostly consumed, for other systems such as the PRICO process presented by [Marmolejo-Correa and Gundersen \(2012\)](#), the simple efficiency does not enable to compute a relevant exergy efficiency. A future paper will present how the intrinsic efficiency can be computed automatically in a process simulation software.

Acknowledgement

Financial support provided by the French National Research Agency (ANR) is gratefully acknowledged.

Appendix A. Exemplified comparison of exergy efficiencies

For a better understanding of this study, the simple efficiency ([Cornelissen, 1997](#)), the intrinsic efficiency ([Brodyansky et al., 1994](#)) and the fuel-product efficiency ([Tsatsaronis, 1993](#)) will be illustrated through four different examples from the chemical engineering, selected to represent most of the situations occurring in industrial sites.

• Turbine

The exergy balance of a turbine, which is representative of systems generating an output shaft-work stream, is presented in [Table A.1](#). Running conditions of this unit operation have been chosen in such a way that this turbine is a 'cross-ambient' unit operation, i.e. operating conditions go through the ambient temperature, T^{00} .

• Below-ambient and above-ambient heat-exchangers

The heat-exchanger is another commonly used unit operation in industrial processes. Two different running conditions have been applied: a 'below-ambient' heat-exchanger whose exergy balance is summarized in [Table A.2](#) and an 'above-ambient' case presented in [Table A.3](#). Unlike the above-ambient system, a below-ambient system means that all temperatures are below the ambient temperature.

The distinction between utilized and waste streams in exergy-based efficiency can be illustrated by the hot output stream in the above-ambient case, which is considered to be a waste stream. Furthermore, the inevitable exergy destruction for the below-ambient heat-exchanger has been computed according to the methodology presented in [Tsatsaronis and Park \(2002\)](#), the minimum temperature approach is 5 °C.

• Chemical reactor

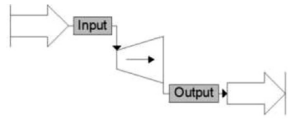
It is worth stressing that no chemical change takes place in the unit operations formerly presented. To complete this study, the last example is an adiabatic reactor where the reaction of combustion of methane and air with a conversion rate of 30% occurs. [Table A.4](#) provides the exergy balance of this reactor.

[Table A.5](#) summarizes the different situations that are treated in the examples.

A.1. Simple efficiency


The simplest way to define exergy efficiency is to express it as the ratio between all exergy outputs and all exergy inputs. Waste

Table A.1
Exergy balance of the turbine (perfect gas).



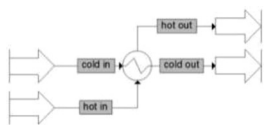
	Flow rate	Temperature	Pressure	Molar fractions		Chemical exergy	Thermal exergy	Mechanical exergy
				N ₂	O ₂			
	kmol/h	K	atm	-	-	kW	kW	kW
In	100.0	320.00	8.0	0.80	0.20	2.21	0.62	143.19
Out	100.0	252.08	2.0	0.80	0.20	2.21	3.22	47.73
Shaft-work (kW)								55.01
Irreversibility (kW)								37.85

Table A.2
Below-ambient heat-exchanger (perfect gas).



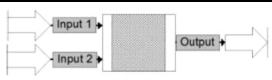
	Flow rate	Temperature	Pressure	Molar fraction	Chemical exergy	Thermal exergy	Mechanical exergy	
				C ₃ H ₈				
	kmol/h	K	atm	-	kW	10 ⁻³ kW	kW	
Cold in	1.0	283.15	1.0	1.00	597.47	7.80	0.00	
Cold out	1.0	293.15	1.0	1.00	597.47	0.86	0.00	
Hot in	2.0	298.15	1.0	1.00	1194.94	0.00	0.00	
Hot out	2.0	293.24	1.0	1.00	1194.94	1.66	0.00	
Irreversibility (10 ⁻³ kW)								5.3
Inevitable irreversibility (10 ⁻³ kW)								3.5

Table A.3
Above-ambient heat-exchanger (perfect gas).



	Flow rate	Temperature	Pressure	Molar fraction	Chemical exergy	Thermal exergy	Mechanical exergy	
				C ₃ H ₈				
	kmol/h	K	atm	-	kW	kW	kW	
Cold in	1.0	298.15	1.0	1.00	597.47	0.00	0.00	
Cold out	1.0	448.15	1.0	1.00	597.47	0.73	0.00	
Hot in	2.0	573.15	10.0	1.00	1194.94	4.85	3.09	
Hot out	2.0	518.21	10.0	1.00	1194.94	3.18	3.09	
Irreversibility (kW)								0.94

Table A.4
Exergy balance of the chemical reactor (perfect gas).



	Flow rate	Temperature	Pressure	Molar fractions					Chemical exergy	Thermal exergy	Mechanical exergy	
				O ₂	CH ₄	CO ₂	H ₂ O	N ₂				
	kmol/h	K	atm	-	-	-	-	-	kW	kW	kW	
Input 1	0.2	298.15	1.1	0.00	0.90	0.00	0.00	0.10	41.56	0.00	0.01	
Input 2	1.8	323.15	1.1	0.20	0.00	0.00	0.00	0.80	0.04	0.01	0.12	
Output	2.0	974.56	1.1	0.13	0.06	0.03	0.05	0.73	28.97	6.07	0.13	
Irreversibility (kW)												6.58

Table A.5
Operating conditions in the examples.

Particularities	Examples			
	Turbine	Below-ambient heat-exchanger	Above-ambient heat-exchanger	Chemical reactor
Temperature	Across T^{00}	Below T^{00}	Above T^{00}	Above T^{00}
Chemical Changes	No	No	No	Yes
Waste Stream	No	No	Yes (output hot stream)	No
Unavoidable irreversibility	No	Yes	No	No

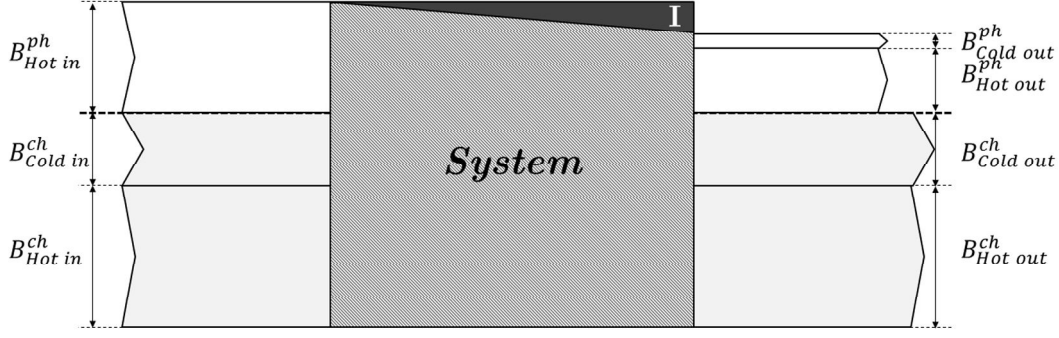


Fig. A.1. Grassmann diagram of the sur-ambient heat-exchanger.

Table A.6
Simple efficiency examples.

	Turbine	Below-ambient heat-exchanger	Above-ambient heat-exchanger	Reactor
Mathematical expression	$\frac{B_{out}^{ch} + B_{out}^{ph} + W_{out}}{B_{in}^{ch} + B_{in}^{ph}}$	$\frac{B_{cold out} + B_{hot out}}{B_{cold in} + B_{hot in}}$	$\frac{B_{cold out}}{B_{cold in} + B_{hot in}}$	$\frac{B_{out}^{ch} + B_{out}^{ph}}{B_{in}^{ch} + B_{in}^{ph}}$
Value (%)	74.08	100.00	33.23	84.24

exergy is excluded from the output exergy (Gong and Wall, 1997). In this condition, Eq. (A.1) represents the definition of simple efficiency (Cornelissen, 1997).

$$\eta_e = \frac{\sum \text{Exergy output}}{\sum \text{Exergy input}} = \frac{B_{out}}{B_{in}} = 1 - \frac{I}{B_{in}} - \frac{B_{out}^{waste}}{B_{in}} \quad (\text{A.1})$$

First of all, notice that the formulation of this exergy efficiency definition is the same whatever the system is, thereby potentially making it a good candidate for an implementation in a process simulation software. This coefficient of performance has been applied in each example. Results and formulations are tabulated in Table A.6.

As stated in Cornelissen (1997), Marmolejo-Correa and Gundersen (2012), Szargut et al. (1988), and shown by the examples of below-ambient heat-exchanger, simple efficiency can give the engineer the wrong impression of the thermodynamic perfection of a given process. When the untransformed exergy is in minority, i.e. when almost all the entering exergy is transformed, simple efficiency may provide quite a good representation of the performance of the system, which is the case, for example, with the turbine or the compressor. However the sensitivity of simple efficiency reduces with increasing quantities of untransformed components, which makes this kind of efficiency unsuitable. In the Grassmann diagram represented in Fig. A.1, the chemical exergy remains unchanged through the heat-exchanger, thus skewing the exergetic efficiency for comparative purposes.

To conclude, this performance criterion can result in misleading conclusions about the thermodynamic performance of the process. This is mostly because in a single unit operation only part of the input exergy participates in the transformation while the other part remains constant. Some authors "neglected" the chemical exergy to make it more relevant (Marmolejo-Correa and Gundersen, 2012). However, in a process simulation software, the user does not know beforehand which form of exergy is to be neglected or not! Nevertheless, as stated by Tsatsaronis (1993), this approach can be successfully applied when the studied process consists of a large number of unit operations.

Unlike input-output efficiency, the produced-consumed efficiency considers that all the exergy exiting the system is not always equal to the exergy produced. Then, produced-consumed efficiencies enable to overcome the limitations of the input-output efficiencies.

A.2. Intrinsic efficiency

It has been observed that the simple efficiency can be overestimated. In particular, this efficiency may assume a value close to one for operation which, from an engineering point of view, has a poor performance; for example, a heat exchanger with a high chemical exergy input. The reason is the fact that only a part of the exergy output is produced by the system in the accomplishment of all the physico-chemical phenomena which take place within its boundaries. The rest of the exergy leaving the system is part of the exergy input which has simply gone through the system without undergoing any transformation (see Fig. A.2). The name transit exergy, first introduced by Kostenko (1983), has been given to this fraction of exergy supplied to the system. Typically, in a chemical reactor, part of the transit exergy is made up of the exergies associated with unreacted feed or inert.

As illustrated in the Grassmann diagram in Fig. A.2, only part of the input exergy is consumed by the system to produce new forms of exergy. On the basis of these observations, Brodyansky et al. (1994) defined a new exergetic efficiency called intrinsic efficiency and expressed by Eq. (A.2).

$$\eta_{int} = \frac{\Delta B^{produced}}{\Delta B^{consumed}} = \frac{B_{out}^{useful} - B^{tr}}{B_{in} - B^{tr}} \quad (\text{A.2})$$

Intrinsic efficiency is the measure of the true ability of the system to produce new exergy from a given amount of consumed exergy. It considers that all the exergy produced is useful and desired. Brodyansky et al. (1994) and then Sorin et al. (1998) who further developed and characterized the concept of transit exergy, provided us with algorithms and formulas for its computation in unit operation. In cases when it is possible to clearly determine which input stream forms the output stream, the transit chemical exergy and transit physical exergy are given by the following equations (Sorin et al., 1998):

$$B_{in,out}^{ch,tr} = \sum_{i=1}^{N_c} \min(n_{in,i}; n_{out,i}) \cdot \min(b_{in,i}^{ch}; b_{out,i}^{ch})$$

$$B_{in,out}^{ph,tr} = \min(n_{in}; n_{out}) \cdot \min(b^{ph}(T^{tr}, P_{in}, Z_{in}), b^{ph}(T^{tr}, P_{in}, Z_{out}), b^{ph}(T^{tr}, P_{out}, Z_{in}), b^{ph}(T^{tr}, P_{out}, Z_{out}))$$

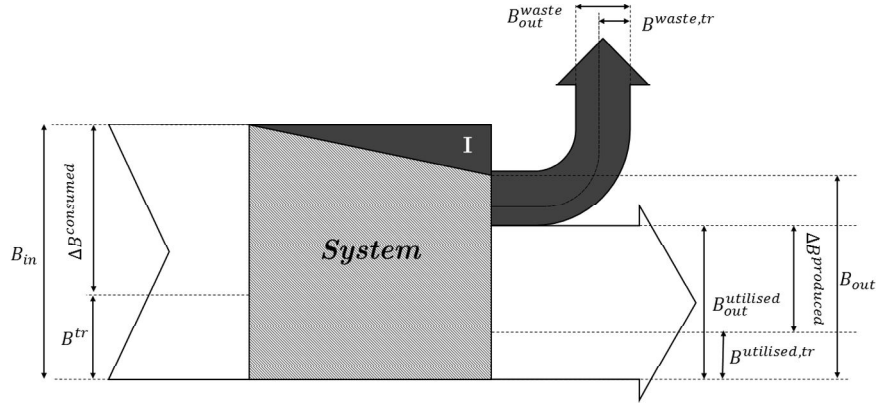


Fig. A.2. Transit exergy.

where

- $T^{tr} = \min(T_{in}, T_{out})$ if $T_{in} > T^{00}$ and $T_{out} > T^{00}$,
- $T^{tr} = \max(T_{in}, T_{out})$ if $T_{in} < T^{00}$ and $T_{out} < T^{00}$,
- else $T^{tr} = T^{00}$.

In cases when such a determination is impossible, Brodyansky et al. (1994) preferred using the following equations:

$$B_{in,out}^{ch,tr} = \sum_{i=1}^{Nc} \min \left(\sum_{j=1}^{N_{in}} B_{j,i}^{ch}, \sum_{k=1}^{N_{out}} B_{k,i}^{ch} \right)$$

$$B_{in,out}^{ch,tr} = \min \left(\sum_{j=1}^{N_{in}} B_j^{ph}, \sum_{k=1}^{N_{out}} B_k^{ph} \right)$$

Let us apply the computation of transit exergy and intrinsic efficiency to the examples.

- The turbine

The turbine is a cross-ambient unit operation then $T^{tr} = 25^\circ\text{C}$. Transit exergy is then given by:

$$B_{(in,out)}^{tr} = B_{(in,out)}^{tr,ch} + B_{(in,out)}^{tr,ph} = B_{in}^{ch} + \min(B_{in}^{ph}(T^{tr}, P_{in});$$

$$B_{out}^{ph}(T^{tr}, P_{out})) = B_{in}^{ch} + B_{out}^{\Delta P}$$

Then, the resulting intrinsic efficiency can be computed thanks to Eq. (A.3).

$$\begin{aligned} \eta_{int} &= \frac{B_{out} + W_{out} - B^{tr}}{B_{in} - B^{tr}} \\ &= \frac{B_{out} + W_{out} - (B_{out}^{\Delta P} + B_{in}^{ch})}{B_{in} - (B_{out}^{\Delta P} + B_{in}^{ch})} = \frac{B_{out}^{\Delta P} + W_{out}}{B_{in}^{ph} - B_{out}^{\Delta P}} = 60.60\% \end{aligned} \quad (A.3)$$

- The heat-exchangers

Analogously to the turbine, the chemical exergy delivered to the systems does not participate to the transformation and thus remains constant through the system. For the above-ambient heat exchanger and according to equations supplied in Sorin et al. (1998), the transit exergy is given by:

$$B^{tr} = B^{tr,ch} + B^{tr,ph} = B_{cold\ in}$$

Table A.7

Partial chemical exergies of the chemical reactor (kW).

	Input 1	Input 2	Output
O ₂	0.000	-0.007	-0.081
CH ₄	41.588	0.000	28.883
CO ₂	0.000	0.000	0.164
H ₂ O	0.000	0.000	0.028
N ₂	-0.028	0.047	-0.021

Note that the transit exergy is computed only on the useful exergy output. The intrinsic efficiency for the above-ambient heat exchanger is then expressed as follow:

$$\begin{aligned} \eta_{int} &= \frac{B_{out}^{useful} - B^{tr}}{B_{in} - B^{tr}} = \frac{B_{cold\ out}^{ph} - (B_{cold\ in}^{ph})}{B_{hot\ in}^{ph} + B_{cold\ in}^{ph} - (B_{cold\ in}^{ph})} \\ &= \frac{B_{cold\ out}^{ph} - B_{cold\ in}^{ph}}{B_{hot\ in}^{ph}} = 0.06\% \end{aligned}$$

Considering now the below-ambient heat-exchanger, one may obtain the following expressions:

$$B^{tr} = B^{tr,ch} + B^{tr,ph} = B_{hot\ in} + B_{cold\ out}$$

$$\begin{aligned} \eta_{int} &= \frac{B_{out} - B^{tr}}{B_{in} - B^{tr}} = \frac{B_{cold\ out} + B_{hot\ out} - (B_{hot\ in} + B_{cold\ out})}{B_{cold\ in} + B_{hot\ in} - (B_{hot\ in} + B_{cold\ out})} \\ &= \frac{B_{hot\ out}^{ph} - B_{hot\ in}^{ph}}{B_{cold\ in}^{ph} - B_{cold\ out}^{ph}} = 23.93\% \end{aligned}$$

- The chemical reactor

To compute the transit exergy of the chemical reactor and according to equations in Brodyansky et al. (1994), one needs to have the partial chemical exergies as summarized in Table A.7. For the chemical reactor, and differently from the turbine and the heat-exchanger, a chemical transformation occurs in the reactor. The transit chemical exergy is given by:

$$\begin{aligned} B_{input-output}^{tr,ch} &= \min(B_{in_1}^{ch,O_2} + B_{in_2}^{ch,O_2}; B_{out}^{ch,O_2}) \\ &\quad + \min(B_{in_1}^{ch,CH_4} + B_{in_2}^{ch,CH_4}; B_{out}^{ch,CH_4}) \\ &\quad + \min(B_{in_1}^{ch,CO_2} + B_{in_2}^{ch,CO_2}; B_{out}^{ch,CO_2}) \\ &\quad + \min(B_{in_1}^{ch,H_2O} + B_{in_2}^{ch,H_2O}; B_{out}^{ch,H_2O}) \\ &\quad + \min(B_{in_1}^{ch,N_2} + B_{in_2}^{ch,N_2}; B_{out}^{ch,N_2}) \\ &= B_{out}^{ch,O_2} + B_{out}^{ch,CH_4} + B_{out}^{ch,N_2} \end{aligned}$$

Table A.8
Intrinsic efficiency examples.

Unit operation	Transit exergy	Efficiency formulation	Value (%)
Turbine	$B_{out}^{\Delta P} + B_{out}^{ch}$	$\frac{B_{out}^{\Delta T} + W_{out}}{B_{out}^{ph} - B_{in}^{\Delta T}}$	60.60
Below-ambient heat-exchanger	$B_{hot\ in} + B_{cold\ out}$	$\frac{B_{hot\ out}^{ph} - B_{hot\ in}^{ph}}{B_{cold\ in}^{ph} - B_{cold\ out}^{ph}}$	23.93
Above-ambient heat-exchanger	$B_{cold\ in}$	$\frac{B_{cold\ out} - B_{cold\ in}}{B_{hot\ in}}$	0.06
Reactor	$B_{in_1}^{\Delta T} + B_{in_2}^{\Delta T} + B_{out}^{\Delta P} + B_{out}^{ch, O_2} + B_{out}^{ch, CH_4} + B_{out}^{ch, N_2}$	$\frac{B_{out}^{ch, CO_2} + B_{out}^{ch, H_2O} + B_{out}^{\Delta T} - (B_{in_1}^{\Delta T} + B_{in_2}^{\Delta T})}{B_{in_1}^{ch} + B_{in_2}^{ch} + B_{in_1}^{\Delta P} + B_{in_2}^{\Delta P} - (B_{out}^{\Delta P} + B_{out}^{ch, O_2} + B_{out}^{ch, CH_4} + B_{out}^{ch, N_2})}$	48.67

The transit physical exergy for the reactor can be calculated as below:

$$B_{input-output}^{tr, ph} = \min(B_{in_1}^{\Delta T} + B_{in_2}^{\Delta T}; B_{out}^{\Delta T}) + \min(B_{in_1}^{\Delta P} + B_{in_2}^{\Delta P}; B_{out}^{\Delta P})$$

$$= B_{in_1}^{\Delta T} + B_{in_2}^{\Delta T} + B_{out}^{\Delta P}$$

Finally, computing the intrinsic efficiency (Eq. (A.4)) gives a value of 48.67

$$\eta_{int} = \frac{B_{out}^{ch} + B_{out}^{ph} - (B_{in_1}^{\Delta T} + B_{in_2}^{\Delta T} + B_{out}^{\Delta P} + B_{out}^{ch, O_2} + B_{out}^{ch, CH_4} + B_{out}^{ch, N_2})}{B_{in_1}^{ch} + B_{in_2}^{ch} + B_{in_1}^{ph} + B_{in_2}^{ph} - (B_{in_1}^{\Delta T} + B_{in_2}^{\Delta T} + B_{out}^{\Delta P} + B_{out}^{ch, O_2} + B_{out}^{ch, CH_4} + B_{out}^{ch, N_2})}$$

$$= \frac{B_{out}^{ch, CO_2} + B_{out}^{ch, H_2O} + B_{out}^{\Delta T} - (B_{in_1}^{\Delta T} + B_{in_2}^{\Delta T})}{B_{in_1}^{ch} + B_{in_2}^{ch} + B_{in_1}^{\Delta P} + B_{in_2}^{\Delta P} - (B_{out}^{\Delta P} + B_{out}^{ch, O_2} + B_{out}^{ch, CH_4} + B_{out}^{ch, N_2})} = 48.67\%$$
 (A.4)

The efficiency divides the chemical exergy into partial chemical exergies. At this point we can exactly define the amount of exergy produced and consumed (Table A.8).

A.3. Fuel-product efficiency

Contrary to intrinsic efficiency, the fuel-product efficiency which is based on the concepts of fuel and product exergy does not consider all the exergy increases as a desired result produced. As mentioned by Lazzaretto and Tsatsaronis (2006), the fuel-product approach is particularly adequate for the analysis of thermal system. In a process simulation software, the user may model and simulate any kind of processes including thermal but also chemical systems. According to Lazzaretto and Tsatsaronis (2006), the product represents the (net) desired result produced by the system, then the definition of the product must be consistent with the purpose of purchasing and using the system. The fuel-product efficiency can be expressed according to Eq. (A.5)

$$\eta_e = \frac{\text{Product exergy}}{\text{Fuel Exergy}} \quad (A.5)$$

The product exergy is defined by Eq. (A.6) whereas the fuel exergy of a system can be calculated thanks to Eq. (A.7) (Lazzaretto and Tsatsaronis, 2006).

$$\text{Product exergy} = \text{Desired exergy output} + \text{desired exergy increases} \quad (A.6)$$

$$\text{Fuel exergy} = \text{necessary exergy input} + \text{necessary exergy decrease} - \text{undesired exergy increase} \quad (A.7)$$

Let us apply this approach to examples presented above.

• Turbine

The objective of a turbine is to simultaneously decrease the pressure of the input stream and generate a work flow. By analyzing exergy balance, one assumes that the decrease of pressure is a necessary exergy decrease while the production of work is the desired exergy production. Consequently, the product exergy is given by Eq. (A.8).

$$\text{product exergy} = W \quad (A.8)$$

Applying the exergy balance, we obtain the fuel exergy in Eq. (A.9).

$$\text{fuel exergy} = B_{in}^{ph} - B_{out}^{ph} \quad (A.9)$$

Then the fuel-product efficiency of the turbine can be computed thanks to Eq. (A.10), and one may obtain 59.24%.

$$\eta_e = \frac{W}{B_{in}^{ph} - B_{out}^{ph}} = 59.24\% \quad (A.10)$$

However, computing efficiency with Eq. (A.10), does not allow us to consider that the thermal exergy reaches a minimum at the ambient temperature T^0 . As mentioned in Marmolejo-Correa and Gundersen (2012), fuel-product efficiency does not explicitly give efficiency expressions for cross-ambient and below-ambient operations.

The evaluation of this kind of efficiency is a much trickier task as it requires the definition of the product exergy by a given system. Moreover, because physical exergy is not a monotonic function of the temperature, the formulation of the fuel-product efficiency can differ depending on operating conditions.

• Heat-exchanger

The heat-exchanger shown in Fig. A.3 provides quite a good illustration of the dependence of fuel-product efficiency on operating conditions. In this example, the chemical exergy is assumed to be constant all along the transformation.

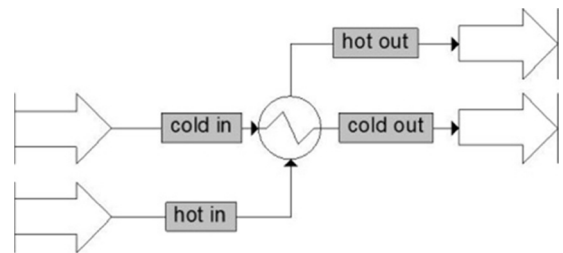


Fig. A.3. Typical heat-exchanger.

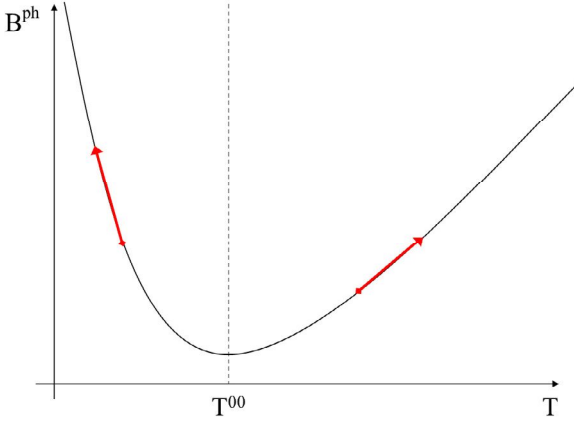


Fig. A.4. Physical exergy vs. temperature.

Is the function of a heat-exchanger to cool the hot stream or to heat the cold stream? Fig. A.4 represents the evolution of physical exergy as a function of the temperature for a monophasic stream.

For an above-ambient heat-exchanger, the increase of exergy is linked to the increase of temperature. Thus *product exergy* is defined by the difference between the output physical exergy and the input physical exergy of the cold stream. Rewriting the exergy balance around the above-ambient heat-exchanger enables us to define the amount of exergy consumed *fuel exergy* as the difference between the input physical exergy and the output physical exergy of the hot stream. Finally, for such a heat-exchanger, the fuel-product efficiency is given by Eq. (A.11).

$$\eta_e = \frac{B_{cold\ out}^{ph} - B_{cold\ in}^{ph}}{B_{hot\ in}^{ph} - B_{hot\ out}^{ph}} \quad (A.11)$$

Considering the hot output stream ('hot out') as a waste stream, the fuel-product efficiency of the sur-ambient heat-exchanger then becomes as formulated in Eq. (A.12).

$$\eta_e = \frac{B_{cold\ out}^{ph} - B_{cold\ in}^{ph}}{B_{hot\ in}^{ph}} = 0.06\% \quad (A.12)$$

Considering now a below-ambient heat-exchanger, *product exergy* is defined as the difference between the output physical exergy and the input physical exergy of the hot stream. Analogously to the above-ambient heat-exchanger, one can obtain the expression given by Eq. (A.13) to define the fuel-product efficiency of a below-ambient heat-exchanger.

$$\eta_e = \frac{B_{hot\ out}^{ph} - B_{hot\ in}^{ph}}{B_{cold\ in}^{ph} - B_{cold\ out}^{ph}} \quad (A.13)$$

With this formulation the fuel-product efficiency obtained is 23.92%, which is a much more significant value than the simple

$$\eta_e = \frac{B_{out}^{\Delta T} - B_{in}^{\Delta T}}{B_{in}^{\Delta P} - B_{out}^{\Delta P} + B_{in}^{ch,O_2} - B_{out}^{ch,O_2} + B_{in}^{ch,CH_4} - B_{out}^{ch,CH_4} + B_{in}^{ch,CO_2} - B_{out}^{ch,CO_2} + B_{in}^{ch,H_2O} - B_{out}^{ch,H_2O} + B_{in}^{ch,N_2} - B_{out}^{ch,N_2}}$$

$$\eta_e = \frac{B_{out}^{\Delta T} - B_{in}^{\Delta T}}{B_{in}^{ch} - B_{out}^{ch} + B_{in}^{\Delta P} - B_{out}^{\Delta P}} = 47.98\%$$

efficiency formerly obtained (99%). Unlike simple efficiency, the fuel-product efficiency in the case of heat-exchanger only deals with physical exergy, which is the exergy associated with temperature and pressure, and does not include in the ratio the chemical exergy term which is not modified in the heat-exchanger (Fig. A.1). However, if the amount of exergy produced is defined without a

previous analysis of exergy evolution, this definition of efficiency can lead to insignificant results. Indeed when applying the exergy efficiency of the over-ambient heat-exchanger to the sub-ambient heat-exchanger, one may obtain an efficiency of 350%. This value means that physical exergy has been generated through the system, which is thermodynamically impossible.

Considering now the unavoidable exergy destruction, the fuel-product efficiency is given by Eq. (A.14) and is equal to 48.3%.

$$\eta_e = \frac{B_{hot\ out}^{ph} - B_{hot\ in}^{ph}}{B_{cold\ in}^{ph} - B_{cold\ out}^{ph} - I_{Un}} \quad (A.14)$$

This new kind of efficiency enables to measure the true potential for improvement of a given process.

• Chemical reactor

The chemical reactor example is treated in order to deal with chemical change at least once in the computing of fuel-product efficiency. To recap, this reactor is a methane combustion chamber. Thus the function of a system can be defined as the increase of temperature to generate, for example, a hot utility stream. It could also be defined as the production of water and carbon dioxide. In the fuel-product approach a distinction is made between reactive chemical exergy and non-reactive chemical exergy (Tsatsaronis, 2007). According to Lazzaretto and Tsatsaronis (2006), to define the fuel and product exergy, a decision must be initially made for each reactive chemical exergy stream whether the fuel is a difference between the inlet and the outlet or the total inlet exergy stream. There is no systematic approach when dealing with chemical system.

The exergy balance of the chemical reactor can be rewritten as follow:

$$[B_{in}^{\Delta T} + B_{in}^{\Delta P} + B_{in}^{ch,O_2} + B_{in}^{ch,CH_4} + B_{in}^{ch,CO_2} + B_{in}^{ch,H_2O} + B_{in}^{ch,N_2}] - [B_{out}^{\Delta T} + B_{out}^{\Delta P} + B_{out}^{ch,O_2} + B_{out}^{ch,CH_4} + B_{out}^{ch,CO_2} + B_{out}^{ch,H_2O} + B_{out}^{ch,N_2}] = I$$

Considering the increase in thermal exergy as the desired exergy product, one may obtain:

$$[B_{in}^{\Delta P} + B_{in}^{ch,O_2} + B_{in}^{ch,CH_4} + B_{in}^{ch,CO_2} + B_{in}^{ch,H_2O} + B_{in}^{ch,N_2}] - [B_{out}^{\Delta P} + B_{out}^{ch,O_2} + B_{out}^{ch,CH_4} + B_{out}^{ch,CO_2} + B_{out}^{ch,H_2O} + B_{out}^{ch,N_2}] = I + B_{out}^{\Delta T} - B_{in}^{\Delta T}$$

Then the fuel-product efficiency can be expressed as given by the following equation:

$$\eta_e = \frac{B_{out}^{\Delta T} - B_{in}^{\Delta T}}{B_{in}^{\Delta P} - B_{out}^{\Delta P} + B_{in}^{ch,O_2} - B_{out}^{ch,O_2} + B_{in}^{ch,CH_4} - B_{out}^{ch,CH_4} + B_{in}^{ch,CO_2} - B_{out}^{ch,CO_2} + B_{in}^{ch,H_2O} - B_{out}^{ch,H_2O} + B_{in}^{ch,N_2} - B_{out}^{ch,N_2}}$$

$$\eta_e = \frac{B_{out}^{\Delta T} - B_{in}^{\Delta T}}{B_{in}^{ch} - B_{out}^{ch} + B_{in}^{\Delta P} - B_{out}^{\Delta P}} = 47.98\%$$

Computing the fuel-product thank to the above equation gives an efficiency of 47.98%.

From this equation, one may note the distinction between the intrinsic efficiency and the fuel-product efficiency. However, in order to get such an equation, a choice/decision has to be initially made to determine the purpose of the unit operation.

Table A.9
Fuel-product efficiency examples.

	Turbine	Sub-ambient heat-exchanger	Sur-ambient heat-exchanger	Reactor
Mathematical expression	–	$\frac{B_{hot\ out}^{ph} - B_{hot\ in}^{ph}}{B_{cold\ in}^{ph} - B_{cold\ out}^{ph} - I_{un}}$	$\frac{B_{cold\ out}^{ph} - B_{cold\ in}^{ph}}{B_{hot\ in}^{ph}}$	$\frac{B_{out}^{\Delta T} - B_{in}^{\Delta T}}{B_{in}^{ch} - B_{out}^{ch} + B_{in}^{\Delta P} - B_{out}^{\Delta P}}$
Value (%)	–	48.3	0.06	47.98

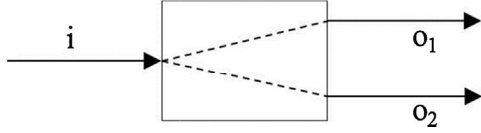


Fig. B.1. Simple unit operation with a single input stream and several output streams ('SIMO' system).

However, if the desired exergy effect is the increase in temperature and the production of water, the fuel product efficiency might be given by the following expression:

$$\eta_e = \frac{B_{out}^{\Delta T} - B_{in}^{\Delta T} + B_{in}^{ch, H_2O} - B_{out}^{ch, H_2O}}{B_{in}^{\Delta P} - B_{out}^{\Delta P} + B_{in}^{ch, O_2} - B_{out}^{ch, O_2} + B_{in}^{ch, CH_4} - B_{out}^{ch, CH_4} + B_{in}^{ch, CO_2} - B_{out}^{ch, CO_2} + B_{in}^{ch, N_2} - B_{out}^{ch, N_2}}$$

The fuel product efficiency highly depends on the engineer's choice in defining the product exergy.

Results and expressions of fuel-product efficiencies are summarized in Table A.9.

To conclude, the fuel-product efficiency is a very interesting formulation of exergy efficiency as it enables to consider the true purpose of the system. However this kind of efficiency needs the engineers to previously take a decision about the purpose of the system. This might be a difficult step in the formulation of exergy efficiency. Moreover, the examples of heat exchanger show that a wrong decision in the definition of product exergy can lead to misleading results. As stated in the several examples, although this proposal for computing exergetic efficiency may provide a better comparison criterion for process analysis than the simple or the intrinsic efficiency efficiencies, the reasoning for deducing the fuel-product efficiency is not generic, and not as easy as claimed by authors, to be implemented in a process simulator. All these limitations prevent from automatic calculations of the efficiency of a system.

Appendix B. Generalization of the methodology – concept of materially connected streams

Let us consider a splitter represented in Fig. B.1. The splitter is representative to 'SIMO' unit operations composed of a single input stream and several output streams.

Note that exergy may transit from stream i to stream o_1 and from stream i to stream o_2 . There is no transit exergy between streams o_1 and o_2 . It is then possible to define the pairs (i, o_1) and (i, o_2) as two pairs of *materially connected streams*. Two streams are said to be *materially connected* if, and only if, the studied output stream is entirely or partly constituted by the considered input stream.

For each pair, the input is only composed of a single input stream. Consequently it is possible to compute transit exergy using equations of case 1 as reported in Table 2. Finally, the overall transit exergy on the splitter is given by Eq. (B.1), i.e. as the sum of transit exergies.

$$B_{splitter}^{tr} = B_{i, o_1}^{tr} + B_{i, o_2}^{tr} = B_{i, o_1}^{tr, \Delta T} + B_{i, o_2}^{tr, \Delta T} + B_{i, o_1}^{tr, \Delta P} + B_{i, o_2}^{tr, \Delta P} + B_{i, o_1}^{tr, ch} + B_{i, o_2}^{tr, ch} \quad (B.1)$$

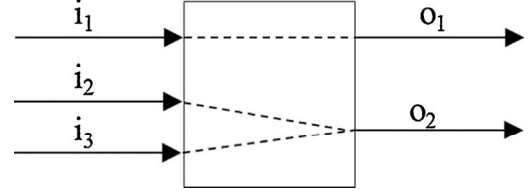


Fig. B.2. Example of a jacketed reactor vessel for the computation of transit exergy ('MIMO' system).

Assume now a 'MIMO' unit operation shown in Fig. B.2. It may represent, for example, a jacketed reactor vessel with several input streams and several output streams.

By analyzing the system represented in Fig. B.2, it is possible to define two sets of materially connected streams. The first one is the pair (i_1, o_1) . There is a single input stream, the transit exergy may be then computed using equations of case 1 of Table 2. The second set of materially connected streams is defined by $(i_2 + i_3, o_2)$. In this case the input is a set of input streams. Consequently to compute the transit exergy, one needs to use equations of case 2 as reported in Table 2. Analogously to the splitter, the overall transit exergy on the jacketed reactor vessel is given by Eq. (B.2).

$$B_{reactor}^{tr} = B_{i_1, o_1}^{tr} + B_{i_2+i_3, o_2}^{tr} = B_{i_1, o_1}^{tr, \Delta T} + B_{i_2+i_3, o_2}^{tr, \Delta T} + B_{i_1, o_1}^{tr, \Delta P} + B_{i_2+i_3, o_2}^{tr, \Delta P} + B_{i_1, o_1}^{tr, ch} + B_{i_2+i_3, o_2}^{tr, ch} \quad (B.2)$$

To recap, the first step of computing transit exergy is to identify sets of materially connected streams, i.e. inlet streams constituting an output stream. While pairs of materially connected streams are identified, one may applied equations reported in to compute transit exergy on each of them.

A generalized formulation for computing transit exergy in an unit operation is given by Eq. (B.3) where N_{SMCS} is the number of sets of materially connected streams, l is a set of materially connected streams (m, o) where m may be a single input stream, i , or several input streams, "in", and o is a single output stream. When m is a set of input streams, Eq. (29) might be used, otherwise Eq. (21) is preferable.

$$B^{tr} = \sum_{l=1}^{N_{SMCS}} B_l^{tr} = \sum_{l=1}^{N_{SMCS}} B_l^{tr, \Delta T} + B_l^{tr, \Delta P} + B_l^{tr, ch} \quad (B.3)$$

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