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A Way to Enhance Process Energy Integration

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ABSTRACT

Energy issue is becoming increasingly crucial for industrial sector that consumes large quantities of utilities. Although the scientific world should continue to look for alternate sources of energy, a short-term solution would rather rely on a more rational use of energy. To face this challenge, exergy analysis appears a very efficient tool as it would enable to increase efficiency and reduce environmental impact of industrial processes. Unfortunately, contrary to enthalpy, this concept is rather difficult to handle and exergy analysis is rarely implemented in process simulators. In this context, the major objective of the study presented in this dissertation is to make exergy analysis more understandable by coupling it with the use of a process simulator and also to demonstrate the value of this approach for analysis of energy efficiency of processes and utilities.

This dissertation presents a generic formulation for exergy of material streams that does not depend on the thermodynamic model, so that it could be easily implemented in a process simulator. The different contributions of exergy (thermal, mechanical and chemical) have been developed and new concept such as the maximal thermal and mechanical recovery potential has been introduced in order to pave the way for exergy analysis.

The formulations of exergy balances on a real process are presented. For that purpose, the formulation of exergy for heat and work flux is developed. The formulation of exergy balances has been introduced for both design and retrofit situations and then a set of hints for the interpretation of this exergy balance has been given. Synthetic tables providing solutions to reduce irreversibilities and external losses have been introduced. Moreover, different kinds of exergy efficiency have been defined to provide a new criterion for the optimization of the process. A new structured methodology for exergy analysis is developed to overcome the limitations of existing methodologies.

To make exergy analysis easier for any engineer, a first prototype has been developed to implement the calculation of exergy for the material streams in a process flowsheet modeled in ProSimPlus. Thanks to this prototype, exergy of each material stream appears in a synthesis table next to the traditional thermodynamic values such as the enthalpy.

Finally, a case study on Natural Gas Liquids recovery process is presented to demonstrate the benefit of the exergy analysis for the improvement of existing processes. First, the exergy analysis permits to make an energy diagnosis of the process: it pinpoints the inefficiencies of the process which relies not only on irreversibilities but also on external exergy losses. Then, based upon respective values of internal and external losses and also thanks to the breaking down of exergy into it thermal, mechanical and chemical contributions, some technological solutions are suggested to propose a retrofit process. Finally, the exergy efficiency criteria enable to optimize the operating parameters of the process in order to improve its energy efficiency.

Keywords: Exergy analysis; Process design; Process integration; Process simulator

RÉSUMÉ

Dans un contexte de réduction des émissions de gaz à effet de serre (GES) et de forte volatilité du prix des énergies, les investissements en efficacité énergétique des sites industriels résultent souvent d’un processus de décision complexe. L’industriel doit pouvoir disposer d’outils lui permettant d’élaborer les solutions d’efficacité énergétique envisageables sur son site. Outre la recherche des sources d’énergie alternatives, que sont les énergies renouvelables, qui n’atteindront leur maturité technologique que sur le long terme, une solution à court terme consiste plutôt à favoriser une utilisation plus rationnelle de l'énergie. Pour relever ce défi, l'analyse exergétique apparaît comme un outil très efficace, car elle permet d’identifier précisément les sources d’inefficacité d’un procédé donné et de proposer des solutions technologiques visant à y remédier. Malheureusement, contrairement au concept d’enthalpie traditionnellement utilisé pour réaliser des bilans énergétiques sur un procédé, ce concept demeure assez difficile à appréhender et n’est que très rarement implémenté dans les simulateurs de procédés.

Les travaux présentés dans ce document visent d’abordà rendre l'analyse exergétique plus accessible en l’intégrant dans un simulateur de procédés, puis à démontrer la pertinence d’une telle analyse pour l’amélioration de l’efficacité des procédés et des utilités associées.

Dans un premier temps, une formulation générique et indépendante du choix du modèle thermodynamique pour l’évaluation de l’exergie des flux de matière est introduite. Une méthode de calcul des différentes contributions de l'exergie (contributions thermique, mécanique et chimique) est développée et un nouveau concept visant à évaluer les potentiels de récupérations thermique et mécanique maximales est introduit.

Par la suite, la notion de bilan exergétique sur un système donné (opération unitaire ou procédé complet) est introduite. Pour l’évaluation des exergies des flux de travail et de chaleur, deux cas de figure sont étudiés : le cas de l’amélioration de procédés existants (« retrofitting ») et le cas de la conception de nouveaux procédés (« design»). Dans le cas de l’amélioration de procédés existants et afin d’aider au diagnostic énergétique de ces systèmes, des tableaux synthétiques proposant des solutions technologiques visant à réduire les irréversibilités ou les pertes exergétiques externes du procédé sont proposés. Par ailleurs, après une analyse comparative des différentes formulations d’efficacité exergétiques existant dans la littérature, la notion d’efficacité intrinsèque est retenue comme le critère le plus adapté pour une optimisation de l’efficacité exergétique d’un procédé complexe. Enfin, une nouvelle méthodologie structurée dédiée à l’analyse exergétique et permettant de pallier les lacunes des méthodologies existantes est présentée.

L’ensemble de ces concepts est implémenté dans un premier prototype logiciel écrit en langage VBScript et intégré au simulateur de procédés ProSimPlus. Enfin, l’efficacité de la procédure est démontrée à travers une étude de cas portant sur la production de gaz naturel.

Mots clés: Analyse exergétique; amélioration de procédés existants; conception des procédés; intégration de procédés; simulateur de procédés

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PART I

GENERAL CONTEXT OF THE STUDY

CHAPTER 1

Introduction

The outlook on energy utilization has gone through a drastic change during the last few decades. Nowadays, there is far greater contemplation on provisioning and consumption of energy. This reflection has been brought about by a number of factors such as dwindling reserves of conventional sources of energy, fluctuating energy prices, unavailability of alternative sources of energy and new ecological realities about climate change. Moreover, the industrialization in developing countries and especially that of China and India will increase the global energy demand. In developing countries, the proportion of global energy consumption is projected to increase from 46 to 58 % between 2004 and 2030, at an average annual growth rate of 3%. During the same period industrialized nations will witness annual energy demand growth of 0.9 % (IEA 2011).

1.1 ENERGY CONSUMPTION OF THE INDUSTRIAL SECTOR

Energy consumption can be divided into four main sectors: transport, building (residential and commercial), agriculture and industrial (see Figure 1.1)(Price et al. 2006). On the global scale, the industrial sector accounts for 36 percent of global energy consumption and even using conservative estimates, this trend will remain more or less the same in the future (Agha 2009).

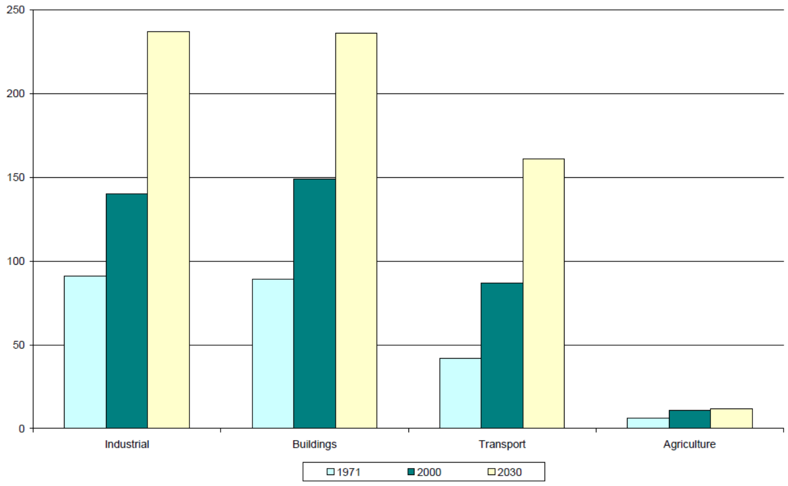


Figure 1.1. Sectorial trends in the world (Price et al. 2006)

Recently in France, the conclusion drawn by the Working Group, “*Lutter contre les changements climatiques et maîtriser l'énergie”* (Fight against climate change and control of energy), gathered at the recent Grenelle de l’environnement (2009) is that, “*beyond the specific actions to improve energy efficiency in Building and Transport sector, there is a source of savings in other sectors which represent 43% of total energy consumption*”. In regard to the industrial sector (which accounts for 21 % of final energy consumption and 20% of emissions of greenhouse gases), the working group recognized that significant efforts had already been made in this sector but pointed out that further progress was still required.

As highlighted in Table 1.1 which classifies the different American industrial subsectors according to their energy consumption, the chemical industry is clearly the greatest user of energy, followed by forest products and petroleum refining. Other principal large consumers include iron and steel mills, food and beverage, mining, aluminum, and transportation equipment manufacturers.

The top three industries share several characteristics that contribute to their high energy consumption. Firstly, in these industries, the core processes used to convert raw materials are characterized by operations performed at high temperatures and high pressures. Secondly, each of these industries consumes vast amounts of energy in form of electricity and steam. Thirdly, due to the technological and thermodynamic limitations, the energy efficiency of several equipments in these processes is quite low.

Table 1.1. Industry ranking based on energy usage (Energetics Inc 2004)

Rank	Sector	Energy usage (TBTU)
1	Chemicals	3729
2	Petroleum Refining	3478
3	Forest Products	3263
4	Iron & Steel Mills	1672
5	Food & Beverage	1156
6	Mining	753
7	Transportation Equipment	488
8	Alumina & Aluminum	441
9	Fabricated Metals	441
10	Textiles	359
11	Cement	355
12	Plastics & Rubber	327
13	Computers, Electronics	321
14	Glass & Glass Products	254
15	Foundries	233
16	Heavy Machinery	213

Moreover, the reliance on fossil fuels as the primary source of energy has huge negative impact on the environment and eco-system of our planet. The studies of Intergovernmental Panel for Climate Change (IPCC) have acknowledged that the main cause for the phenomenon of global warming is the emission of green house gases, which are released in to the atmosphere during burning of fossil fuel. Global warming is considered to the biggest impediment in carrying out sustainable development.

Actually, the industrial sector is faced with multiple challenges. On one hand, the fossil fuel prices have shown radical fluctuations during the last few years with the crude oil price recording the highest ever price of $147.27 per barrel (on July 11, 2008). On the other hand, increased competition and shrinking profit margins are placing increased financial burdens for running sustainable businesses. In addition to this the environmental regulations, influenced by international treaties like Kyoto, European Emission Trading Scheme and Copenhagen Climate Change Conference, are becoming increasingly stringent and hard to satisfy. In order to overcome these multiple challenges, industrial sector needs to look for ways of improving productivity, reducing operational costs and satisfy environmental regulations. To reach these objectives, the efficient utilization of energy has emerged as one of the major point of focus.

1.2 SOLUTION TO THE ENERGY ISSUE IN THE INDUSTRIAL PERSPECTIVE

Since 1990, there have been concentrated efforts in scientific world to find alternative sources of energy. Emphasis is on renewable energy like wind, solar, hydrogen, etc. However, even by the most optimistic assessments, all these alternatives are long-term solutions. The projections of Energy Information Administration (EIA), a statistical agency of the U.S.A department of energy, show that in immediate future fossil fuels will remain as primary sources of energy. Thus, along with the development of alternative energy sources, effort must be made to seek modus operandi that will minimize the damage caused by the fossil fuels. To encourage these researches, Baranzani presented the advantages of applying carbon tax (Baranzini et al. 2000) while Painuly proposed the usefulness of green credits in encouraging the use of renewable sources (Painuly 2001). Initiatives like cleaner production (Kjaerheim 2005) and zero-emissions (Kuehr 2007) are important approaches in this regard. However, another short term solution would consist in improving energy efficiency in industrial processes (IPCC, Intergovernmental Panel on Climate Change 1996).

Concerning the industrial sector, the mode of production and management of utilities provides a great potential source for energy savings. The Working Group (Grenelle de l'Environnement 2009) concluded that "approximately one third of the energy consumption of industrial (or final energy 11Mtep) comes from processes called *"utility"* (steam, hot air, heaters, electricity, etc.). The margins for improving the effectiveness of these processes exist. The dissemination and implementation of best practices can save up to 2 Mtep without requiring technological breakthroughs." In other words, one of the mechanisms identified by the Working Group to reduce energy consumption and emissions of greenhouse gases is **"the establishment of more efficient means of using process utilities**" within production units.

1.3 METHOD AND TOOLS DEDICATED TO ENERGY EFFICIENCY OF PROCESSES

A usual adopted to design processes and make more efficient use of utilities was based upon a **process design hierarchy** (Linnhoff et al. 1982) represented by an "onion diagram" (Figure 1.2). At the heart of this hierarchy is the process design (reactor, separation and recycle system) while the energy considerations are the outer layers (heat recovery system, utilities, etc). In this approach certainly the emphasis is on the process design; the process energy requirements are taken into account a posteriori.

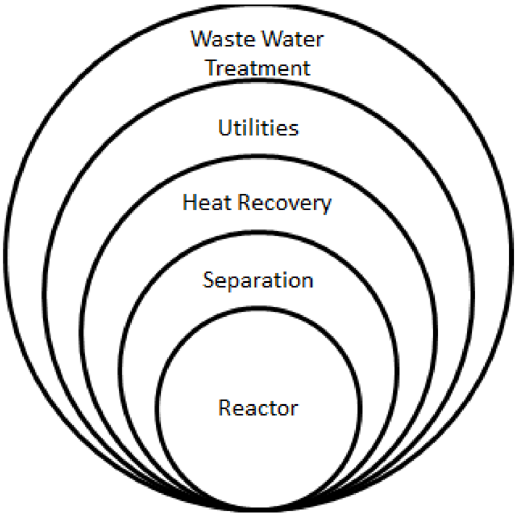


Figure 1.2.The onion model of process design (Smith 2005)

Nowadays, an **integrated approach** tends to replace the hierarchical approach. The "*process integration*" consists in considering the big picture first by looking the whole manufacturing process as an integrated system of interconnected processing units as well as process, utility and waste streams (see Figure 1.3). The research concerning this approach started in the late 1970s and early 1980s with an emphasis on energy conservation (Smith 2000). In the early 1990s, the process integration was synonymous with thermodynamic technique of pinch and energy analysis.

More recently, Gundersen et al. (2000) gave a more general definition for Process Integration: "*Process Integration includes systematic and general methods for designing integrated production systems, ranging from individual process to total sites, with special emphasis on the efficient use of energy and reducing the environmental effects*". Thus, nowadays, Process Integration covers four key areas (Smith 2005):

- Efficient use of raw material to improve the profitability of the process,

- o Emission reduction to obtain a sustainable process,
- o Efficient Process operations to optimize the process control,
- o And high energy efficiency to reduce the energy consumption of the process.

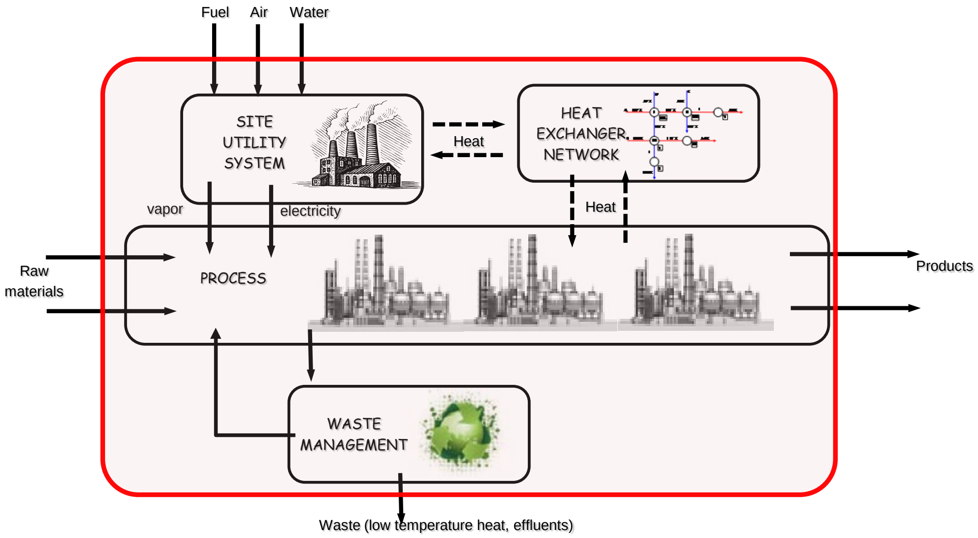


Figure 1.3.Process integration for a global optimization

Process Integration techniques include various approaches. Systematic methods such as **Pinch Analysis** based on the application of thermodynamic principles were developed (Smith 2000). This approach is aimed at increasing process-to-process heat exchanges by the design of heat exchanger networks (HEN). It can be applied to complex industrial sites such as petroleum refineries. It can incorporate complementary techniques such as energy conversion and upgrading.

Later, important contributions were made by applying **mathematical programming techniques** (*Non Linear Programming*, *Linear Programming*) to the HEN problem. Although this was only a small part of the total problem of the synthesis of manufacturing systems in the process industries, it nevertheless was an important phase in the development of process integration techniques. Other areas where significant progress has been made include heat integrated distillation system design, utility system design and optimization, mass exchange networks and water system design.

Another approach that could contribute to process integration is the **Exergy Analysis** (Kotas, 1985; Szargut et al., 1988). Exergy analysis has been investigated in many different applications: the reviews (Sciubba & Wall 2007; Hinderink et al. 1999) demonstrated that exergy analysis can be a very efficient tool to evaluate the sustainability of a process.

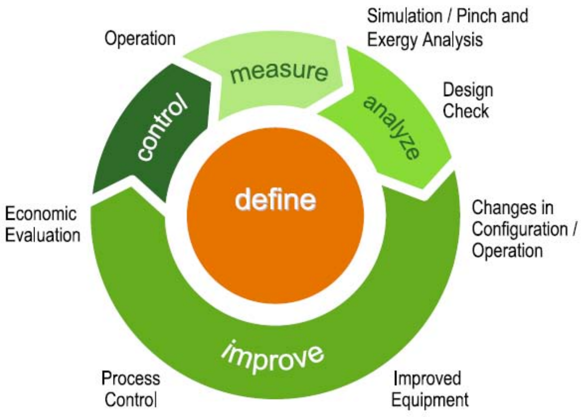


Figure 1.4.Work flow for the analysis of an existing process (Asprion et al. 2011)

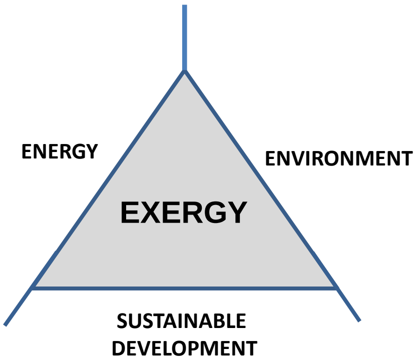


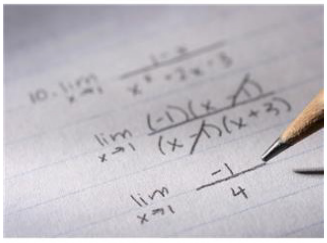
Figure 1.5.The interdisciplinary triangle of exergy (Dincer 2011)

From a thermodynamic point of view, Exergy is 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. Unlike energy, exergy is not subject to a conservation law (except for reversible processes). Rather, exergy is consumed or destroyed due to irreversibilities in any real process. The exergy consumption during a process is proportional to the entropy created. Exergy measures both the quality and quantity of the energy involved in transformations within a system. Thus, exergy analysis, also called "*lost work analysis*" can be a helpful tool in the evaluation of the energy efficiency of a process. With exergy analysis, it is possible to quantify the exergy losses in each process step, to identify units for improvements and to compare different process configurations (Figure 1.4). The exergy analysis could also be used in an early stage in the development of new process (Asprion et al. 2011). Moreover, more meaningful indicator than the traditional energy efficiency can be defined using exergy; thus, exergy efficiency permits to evaluate the degree of perfection of the considered process (Dincer 2002).

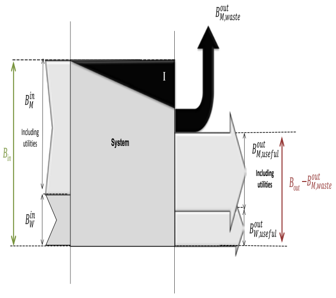
Under these facts, exergy can be considered as an interdisciplinary concept merging energy, environment and sustainable development notions (Figure 1.5) (Dincer 2011; Rosen et al. 2008).

1.4 SCOPE OF THE STUDY

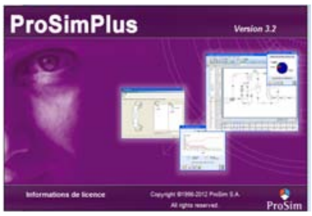
As it has been explained formerly, energy issue is becoming increasingly crucial for industrial sector that consumes large quantities of utilities. Although the scientific world should continue to look for alternate sources of energy, a short-term solution would rather rely on a more rational use of energy. To face this challenge, **exergy analysis** appears a very efficient tool as it would enable to increase efficiency and reduce environmental impact of industrial processes. Unfortunately, contrary to enthalpy, this concept is rather difficult to handle and exergy analysis is rarely implemented in process simulators. In this context, the major objective of the study presented in this dissertation is **to make exergy analysis more understandable** by **coupling it with the use of a process simulator** and also **to demonstrate the value of this approach for analysis of energy efficiency of processes and their utilities.**



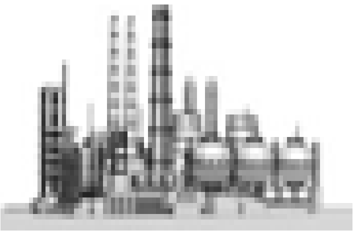
After reviewing basic exergy concepts such as the choice of reference environment, Chapter 2 introduces a generic formulation for exergy calculations of material streams. The formulations introduced in this chapter are not only generic to enable their implementation in a process simulator but they also pave the way for exergy analysis by defining the two major contributions of exergy of a material stream (physical and chemical exergies).



Chapter 3 introduces the formulation of exergy balances on a real process. For that purpose, the formulation of exergy for heat and work flux is developed. Here again, efforts are made to propose a generic approach enabling to implement exergy analysis for both “design” and “retrofitting” situation. Various formulations for exergetic efficiency criteria are presented and compared. Finally, a new structured methodology for exergy analysis is developed to overcome the limitations of existing methodologies.



To make the exergy analysis easier for any engineer, Chapter 4 exploits the concepts developed in the previous chapters to implement exergy calculations and exergy analysis.



Finally, Chapter 5 illustrates the concepts introduced in Chapters 2 and 3 and the tools developed in chapter 4 through a case study. The example is a Natural Gas Liquids (NGL) recovery process coupled to its utility system. Starting from the base process, the methodology permits to propose a retrofit configuration and to optimize its operating parameters in order to improve the energy efficiency of the global process.

PART II

FUNDAMENTAL CONCEPTS: EXERGY OF STREAMS AND EXERGY ANALYSIS

CHAPTER

2

Exergy of Material Streams: Definition and Formulation

2.1 BASIC EXERGY CONCEPTS AND DEFINITIONS

2.1.1 Exergy vs. Enthalpy

The basic concept of exergy requires a comparison between exergy and enthalpy balances must be performed. As illustrated on Figure 2.1 and Figure 2.2 representing material and enthalpy balances, material and energy are conserved in every device or process and cannot be destroyed. Mater entering a system can be accounted for in the products and by-products and energy enter the system in the form of work, heat or raw material and can be found in the output as work, heat or waste, by product and desired products material streams.

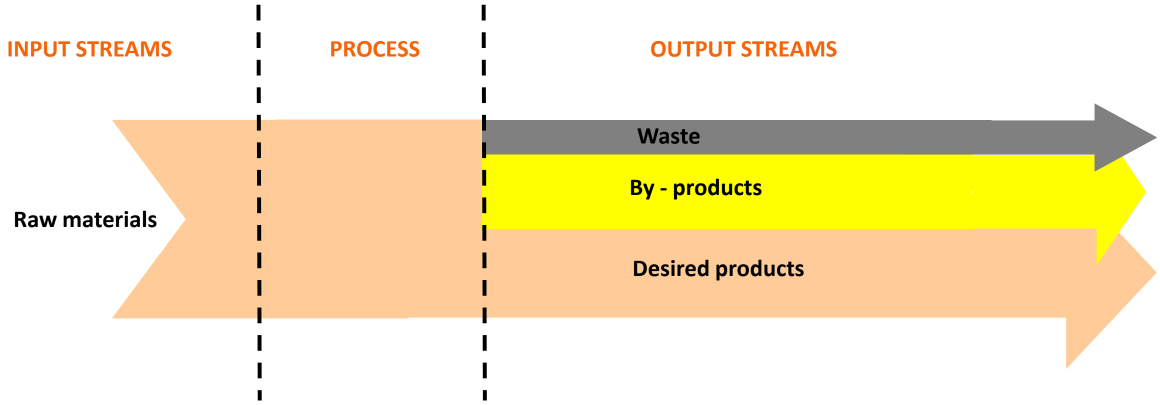


Figure 2.1. Material balance

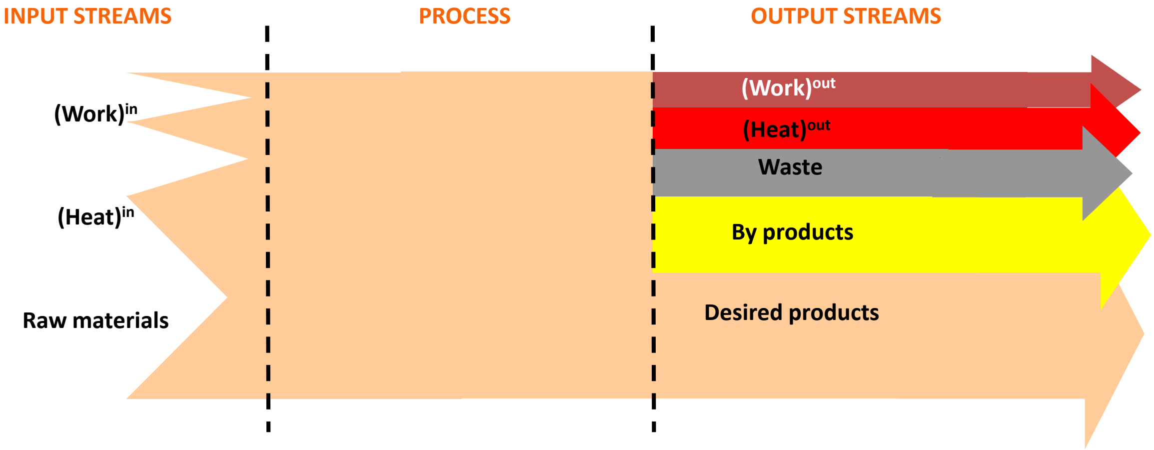


Figure 2.2. Energy balance

However, the energy and mass conservation idea alone is inadequate for depicting some important aspects of resource utilization. This type of process analysis only shows the material or energy flows of the process and does not give insights on how the quality of the energy degrades through the process by dissipation; exergy notion contributes to fill this gap by measuring the quality of energy and then accounting for thermodynamic imperfection of real process. Decreasing the exergy losses of a process means a lower primary fuel consumption so reducing the operating cost and increasing the process efficiency. When considering exergy balances, a Grassmann diagram (Kotas, 1985) such as the one illustrated in Figure 2.3 should be used as it highlights the degradation of the quality of energy (the input arrows are larger than output ones). This diagram will be largely commented in Chapter 3.

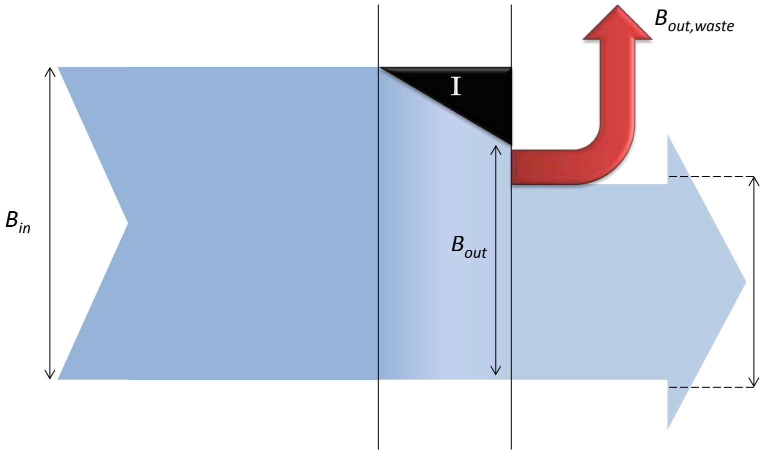


Figure 2.3. Grassmann diagram

Moreover, exergy appears as a precious concept to account for the quality of a given form of energy and to quantify the portion of energy that can be practically recovered. For example, although 10 kJ of LP steam and 10 kJ of electricity are equivalent in energy balance, 10 kJ of electric energy is much more valuable than 10 kJ of thermal energy available at LP steam temperature (≈ 100°C). Electricity is useful whereas, energy of LP steam is valuable until its temperature is brought down to the plant environment temperature (e.g. 25°C).

2.1.2 Brief history of exergy

In a recent paper, Scibba and Wall (2007) presented a really comprehensive history of exergy from early beginning till today. Some key dates are reported in Figure 2.4. It is widely known that the exergy concept has originated from the early work of what would later become Classical Thermodynamic. An exact starting date is 1824, when Carnot stated that "the work that can be extracted of a heat engine is proportional to the temperature difference between the hot and the cold reservoir" (Carnot 1824). This simple statement led later laboring by different works (Clapeyron 1834; Rankine 1851; Thomson 1853) to the position of the second law of thermodynamics (Clausius 1879; Clausius 1960). However, Gibbs, who defined the "available energy", was the first to explicitly introduce the notion of available work, including the diffusion term.

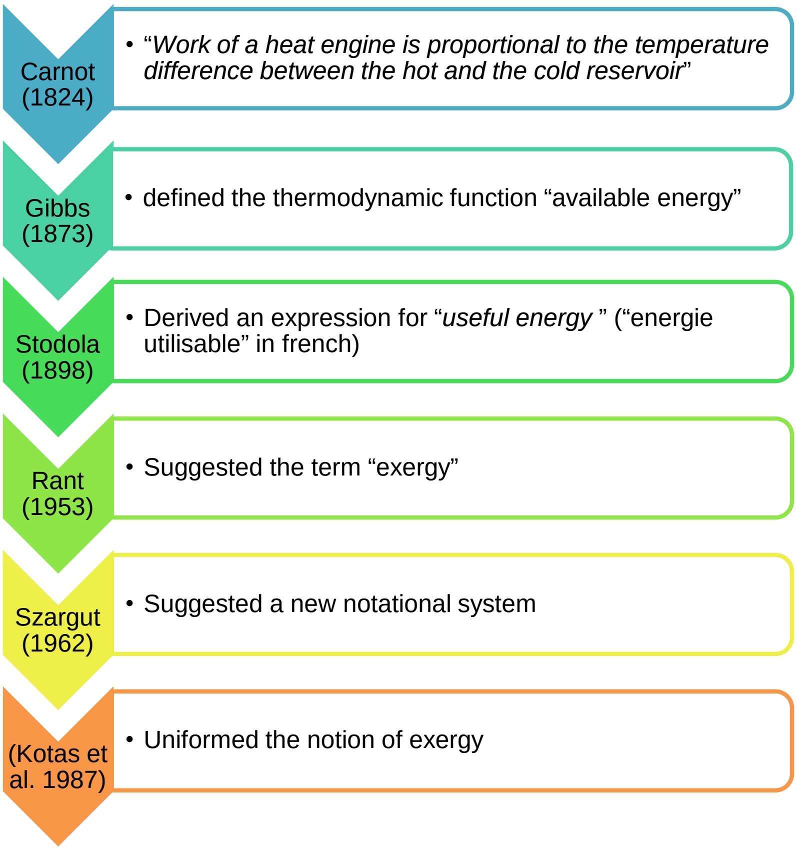
Tait (1868), and Lord Kelvin (Thomson et al. 1962), had also defined something similar to Gibbs availability without extended discussion of the concept (Tait 1877). There have been later some elaborations on Gibbs' availability in France (Duhem 1911) and Germany (Carathéodory 1909).

With no direct reference to Gibbs' work, two researchers (Stodola 1898; Gouy 1901) independently derived an expression for "useful energy" ("énergie utilisable" in French) as the expression $H\text{-}T^{00}\Delta S$ where H, T^{00} and ΔS are respectively the enthalpy of the material stream, the ambient temperature and the change in entropy.

At a scientific meeting in 1953, the term exergy (in German "Exergie") to denote *"technical working capacity*" was suggested by the Slovenian Zoran Rant for the first time. Energy literally means "*internal work*" (from the Greek en [εν] and ergon [εργον]; the prefix ex [εξ] implies instead an "external" quantity.

Rant even published a linguistic essay (Rant 1956) to discuss international equivalent names for this quantity. He proposed exergie in French, exergia in Spanish, essergia in Italian and eksergija in Slavic languages. By adopting this name (i.e. exergy), all previous expressions (e.g. available energy, availability, available work, potential work, useful energy, and potential entropy) could be abandoned. It took 50 years for Rant's denomination to become accepted worldwide. However, some US authors still use the terminology of "availability" instead of 'exergy'.

Two different notational systems was suggested (Szargut 1962; Weingärtner 1969) as a mature topic requires a standard notation system. This problem with notation was formally solved much later (Kotas et al. 1987). Like what we have seen for name of exergy, there were as many definitions of "exergy efficiency" as there were authors in the field. This point will be emphasized later in the manuscript in Chapter 3.



- "*Work of a heat engine is proportional to the temperature difference between the hot and the cold reservoir*"
- defined the thermodynamic function "available energy"
- Derived an expression for "*useful energy* " ("energie utilisable" in french)
- Suggested the term "exergy"
- Suggested a new notational system
- Uniformed the notion of exergy

Figure 2.4. A review of exergy history

2.1.3 Components of exergy

Based on the second law, an opportunity exists for generating work when two systems at different states are allowed to come into equilibrium. Exergy is the maximum theoretical work obtainable as a suitably idealized system called "*exergy reference environment*" or "*environment*" and the system of interest interact to equilibrium (Moran & Shapiro 2006). More recently, the modern definition of exergy has been enounced as follows: "*exergy is the maximum theoretical useful work obtained if a system S is brought into thermodynamic equilibrium with the environment by means of processes in which the system S interacts only with this environment*" (Sciubba & Wall 2007).

- As there are many forms in which energy flows present themselves in nature, there are several corresponding forms of exergy. The most commonly used are listed in Table 2.1. The physical significance of the “exergy equivalence” is given as flows:
- The *kinetic energy* of a system traveling at a speed V with respect to a Galilean frame of reference can be in principle entirely recovered into any other form: potential (principle of the ideal pendulum); heat (friction brake); mechanical (impulse turbine); or electrical (piezoelectric effect). Therefore, quantity of kinetic exergy is equal to quantity of kinetic energy.
- The same applies to gravitational *potential energy* and to all energy forms related to motion in a conservative force field. Therefore, quantity of potential exergy is equal to quantity of potential energy.
- *Mechanical work* and *electrical energy* can also be freely converted into each other. Therefore, quantity of shaft work is equal to quantity of shaft work.
- *Chemical energy* cannot be entirely transformed into mechanical work; the maximum “work” that can be extracted from a system composed of a single pure substance not only depends on the chemical enthalpy of formation of that substance, but also on the difference between its concentration in the system and in the reference environment. This matter will be detailed in Section 2.2.3 of this chapter.
- *Heat* is the “least available” form of energy flow: the portion that can be converted into work depends on both the system and reference temperatures.
- Energy emission from a blackbody at temperature T is σT^4 which can be thought as heat transferred to a sink at 0 K. But the exergy of that radiation in a reference environment at T^{00} is not given by Carnot's efficiency because a radiator at temperature T cannot transfer the amount of heat σT^4 to a heat sink at the same temperature T. In order to avoid any entropy generation, an infinite number of intermediate heat sources at temperature T_i, absorbing radiation at $T_i + dT_i$ and emitting radiation at T_i, can be imagined, with an infinite number of Carnot engines extracting the maximum work from the net heat input at each, $d\left(\sigma T_i^4\right) = 4\sigma T_i^3 dT_i$ (Martínez 2012).

Table 2.1. Exergy components

Type of energy flow	*Molar energy*	*Molar exergy*
Kinetic	$\frac{1}{2}V^2$	$\frac{1}{2}V^2$
Potential	$g(l-l_0)$	$g(l-l_0)$
Heat	q	$q\left(1-\frac{T^{00}}{T}\right)$
Mechanical	w	w
Chemical	Δg	$\mu(T^{00},P^{00},\mathbf{z})-\mu(T^{00},P^{00},\mathbf{z}^{00})$
Radiation	σT^4	$\sigma\left(T^4-\frac{4T^3T_0}{3}+\frac{T_0^4}{3}\right)$

2.1.4 A focus on thermal and chemical processes

Thermal and chemical processes usually deal with material, work and heat streams. Heat and work can directly be considered as energy flows and correspondence between energy and exergy values are directly reported in Table 2.1. It is more complex for a material stream as its exergy can be divided into several components illustrated in Figure 2.5.

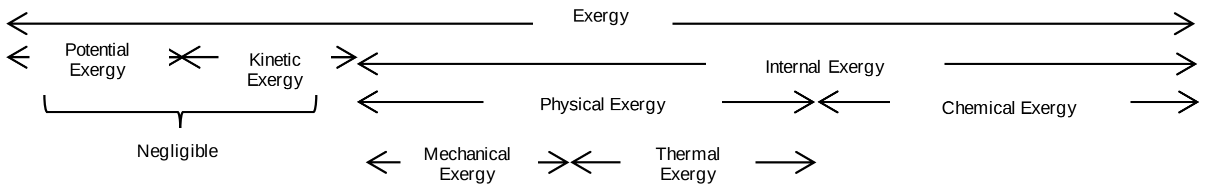


Figure 2.5. Exergy components

When a system undergoes a process without any significant changes in velocity and height between the inlet and outlet conditions, the kinetic and the potential exergies can be neglected. This is the case for most of the processes to be simulated in process simulators. Neglecting kinetic and potential exergy, physical exergy and chemical exergy become the two major contributors of chemical processes. As a consequence, the total exergy of a material stream at given conditions is then expressed as the sum of chemical exergy and physical exergy.

Figure 2.6 illustrates the physical and chemical exergy concept. The definition of both kinds of exergy requires the introduction of three fundamental states:

- *The "process state"* refers to the initial state of the system under study defined by its temperature, pressure and composition *(T,P,**z**).*
- *The "environmental state"* satisfies the conditions of restricted equilibrium with the environment i.e. temperature and pressure equal to that of the environment $(T^{00}, P^{00}, \mathbf{z})$.
- *Finally the "standard dead state" is used* when the conditions of full thermodynamic equilibrium between the system and the environment are reached. In these conditions, the temperature, pressure and composition of the system are respectively equal to $(T^{00}, P^{00}, \mathbf{z}^{00})$ and the value of exergy of the system is equal to zero.

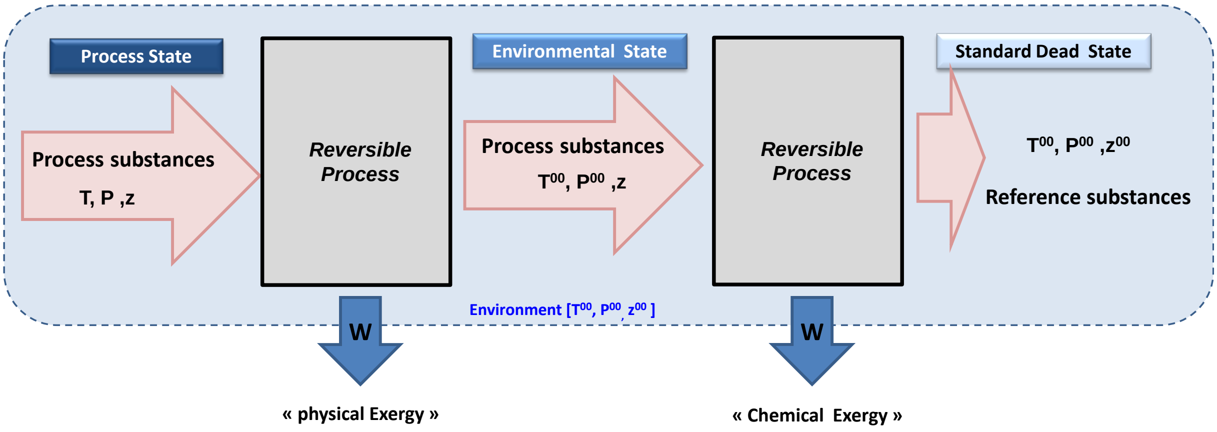


Figure 2.6. Definition of states

Given these definitions, physical and chemical exergies can be defined as follows:

- *Physical exergy* is the work that can be obtained by taking the system from the *process state* to the *environmental state*
- *Chemical exergy* is the work that can be obtained by taking a substance from the *environmental state* to the *standard dead state*. According to Rivero and Anaya (1997), chemical equilibrium has two contributions:
    - A reactional exergy resulting from the chemical reaction necessary to producing species existing as stable components in the environment from the initial composition of the substance;
    - A concentrational exergy, which results from the process required to match chemical concentration of the produced species to their chemical concentration in the environment (Rivero & Anaya 1997).

2.1.5 Reference environment

Whereas the evaluation of the physical exergy of a process stream requires the definition of the temperature and pressure of a reference environment, the calculation of the chemical exergy cannot be performed without a precise description of the substances existing in the environment.

The chemical exergy quantity strongly depends on the reference environment model. Because of the extreme complexity of the physical world, this task remains a big challenge. In the section, several approaches and classes of reference-environment models are briefly described.

2.1.6 Modeling the environment

2.1.6.1 Partial Reference Environments (Partial RE)

The Partial Reference Environment (Partial RE) is defined according to the specific characteristics of the analyzed process. This criterion is based on that being the exergy a parameter that quantifies the theoretical evolution of a system with respect to the R.E., some of the possible evolutions of the system, cannot be attained because of process limitations. Hence, only possibilities of evolution that the system can practically attain are analyzed. The partial R.E. is not a “dead state”.

Natural-environment-subsystem models: These models attempt to simulate realistically subsystems of the natural environment. One of such models consisting of saturated moist air and liquid water in phase equilibrium was proposed (Baehr & Schmidt 1963). An extension of the above model which allowed sulfur-containing materials to be analyzed was proposed (Gaggioli & Petit 1977; Rodriguez 1980). The temperature and pressure of this reference environment are normally taken to be 25◦C and 1 atm, respectively, and the chemical composition is taken to consist of air saturated with water vapor, and the following condensed phases at 25◦C and 1 atm: water (H_2O), gypsum ($CaSO_4 \cdot 2H_2O$) and limestone ($CaCO_3$). The stable configurations of C, O and N respectively are taken to be those of CO_2, O_2 and N_2 as they exist in air saturated with liquid water at T^{00} and P^{00}; of hydrogen is taken to be in the liquid phase of water saturated with air at T^{00} and P^{00}; and of S and Ca respectively are taken to be those of $CaSO_4 \cdot 2H_2O$ and $CaCO_3$ at T^{00} and P^{00}.

Process-dependent models: A model which contains only components that participate in the process being examined in a stable equilibrium composition at the temperature and total pressure of the natural environment was proposed (Bosnjakovic 1963). This model is dependent on the process examined, and is not general. Exergies evaluated for a specific process-dependent model are relevant only to the process; they cannot rationally be compared with exergies evaluated for other process-dependent models.

2.1.6.2 Comprehensive Reference Environments (comprehensive RE)

According to most authors, the model of the reference environments should be as close as possible to the natural environment and should provide an economic indicator for the exergy values; for example, abundant substances in nature should have lower exergies than scarce ones. Different models of comprehensive reference environment have been introduced.

- The '*equilibrium models*' are in thermodynamic equilibrium but their composition and parameters distinctly differ from the natural environment.
- Other models called '*reference substance models*' consider the most abundant species in the real environment but do not assume that these substances are in thermodynamic equilibrium.

Equilibrium models: In these models all the materials present in the atmosphere, oceans and a layer of the crust of the earth are pooled together and an equilibrium composition is calculated for a the environmental temperature (i.e. 25°C) was proposed by Ahrendts (1980). The selection of the thickness of crust considered is subjective and is intended to include all materials accessible to technical processes. Ahrendts (1980) considered thicknesses varying from 1 to 1000 m. First, Ahrendts showed that exergy values obtained using these environments are significantly dependent on the thickness of crust. Furthermore, whatever the considered thickness, the calculated compositions of substances differed significantly from the natural environment. This calculation shows to demonstrate that the natural environment is not in thermodynamic equilibrium. It was explained already by a group of researchers (Valero et al. 2002) why Ahrendt's R.E. was not suitable to evaluate the natural capital on Earth. Most of the metals cannot be evaluated because they form part of the 1% of the Earth's crust neglected by Ahrendts. His obtained R.E. is very different from the real environment and it is very unlikely an eventual evolution towards it, since some processes are kinetically, biologically and/or geologically blocked. As a consequence, it appears that Ahrendts' equilibrium model does not give meaningful exergy values when applied to the analysis of real processes.

Ahrendts (1980) also proposed constrained-equilibrium model, a modified version of his equilibrium environment in which the calculation of an equilibrium composition excludes the possibility of the formation of nitric acid (HNO_3) and its compounds. All chemical reactions in which these substances are formed are in constrained equilibrium, and all other reactions are in unconstrained equilibrium. When a thickness of crust of 1 m and temperature of 25°C were used, the model was similar to the natural environment.

Reference-substance models: A reference environment with the criterion of chemical stability was proposed (Kameyama et al. 1982). The references are the most stable compounds among those with thermo-chemical data and can be integrated in the solid, liquid and gaseous environments. As Szargut stated in (Szargut 1989), some of the most stable compounds selected by Kameyama et al. like nitrates, compounds between rare elements (e.g. $PtBr_2$) or compounds with Fr as the reference species for the elements F, Cl, Br, I should not be recommended, because the probability of their formation in the environment is very small. Therefore, Kameyama et al. R.E. is not very suitable either to evaluate the scarcity of the natural capital.

A new R.E. very close to the real environment based on abundance and following Szargut's criterion was proposed (Ranz 1999). According to Ranz, lots of minerals are compounds with the most common components of the upper continental crust, but are not very stable and do not represent the products of an interaction between the components of the natural environment and the waste products of industrial processes. The solid phase of this new R.E. reproduces accurately the Earth's upper continental crust, since the solid reference species that make up this environment are the same as the most abundant types found in the Earth's upper continental crust. A problem with the Ranz proposed R.E. is that if we assign zero exergy to the most abundant substances, we are decreasing arbitrarily the natural capital, because many abundant minerals like sulfides naturally evolutes to the most stable oxides. Therefore, as proposed by literature (Valero et al. 2002), we must return to Szargut's criterion of using the most stable substance, within the limits fixed by the “Earth similarity criterion".

According to Szargut's criterion, among a group of reasonable abundant substances, the most stable will be chosen if they also complain with the “Earth similarity criterion". Thus for example in the case of Sb, the substance Sb_2S_3 is more abundant than Sb_2O_5, nevertheless, according to Szargut's criterion, Sb_2O_5, which is much more stable, will be taken as reference substance. Therefore, Szargut's dead environment is similar to the real physical environment and should represent the products of an interaction between the components of the natural environment and the waste products of the processes. The most probable products of this interaction should be chosen as reference species.

The model proposed by Szargut (1967) considers species that are in abundance in the real environment. Reference species can either be gaseous component from the atmosphere, species dissolved in the seawater or solid compounds present in the Earth’s surface. Recently, the model proposed by Szargut (1967) for the calculation of the standard chemical exergy of elements and organic and inorganic substances has been revised by Valero et al. (2002) who used more precise data of the concentration of elements in the Earth’s crust; Using these updated data, Rivero & Garfia (2006) established a new database composed of the chemical exergy for each elements (so-called “standard chemical exergy of elements”). This database was compared with the database established by Szargut. Because of some anomalous behavior in the chemical exergy when a different salinity of seawater is assumed, some different reference species than those used in the latest version of the Szargut model were proposed for the following elements: silver, gold, barium, calcium, cadmium, copper, mercury, magnesium, nickel, lead, strontium and zinc. The complete set of updated values of standard chemical exergies of elements for the standard conditions (298.15 K and 1 atm) is reported in Appendix A. Note that the temperature and pressure of all environments are always fixed at 298.15 K and 1 atm in the literature. Therefore, only the definition of concentration of species present in the reference environment influences the chemical exergy.

According to Table 2.2 that summarizes the models for environment, the reference-substance model appears to be the most commonly used class of reference environment. In this study, the recently updated reference-substance model proposed by Rivero & Garfias (2006) and tabulated in Appendix A will be used.

Table 2.2. Different classes of reference-environment models

Type of RE			**Advantages**	**Shortcomings**	**Reference**
Partial	-	Natural-environment-subsystem models	Simulate realistically of environment	- Not updated - Limited chemical elements	(Baehr & Schmidt 1963) (Gaggioli & Petit 1977) (Rodriguez 1980)
		Process-dependent models	- Dependent on the process examined	- Not general	Bosnjakovic (1963)
Comprehensive	***Reference-substance models***	Reference-substance models	- The most commonly used RE - Recently updated - The recent model is similar to the natural environment	- Some of models in this class are not similar to the natural environment	(Szargut 1967) (Szargut et al. 1988) (Sussman 1980) (Rivero & Garfias 2006b)
		Chemical-stable models	- The most stable compounds is chosen as RS	- The probability of formation of some of RS in the environment is very small	(Kameyama et al. 1982).
		Most-abundant-substances models	- Very close to the real environment	- If we assign zero exergy to RS, the natural capital are decreasing	(Ranz 1999)
	Equilibrium models	Equilibrium models	- A model in which all the materials in the atmosphere, oceans and a the earth are in equilibrium	- Does not give meaningful exergy values - The natural environment is far away from such equilibrium - Very high exergy values for oxygen - In disagreement with the “Earth similarity criterion"	(Ahrendts 1980)
		Constrained-equilibrium models	- Similar to the natural environment	- Not updated	(Ahrendts 1980)

2.2 EXERGY OF A MATERIAL STREAM

For the purpose of exergy balance, all types of exergy associated with input streams highlighted in Figure 2.2 (i.e. material, heat and work streams) have to be calculated. This section focuses on the exergy of material streams; Exergy of a material stream is precisely defined and a generic formulation independent of the thermodynamic model and of the physical state of the stream is introduced. This lays the foundations of the implementation of the calculation of a new thermodynamic quantity in Simulis Thermodynamics. As demonstrated formerly, the two major contributions of exergy are the physical exergy and chemical exergy. Both of them will be introduced.

2.2.1 Preliminary remark

In the existing literature dealing with the exergy calculation, the considered material stream is always a monophasic stream (liquid, vapor or solid). As process simulator often include multiphasic streams, it is necessary to know how to deal with such streams. The calculation of usual state function like enthalpy or entropy consists in calculating the enthalpy or entropy of liquid and gas phases and in weighting these contributions with the vapor ratio. To demonstrate the analogy with exergy formulation, let us consider a virtual separation process illustrated in Figure 2.7 whose purpose is to separate the two phases of a liquid vapor equilibrium system.

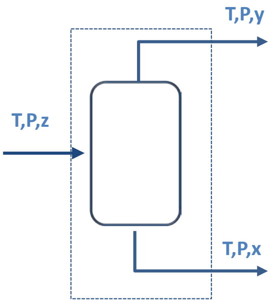


Figure 2.7. Separation of a liquid-vapor equilibrium system

As liquid and vapor phases are in equilibrium, the process is an adiabatic one. Applying the second principle, we can write:

$$s(T,P,z) - ws^v(T,P,y) - (1-w)s^l(T,P,x) + \frac{I}{T^{00}} = 0 \qquad (2.1)$$

Then, the irreversibility I is given by:

$$I = T^{00}[s(T,P,z) - ws^v(T,P,y) - (1-w)s^l(T,P,x)] \qquad (2.2)$$

Moreover, the entropy of a liquid/vapor system is given by:

$$s(T,P,z) = ws^v(T,P,y) + (1-w)s^l(T,P,x) \qquad (2.3)$$

It results from these equations that, the irreversibility of the separation operation of two phases in thermodynamic equilibrium is equal to 0. Then, a reversible operation is a process that does not destroy exergy.

As a consequence, we will conclude that the exergy of a material stream can be handled as enthalpy and entropy state functions and that we can write:

$$b(T,P,z) = wb^{v}(T,P,y) + (1-w)b^{l}(T,P,x) \tag{2.4}$$

To conclude, to evaluate the exergy of material streams, it will be necessary to split multiphasic stream into several monophasic streams and then to calculate the exergy of each monophasic stream. In the following sections, the streams will be supposed to be monophasic.

2.2.2 Physical Exergy

2.2.2.1 General formulation

As illustrated in Figure 2.8, physical exergy can be defined as: “the maximum amount of work obtainable when it is brought from its process state to the environmental state, by physical reversible process involving thermal and mechanical interactions only with the environment”.

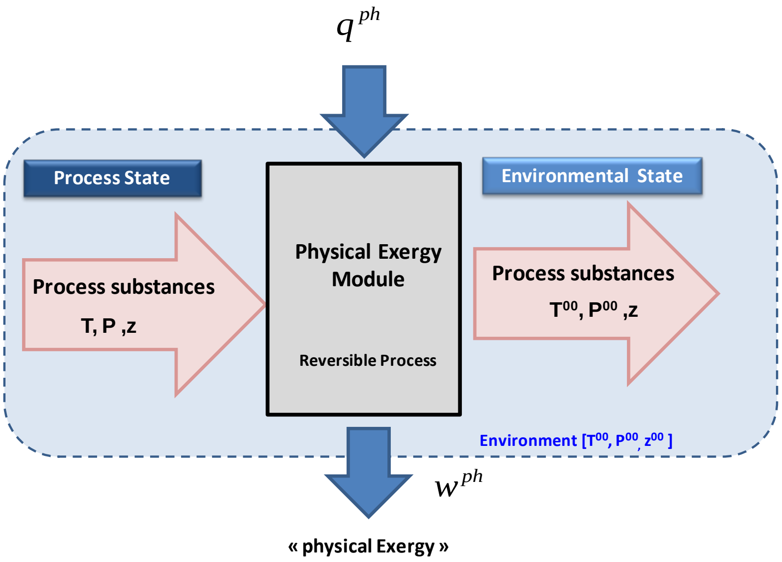


Figure 2.8. Definition of the physical exergy

The *Physical Exergy Module* illustrated in Figure 2.8 represents an ideal device around which the process system is set from the P*rocess State* to the *Environmental State* through a reversible process.

The first law of thermodynamics written on the Physical Exergy Module leads to:

$$h(T,P,\mathbf{z}) - h(T^{00},P^{00},\mathbf{z}) + q^{ph} - w^{ph} = 0 \tag{2.5}$$

Then the second law of thermodynamics gives:

$$s(T,P,\mathbf{z}) - s(T^{00},P^{00},\mathbf{z}) + \frac{q^{ph}}{T^{00}} = 0 \tag{2.6}$$

Eliminating the heat transfer rate between the last two equations, the specific physical exergy b^{ph} can finally be defined as follows:

$$b^{ph} = w^{ph} = h(T,P,\mathbf{z}) - T^{00}s(T,P,\mathbf{z}) - \left[h(T^{00},P^{00},\mathbf{z}) - T^{00}s(T^{00},P^{00},\mathbf{z})\right] \qquad (2.7)$$

As can be seen in Eq. (2.3), the specific physical exergy is a function of enthalpy and entropy difference; as a consequence, the chosen basis for enthalpy and entropy calculation does not impact the value of physical exergy.

Assuming that the material stream behaves like a perfect gas, its physical exergy can be calculated from Eq. (2.8):

$$b^{ph} = c_P\left(T - T^{00}\right) - T^{00}\left(c_P \ln\frac{T}{T^{00}} - R\ln\frac{P}{P^{00}}\right) \qquad (2.8)$$

2.2.2.2 Thermal and mechanical contributions

Some authors express the physical exergy as the sum of thermal and mechanical contributions. This is a very useful approach for the analysis of the recovery potential of waste products. As an example, energy efficiency of processes containing some effluents with a high thermal exergy contribution could be improved through heat integration techniques. On the other hand, a waste product containing a high mechanical exergy would be recovered using a turbine.

To define both contributions, Kotas (1985) arbitrarily chose the thermodynamic path illustrated in Figure 2.9. This path includes an intermediate state (T^{00},P); in that conditions, the thermal exergy is based upon a P^{00} isobar transformation from T to T^{00} (Eq. 2.9) whereas the mechanical exergy corresponds to the T^{00} isotherm transformation from P to P^{00} (Eq. 2.10).

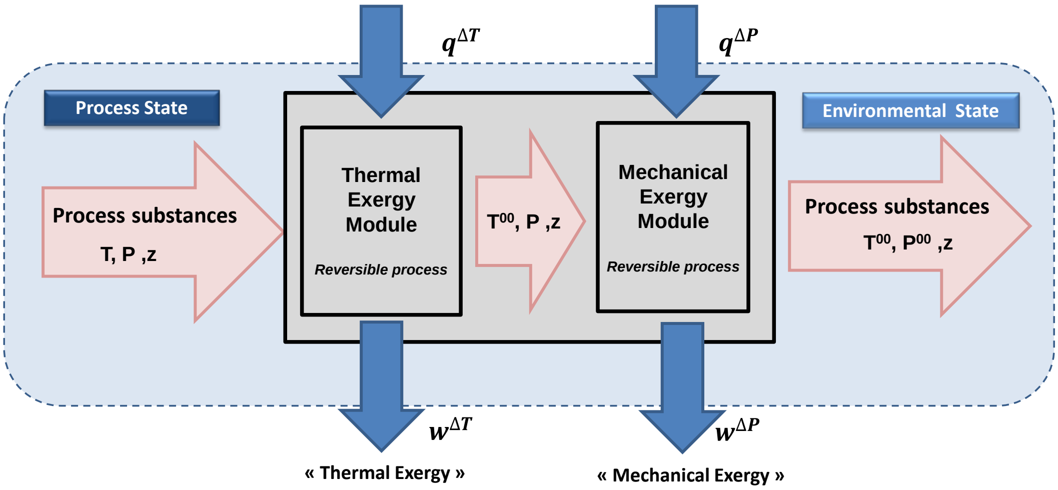


Figure 2.9. Thermal and mechanical exergy (Kotas,1985)

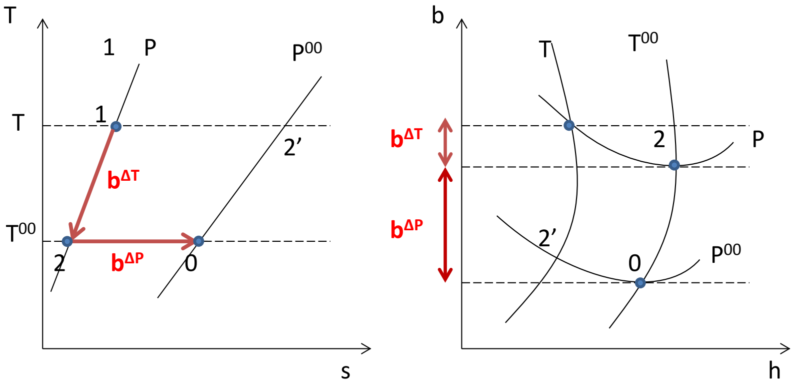


Figure 2.10. Thermodynamic path for thermal and mechanical contributions of physical exergy

As a consequence, we have:

$$b^{\Delta T} = w^{\Delta T} = h(T,P,\mathbf{z}) - T^{00}s(T,P,\mathbf{z}) - \left[h\;(T^{00},P,\mathbf{z}) - T^{00}s\;(T^{00},P,\mathbf{z})\right] \tag{2.9}$$

and

$$b^{\Delta P} = w^{\Delta P} = h(T^{00},P,\mathbf{z}) - T^{00}s(T^{00},P,\mathbf{z}) - \left[h\;(T^{00},P^{00},\mathbf{z}) - T^{00}s\;(T^{00},P^{00},\mathbf{z})\right] \tag{2.10}$$

In that case, the sum of both thermal and mechanical contribution is equal to the physical exergy.

$$b^{ph} = b^{\Delta T} + b^{\Delta P} \tag{2.11}$$

However, the respective values of thermal and mechanical exergies would not be the same while considering the intermediate state (T,P^{00}).

2.2.2.3 Maximal potential for thermal and mechanical recovery

To help the engineer in his analysis of external exergy losses and to enable him to select the best recovery process, we introduce the Maximal Potential for thermal and mechanical recovery (see Figure 2.11).

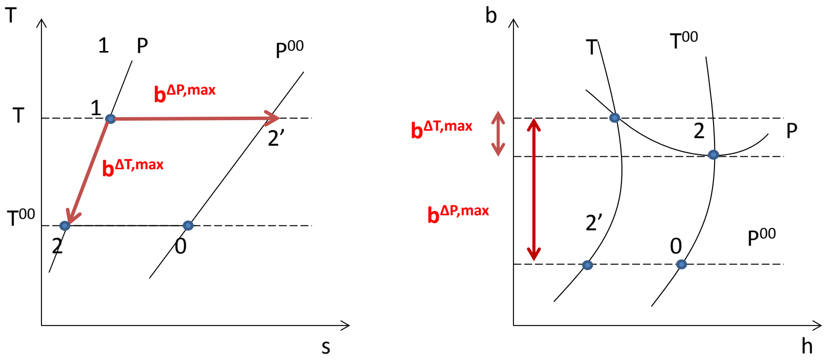


Figure 2.11. Thermodynamic path for maximal potentials for thermal and mechanical recovery

The maximal potentials for thermal and mechanical recovery can be defined as follows:

$$b^{\Delta T,\max} = h(T,P,\mathbf{z}) - T^{00}s(T,P,\mathbf{z}) - \left[h\ (T^{00},P,\mathbf{z}) - T^{00}s\ (T^{00},P,\mathbf{z})\right] \tag{2.12}$$

and

$$b^{\Delta P,\max} = h(T,P,\mathbf{z}) - T^{00}s(T,P,\mathbf{z}) - \left[h\ (T,P^{00},\mathbf{z}) - T^{00}s\ (T,P^{00},\mathbf{z})\right] \tag{2.13}$$

Note that in this case, the sum of both maximal potentials for thermal and mechanical recovery is not equal to the physical exergy.

$$b^{ph} \neq b^{\Delta T,\max} + b^{\Delta P,\max}$$

This calculation is only required to evaluate the maximum recovery potential of a given effluent.

2.2.3 Chemical Exergy

2.2.3.1 Definition of chemical exergy

Starting from the final state used to evaluate the physical exergy of a given stream (i.e. the *environmental state*) one can evaluate the chemical exergy. Chemical exergy is defined as "*the maximum work obtainable when the substance under consideration is brought from* environmental state *to the standard* dead state *by a reversible process involving heat transfer and exchange of substances only with the environment*" (Szargut et al. 1988).

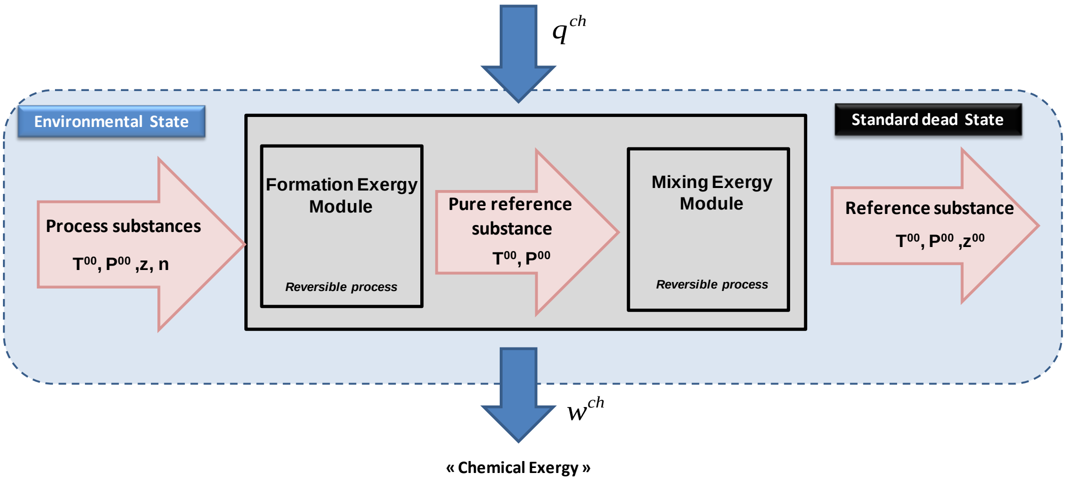


Figure 2.12. Definition of chemical exergy

To assess the chemical *exergy* of a stream the properties of the chemical substance included in the stream must be referred to the properties of some corresponding suitably selected substances in the environment (i.e. *Reference Substances, RS*). Reference Substances can either be gaseous component from the atmosphere, species dissolved in seawater, or solid compounds presents on the earth's surface.

Recall that in this study, the chosen reference environments that introduced by Rivero & Garfias (2006) and described in Appendix A.

Two cases must be considered:

- If the considered process substance is a reference substance (for example CO_2 which is a substance existing in the atmosphere), the calculation of its chemical exergy corresponds to the maximum work obtainable when its process composition is set to the composition of CO_2 in the atmosphere (see the "*Mixing Exergy Module*" in Figure 2.13).
- If the considered process substance does not belong to the reference substances, the calculation of its chemical exergy first requires the modeling of a reversible chemical reaction that would transform the process substance into several pure reference substances (see the "*Formation Exergy Module*" in Figure 2.13). Then, the "Mixing Exergy Module" sets the composition of these pure reference substances to the environmental composition.

To illustrate this concept, let us take an example illustrated in Figure 2.13 where a process stream composed of CO and H_2 is considered. To be set to the standard dead state, CO and H_2 need to be transformed to the substances found in the reference environment. Two reversible chemical reactions occur in the Formation Exergy Module to transform respectively the CO into pure CO_2 and pure H_2O and H_2 into pure H_2O with the aid of O_2 brought from the environment. Then the Mixing Exergy Module contributes to set these pure reference substances to their environmental composition.

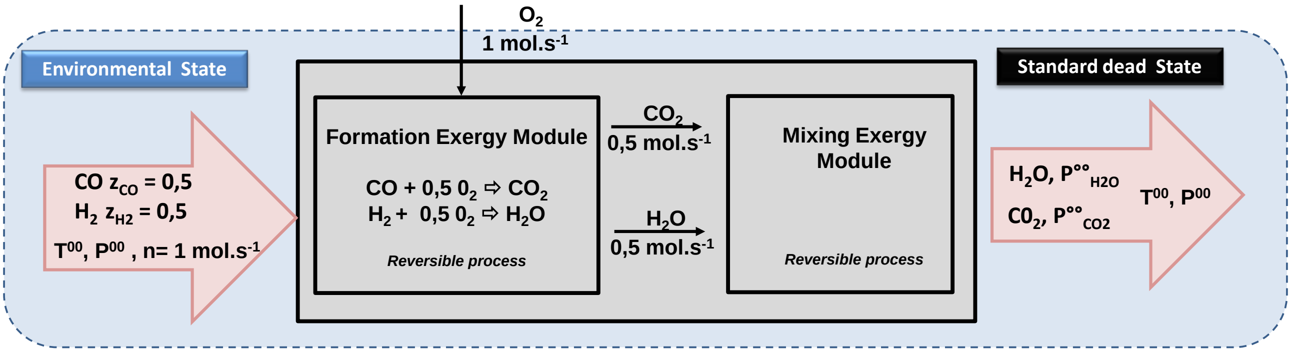


Figure 2.13. An example for chemical exergy

2.2.3.2 Formulation of chemical exergy

The general formulation of the chemical exergy of a given mixture can be deduced from this former simple example. Let us consider fist the case of a vapor mixture in the environmental state. At T^{00},P^{00}, the vapor mixture behaves as a perfect gas and the chemical exergy; given the molar flowrate of the process stream n, the chemical exergy of the mixture $b^{ch,*}$can be expressed as follows :

$$b^{ch,*}(T^{00},P^{00},z) = h(T^{00},P^{00},z) - s(T^{00},P^{00},z) - \frac{1}{n}\sum_{i}^{Nc}\left[\sum_{j=1}^{N_{ref,i}} n_{j,i}\left[h_j(T^{00},P^{00},z^{00}\right] - T^{00}s(T^{00},P^{00},z^{00})\right] \tag{2.14}$$

where,

- $n_{j,i}$ is the flowrate of the reference substance j generated by the process substance i

- $N_{ref,i}$ is the number of reference substances j generated by the process substance i

Expressing the specific entropy as a function of activities a_i,,Eq. (2.14) can be written as follows:

$$b^{ch,*}(T^{00},P^{00},z) = \sum_{i}^{Nc} y_i \left[h_i^{\circ}(T^{00},P^{00}) - T^{00} s_i^{\circ}(T^{00},P^{00}) - RT^{00} l\,n[a_i(T^{00},P^{00},z)] - \sum_{j=1}^{N_{ref,i}} \frac{n_{j,i}}{ny_i} \left[h_j(T^{00},P^{00},z^{00}) - T^{00} s(T^{00},P^{00},z^{00}) \right] \right] \tag{2.15}$$

According to Eq. (2.10), the calculation of chemical exergy requires to be able to calculate the enthalpy and entropy of reference substances in the standard dead state. These calculations have been made by Rivero & Garfias (2006) starting from the knowledge of concentration of reference substances in environment and thanks to complex thermodynamic calculations. To simplify the exergy calculations, Szargut et al. (2005) introduced the concept of molar standard chemical exergy.

> The molar standard chemical exergy $b_i^{\circ *}$ of a reference substance is the molar chemical exergy obtained at (T^{00},P^{00}) of the pure substance in the gas state

We can write,

$$b_i^{\circ *} = h_i^{0*}(T^{00},P^{00}) - T^{00} s_i^{0*}(T^{00},P^{00}) - \sum_{j=1}^{N_{ref,i}} \frac{n_{j,i}}{n_i} \left[h_j(T^{00},P^{00},z^{00}) - T^{00} s(T^{00},P^{00},z^{00}) \right] \tag{2.16}$$

Integrating the molar standard chemical exergy $b_i^{\circ *}$ in Eq.(2.15), we finally obtain

$$b^{ch,*}(T^{00},P^{00},z) = \textstyle\sum_i^{Nc} y_i [b_i^{0*} + RT^{00} ln(a_i)] \tag{2.17}$$

Generalizing this equation for a multiphasic mixture composed of N^{ϕ} phases à T^{00}, P^{00}, we can write

$$b^{ch}(T^{00},P^{00},z) = \textstyle\sum_1^{N\varphi} w^{\varphi} \left(\sum_i^{Nc} z_i \left[b_i^{0\varphi} + RT^{00} ln(a_i) \right] \right) \tag{2.18}$$

where

$$b_i^{\circ\varphi} = b_i^{0*} + \Delta G_{v\to\varphi} \tag{2.19}$$

The evaluation of the activity depends on the considered phase :

o In the case of a gas phase, a_i is given by :

$$a_i = \frac{f_i^V(T^{00}, P^{00}, y)}{f_i^{0,V}(T^{00}, P^{00})} \qquad (2.20)$$

At T^{00}=298.15 K and P^{00}=1 atm, the gas can be considered as a perfect gas and the fugacity is equal to the pressure P^{00}. Then, we finally have:

$$a_i = \frac{f_i^V(T^{00}, P^{00}, y)}{P^{00}} \qquad (2.21)$$

- In the case of a liquid phase, a_i is given by :

$$a_i = \frac{f_i^l(T^{00}, P^{00}, y)}{f_i^{0,l}(T^{00}, P^{00})} = \gamma_i(T^{00}, P^{00}, x).x_i \qquad (2.22)$$

- Finally for a solid phase, we have

$$a_i = 1 \qquad (2.23)$$

This is precisely the equation that will be used to calculate the chemical exergy of a given mixture. In this equation, the standard chemical exergy of element must be known.

2.2.3.3 Calculation of the molar standard chemical exergy

As explained formerly, the molar standard chemical exergy of a reference substance are deduced from the conventional mean concentration of the reference species in the environment. Moreover, molar standard chemical exergies of element can be deduced from molar standard chemical exergy of species using the following expression:

$$b_i^{0*} = \Delta G_f^{\circ} + \sum_{j=1}^{N_{el,i}} n_{i,j} b_j^{\circ *} \qquad (2.24)$$

Note that in this equation the free formation Gibbs enthalpy is given for a substance i in the gas state. As a consequence, the molar standard chemical exergies obtained are gas molar standard chemical exergies.

Figure 2.14 illustrates this concept by explaining the process enabling to calculate the molar standard chemical exergy of element phosphorus starting from the concentrations of H_2O and O_2 in atmosphere and concentration of HPO_4 in hydrosphere.

Starting with the partial pressure of the Reference Substance O_2 in the atmosphere, one can calculate the standard chemical exergy of element.

$$b_{O_2}^{0*} = \frac{RT^{00}}{2} \ln\left(\frac{P_{O2}^{\circ}}{P^{00}}\right) \qquad (2.25)$$

where $P_{O_2}^0$ represents the partial pressure of oxygen in the atmosphere.

Then b_O^0 can be deduced as follows:

$$b_O^{0*} = \frac{b_{O_2}^0}{2} \tag{2.26}$$

In the same way, starting from the partial pressure of H_2O in the atmosphere, we have:

$$b_{H_2O}^{0*} = RT^{00} \ln P_{H_2O}^0 \tag{2.27}$$

and b_H^0 can be deduced:

$$b_H^{0*} = \frac{b_{H_2O}^{0*} - \Delta G_{f_{H2O}}^0 + b_O^{0*}}{2} \tag{2.28}$$

Finally, this two molar standard chemical exergy of elements O and H, can be used to calculate exergy of phosphorus. Using an electrolytic model the standard chemical exergy of HPO_4, $b_{HPO4}^0$is deduced from the mean concentration of this component in the seawater. Then, we can write:

$$b_{HPO4}^{0L} = \Delta G_{f,HPO4}^{*} + b_H^{0*} + b_P^{0*} + 4b_O^{0*} \tag{2.29}$$

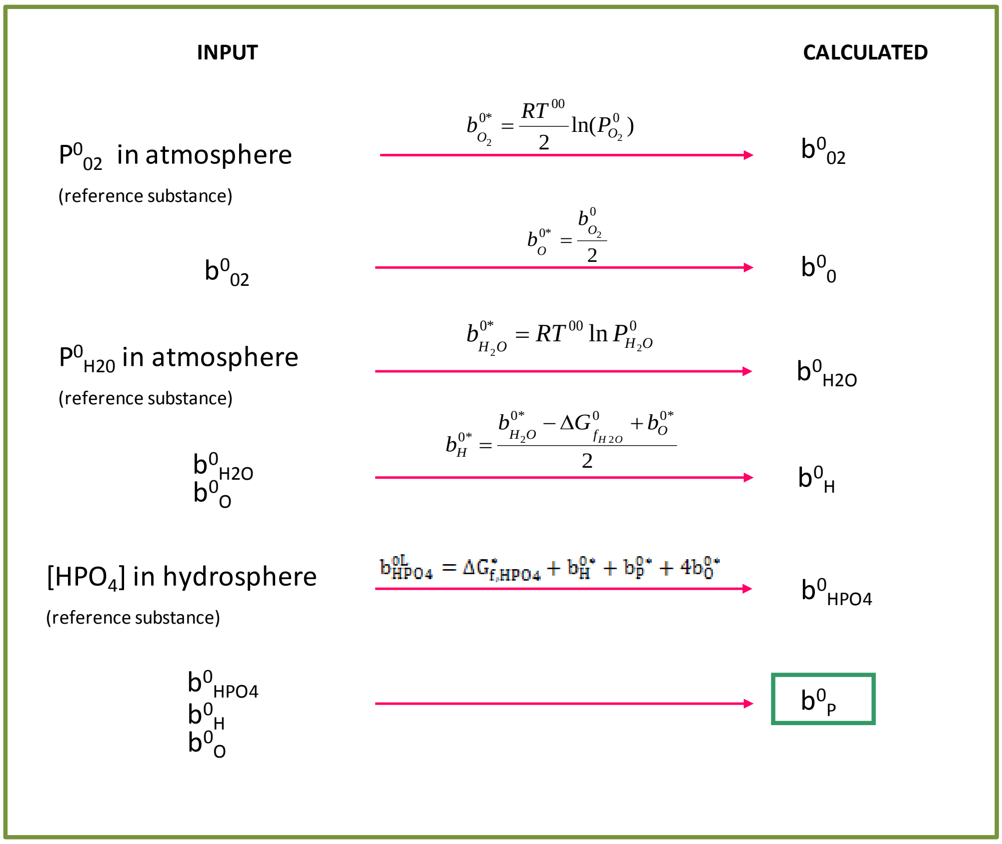


Figure 2.14. An example for chemical exergy calcuation

This example highlights the complexity of calculation of standard chemical exergy of each element and shows that the chemical exergy of chemical elements are strongly interconnected. The sequence formerly explained needs to be done for each chemical element and starting from the mean concentration of several reference substances. Figure 2.15 illustrates the sequence for the calculation of standard chemical exergy of elements, according to the different mediums (i.e. atmosphere, hydrosphere or lithosphere) in which the reference species is found. It can be seen that the standard chemical exergy of most of the elements depends on the standard chemical exergy of oxygen and hydrogen. Besides, the standard chemical exergy values of fluorine and magnesium are the most dependent on the chemical exergy of other elements. Due to the fact that the elements calcium, iron and silicon, are contained in the reference species of elements fluorine, cobalt, aluminum, beryllium, magnesium and zirconium, the standard chemical exergy of those should be calculated before the one of these.

From this strong dependency it might be concluded that if chemical exergy of one element in another temperature and pressure than the standard ones are needed, all of this calculation should be redone. This means that changes in temperature and pressure needs new standard table. As this is quite a cumbersome task, in our work we have decided to prohibit the change of reference temperature, pressure and composition for chemical exergy.

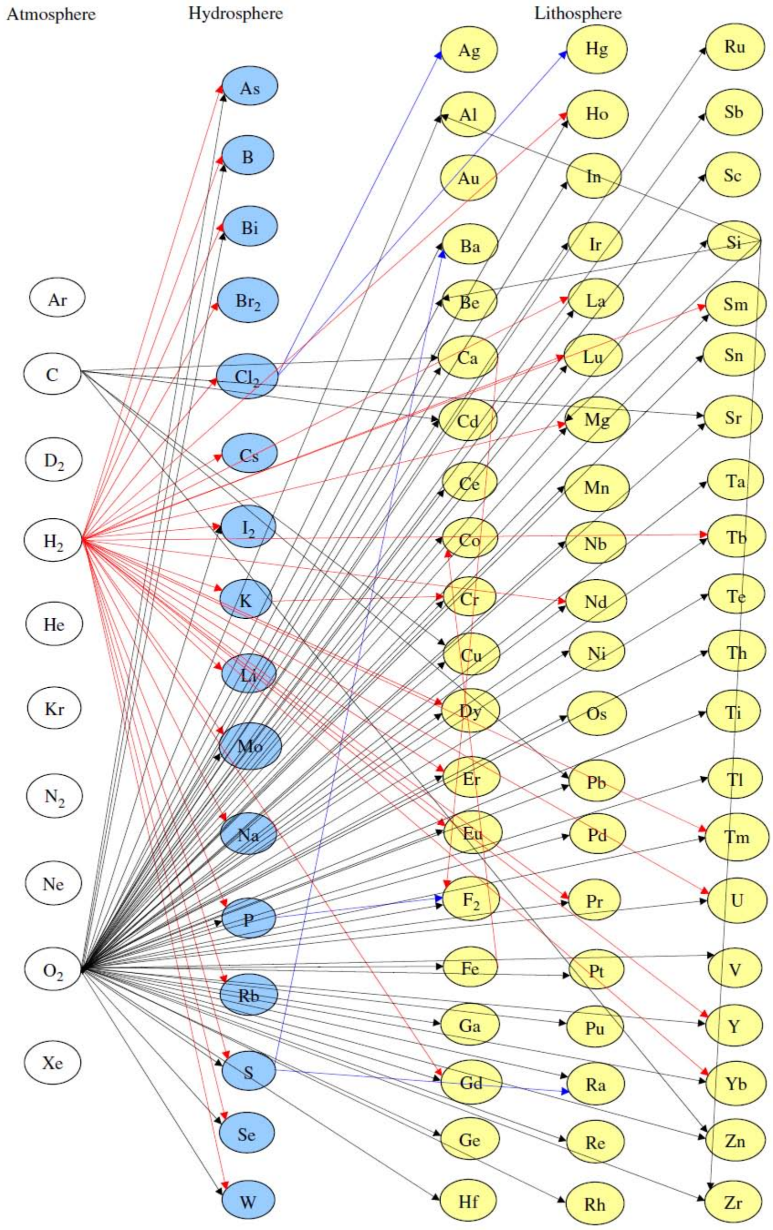


Figure 2.15. Route for the standard chemical exergy calculation of elements (Rivero & Garfias 2006)

2.2.3.4 Chemical exergy and heating value

Specific chemical exergy is an important fuel property in exergy analysis and performance optimization of energy conversion systems. The common basis for calculating efficiencies of power processes is to use the lower heating value (LHV). However, the LHV is not the same as the chemical exergy and should therefore not be used in exergy calculations (Aspelund & Gundersen 2009). To estimate specific chemical exergy of fuels, some correlations have been proposed.

A constant ratio of chemical exergy to calorific value for solid and (separately) liquid fuels, is proposed (Rant 1961). However, the calculation for different organic substances showed the ratio depends significantly on the chemical composition (Szargut & Styrylska 1964). Rant's correlations by taking the chemical composition of fuels into account using statistical method, is corrected (Szargut & Styrylska 1964).

Although Szargut and Styrylska's correlations have been commonly used for evaluation of chemical exergy of fuels in previous works (Feng et al. 2004; Prins et al. 2007; Panopoulos et al. 2006), there are some drawbacks. Firstly, the correlations do not involve the effect of nitrogen on liquid fuels and sulfur on solid fuels, respectively, because of the lack of relevant thermodynamic data. Secondly, the states of some organic compounds had been mistaken in Szargut's source data (Szargut et al. 1988) according to the new edition of handbook of organic chemistry (Gokel 2004). Finally, the correlations are limited to Szargut's reference environmental (R.E.) model theoretically.

To overcome these limitations, recently a unified simple correlation for estimating specific chemical exergy of solid and liquid fuels on dry basis, is developed (Song et al. 2012). In this method, the specific chemical exergy of a dry fuel was split into two contributions: chemical exergies of organic matter and inorganic matter, respectively. To estimate chemical exergy of organic matter, a correlation for estimating standard entropy of organic matter of solid and liquid fuels was derived. A system of linear equations for estimating the numbers of moles of selected inorganic compounds from ash analysis data was established for estimating chemical exergy of inorganic matter.

2.3 CONCLUSION

In this chapter, a set of equations is developed to calculate exergy for the two major contributions of exergy of a material stream (i.e. the physical and chemical exergies). In order to calculate the chemical exergy, after reviewing the all existing reference environment models, the most recently updated reference-substance model has been chosen to model the natural environment as a reference environment. Then, general formulations of both physical and chemical exergy for any material stream are given. These equations are general and independent of equation of state. It means that these equations can be implemented in any process simulator. The new general formulations pave the way for exergy analysis as it will be shown in next chapters. For example, the new definitions such as the maximal thermal and mechanical contribution of physical exergy will be useful in the exergy analysis. These points will be discussed in detail in Chapter 3 and will be applied to an academic case study in Chapter 5.

CHAPTER 3

Exergy Balance and Exergy Analysis

3.1 EXERGY BALANCE: BASIC CONCEPTS

According to Tsatsaronis (1993), "*the second law of thermodynamics complements and enhances the energy balance by enabling evaluation of both the thermodynamic value of an energy carrier, and the real thermodynamic inefficiencies and losses of processes or systems*". In this section, the second part of this postulate will be demonstrated by introducing the exergy balances formulations and proposing hints for its interpretation.

3.1.1 General formulation of an exergy balance

As explained in the beginning of Chapter 2, an exergy balance relies on the decomposition of input and output streams in material, work and heat streams. Moreover, output streams can be also split into waste streams and useful ones. Waste streams include all streams rejected to the environment without being recycled or reused whereas useful streams are material, heat or work streams used in a downstream process.

Contrary to energy balances which are directly deduced from the first law of thermodynamics, exergy balances are deduced from a combined formulation of the first and the second laws of thermodynamics. The generic system studied through exergy balances is illustrated in Figure 3.1. In this system that can either represent a single unit operation, a global process or a part of a process, inputs (material, heat and work) are transformed into outputs (material, heat and work) by thermal and chemical operations.

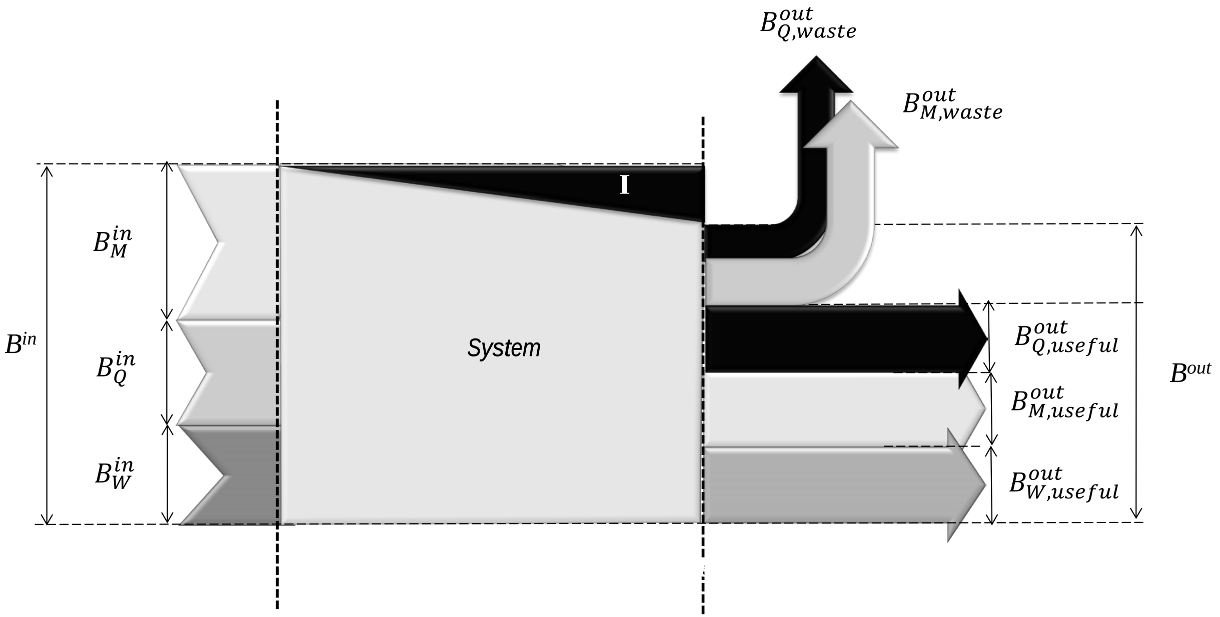


Figure 3.1. A General Grassmann representation of a process or system

As stated in Eq. (3.1), energy balance deduced from the first law of thermodynamics can be written as follows:

$$H_M^{in} + Q^{in} + W^{in} = H_M^{out} + Q^{out} + W^{out} \tag{3.1}$$

As illustrated in Figure 3.1, exergy balance includes another term I, usually called “*internal exergy loss*», corresponding to the exergy destroyed inside the system because of irreversibilities of the process:

$$B^{in} = B^{out} + I \tag{3.2}$$

In this equation, total exergy input B^{in} and total exergy output B^{out} are respectively given by the sum of input and output exergies associated with material (NS_M streams), work (NS_W streams) and heat streams (NS_Q streams):

$$B^{\mathrm{in}} = \sum_{i=1}^{NS_M^{in}} B_{\mathrm{M,i}}^{\mathrm{in}} + \sum_{i=1}^{NS_Q^{in}} B_{Q,i}^{in} + \sum_{i=1}^{NS_W^{in}} B_{W,i}^{in} \tag{3.3}$$

$$B^{\mathrm{out}} = \sum_{i=1}^{NS_M^{out}} B_{\mathrm{M,i}}^{\mathrm{out}} + \sum_{i=1}^{NS_Q^{out}} B_{Q,i}^{out} + \sum_{i=1}^{NS_W^{out}} B_{W,i}^{out} \tag{3.4}$$

In these equations:

- $B_{Q,i}^{in}$ refers to the exergy of the ith input heat streams also called **utility heat stream,**
- $B_{Q,i}^{out}$ refers to the exergy of the ith output heat stream,
- $B_{W,i}^{in}$ and $B_{W,i}^{out}$ respectively refer to exergy of ith input and output work streams.
- In addition, $B_{\mathrm{M,i}}^{\mathrm{in}}$ and $B_{\mathrm{M,i}}^{\mathrm{out}}$ correspond to the exergy of the i-th material stream at the inlet and outlet, respectively.

Using the “*useful/waste*” concept, Eq. (3.2) can also be written as follows:

$$B^{in} = B_{useful}^{out} + \underline{B_{waste}^{out}} + I \tag{3.5}$$

where underlined term is called “*external exergy loss*”. The terms corresponding to “internal exergy loss” and “external exergy loss” will be discussed in detail in the next sections.

Assuming that the exergy flow corresponding to work output is always useful exergy, the exergy balance can finally be expressed as follows:

$$\sum_{\mathrm{i}=1}^{NS_M^{in}} B_{\mathrm{M,i}}^{\mathrm{in}} + \sum_{i=1}^{NS_Q^{in}} B_{Q,i}^{in} + \sum_{i=1}^{NS_W^{in}} B_{W,i}^{in} = \sum_{i=1}^{NS_{M,useful}^{out}} B_{\mathrm{M,useful,i}}^{\mathrm{out}} + \sum_{\mathrm{i}=1}^{NS_{M,waste}^{out}} B_{\mathrm{M,waste,i}}^{\mathrm{out}} + \sum_{\mathrm{i}=1}^{NS_{Q,useful}^{out}} B_{Q,useful,i}^{out} + \sum_{\mathrm{i}=1}^{NS_{Q,waste}^{out}} B_{Q,waste,i}^{out} + \sum_{\mathrm{i}=1}^{NS_W^{out}} B_{W,i}^{out} + I \tag{3.6}$$

To establish exergy balances on a given system (representing an unit operation, a set of unit operations or a global process), one needs to evaluate all the terms of this equation:

- First, the term B_M^{in} is deduced from equations established in the Chapter 2 for exergy of material streams,
- To evaluate the terms $B_{M,useful}^{out}$ and $B_{M,waste}^{out}$ which are also exergies of material streams, one needs to distinguish waste material streams from useful ones; this classification will have to be suggested by the engineer according to his knowledge of the process.
- Finally, it will also be necessary to evaluate the exergy flows related to heat and work streams and to precisely distinguish utilities, waste and useful heat streams. These points will also be discussed in the next sections.

3.1.2 Exergy of work streams

Exergy is defined as the equivalent work of a given energy form. Consequently, shaft-work (either mechanical or electrical work) is equivalent to exergy (Dinçer & Rosen 2007).

$$B_W = W \tag{3.7}$$

3.1.3 Exergy of heat streams

3.1.3.1 General definition

The exergy of a heat stream is determined by the maximum work that could be obtained from it, using the environment as a reservoir of zero-grade thermal energy. To transform this heat stream, one must consider a Carnot Heat engine operating between the temperature T of the heat stream and the temperature T^{00} of the environment. Two situations must be considered: the case of an “above-ambient stream” and the case of a “sub-ambient” stream.

- Case of a “above-ambient” stream (see Figure 3.2)

The first case concerns a heat stream whose temperature is higher than the environment temperature. For the specified control surface of the Carnot cycle shown in Figure 3.2, first and second laws of thermodynamics respectively result in Eqs. (3.8) and (3.9). To obtain the right values and to be independent of the thermodynamic convention, the absolute values are used in these equations.

$$Q \ - W - Q^{00} = 0 \tag{3.8}$$

$$\frac{Q}{T} - \frac{Q^{00}}{T^{00}} = 0 \tag{3.9}$$

Combining Eqs. (3.8) and (3.9), we finally obtain:

$$B_{Q,sur} = W = Q\left(1 - \frac{T^{00}}{T}\right) \tag{3.10}$$

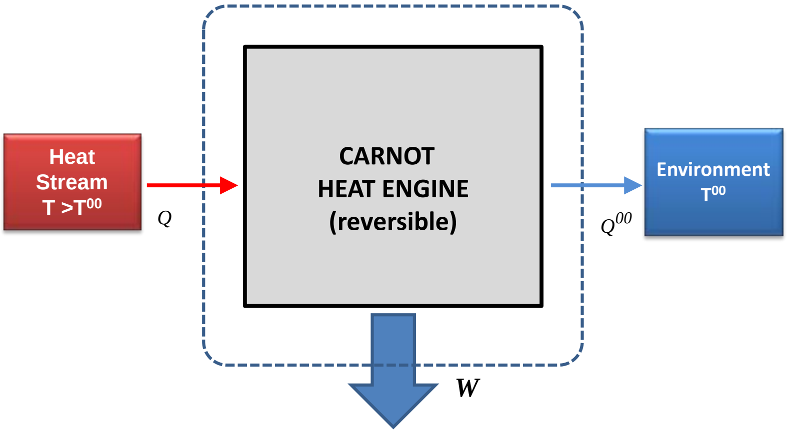


Figure 3.2. Carnot cycle for an "above-ambient" temperature

- Case of a "sub-ambient" stream (see Figure 3.3)

For "*sub-ambient*" heat streams the Carnot heat engine can be represented as illustrated in Figure 3.3.

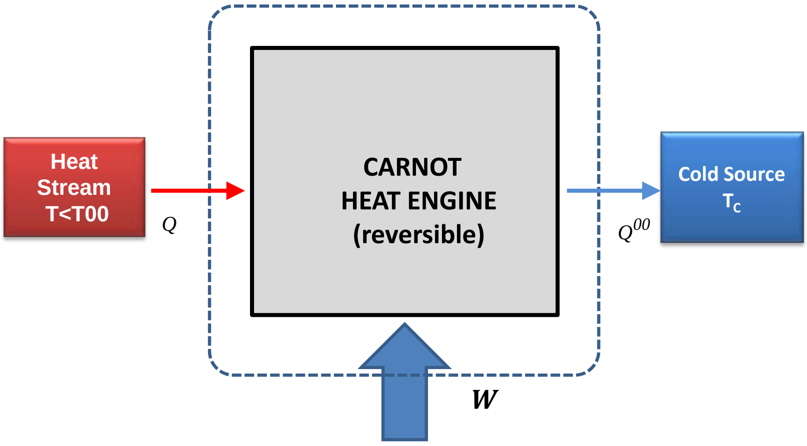


Figure 3.3. Carnot cycle for a "sub-ambient" temperature

In that situation, we can write:

$$Q \ + W - Q^{00} = 0 \qquad (3.11)$$

$$\frac{Q}{T} - \frac{Q^{00}}{T^{00}} = 0 \qquad (3.12)$$

Here, combining Eqs. (3.11) and (3.12) leads to the following formulation:

$$W = Q\left(\frac{T^{00}}{T} - 1\right) \qquad (3.13)$$

According to the definition, the exergy of a heat stream is the maximum work that could be obtained from it, using the environment as a reservoir of zero-grade thermal energy, for “sub-ambient” heat streams, the exergy is of opposite sign compared to heat flux. Consequently, we have:

$$B_{Q,sub} = -W = Q\left(1 - \frac{T^{00}}{T}\right) \qquad (3.14)$$

> *As a consequence, the exergy of a heat flux can be defined by a single formula whatever the temperature of this flux, and given by Eq. (3.15).*
>
> $$B_Q = Q\left(1 - \frac{T^{00}}{T}\right) \qquad (3.15)$$
>
> *In this equation, it is important to note that the exergy flux is defined by an algebraic value which can be positive when considering an input flux and negative when considering an output flux.*

The major difficulty in Eq. (3.15) relies on the determination of the temperature T of the hot source. Let’s illustrate this postulate by considering the two heat exchange situations illustrated in Figure 3.4.

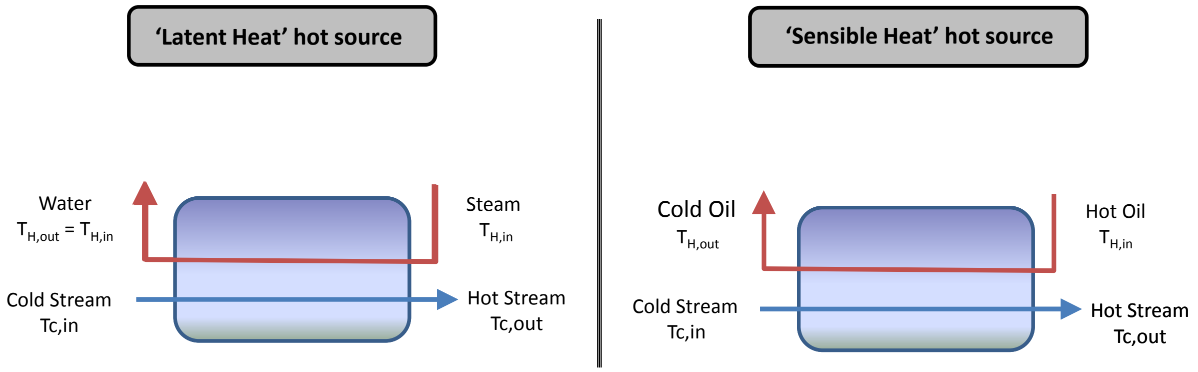


Figure 3.4. Latent heat and sensible heat hot sources

- In the first case, the hot source is a '*latent heat*' source; the temperature of the hot source is the same all along the exchanger. In that case, $T = T_H = T_H^{in}$.
- On the other hand, in the second case, the hot source is a '*sensible heat*' utility. In this situation, the evaluation of the exergy for such a heat stream is not as easy as claimed by some references (Kotas 1985): is T equal to T_H^{in}, T_H^{out} or a mean value ?

Actually, two cases must be distinguished:

- The "*design case"* corresponds to the exergy analysis of a future process; in this situation, some details of the process or of the part of the process – such as technological choices, kind of required utilities or heat integration schemes –are not yet under examination. To handle such situation, B_Q term will be evaluated assuming reversible heat exchanges.
- The "*retrofitting case*", where exergy analysis intends to evaluate and optimize the exergy efficiency of current processes. In this situation, technological choices and utilities used in different part of the process and heat exchanger networks are perfectly defined. As we will see in the following sections, in this situation, B_Q terms will disappear and will be replaced by B_M terms.

3.1.3.2 "Design case": Evaluation of the B_Q terms

- *Evaluation of the thermodynamic average temperature*

When designing a new process, the most adequate utility is not always known for each heat exchange. In this situation, a solution would consist in considering a thermodynamic average temperature ($\overline{T}$) (Tsatsaronis 1993). This temperature corresponds to the temperature of the utility assuming a reversible heat exchange with the process stream. The evaluation of this thermodynamic average temperature for hot and cold utilities is illustrated in Figure 3.5. Note that in this figure *Q* is an algebraic term that can be positive or negative. Combining first and second laws of thermodynamics on the balance region and assuming a reversible process, we obtain:

$$H_p^{out} - H_p^{in} - Q = 0 \tag{3.16}$$

$$S_p^{out} - S_p^{in} - \frac{Q}{\overline{T}} = 0 \tag{3.17}$$

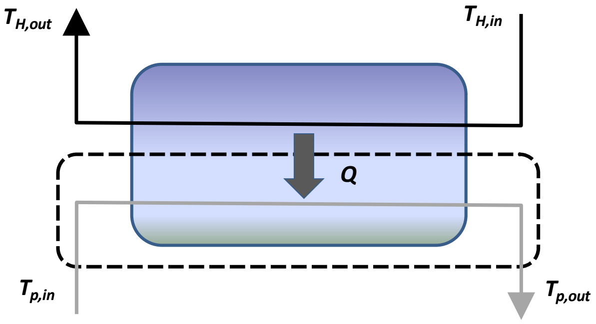


Figure 3.5. Evaluation of the thermodynamic average temperature of a "hot source"

Substituting Eq. (3.16) in Eq. (3.17), $\overline{T}$ can then be evaluated:

$$\overline{T} = \frac{H_P^{out} - H_P^{in}}{S_P^{out} - S_P^{in}} \tag{3.18}$$

As we can see, the "*thermodynamic average temperature*" defined by Eq. (3.18), is expressed as a function of the enthalpy and entropy flows of input and output process streams.

> *When performing an exergy analysis for a new process ("design case"), the heat transfers and other phenomena concerning the process streams are assumed to operate under reversible conditions, then generating no irreversibility. This approach, via enthalpy and entropy calculations, provides the engineer with some hint prior to detailed design of utility system. As a consequence, in the "design case" and compared to the original form, the Grassmann diagram does not display irreversibility I anymore.*

For a heater, the resulting thermodynamic average temperature corresponds to the minimum temperature required to drive the heat transfer. For a cooler, the same calculation can result in the maximum required temperature

❖ *Classification of heat streams exergies: utility, waste output or useful output*

To classify heat streams according to their role in the studied process, one needs to determine the sign of B_Q (Eq. 3.11); let's consider different situations illustrated in Figure 3.6.

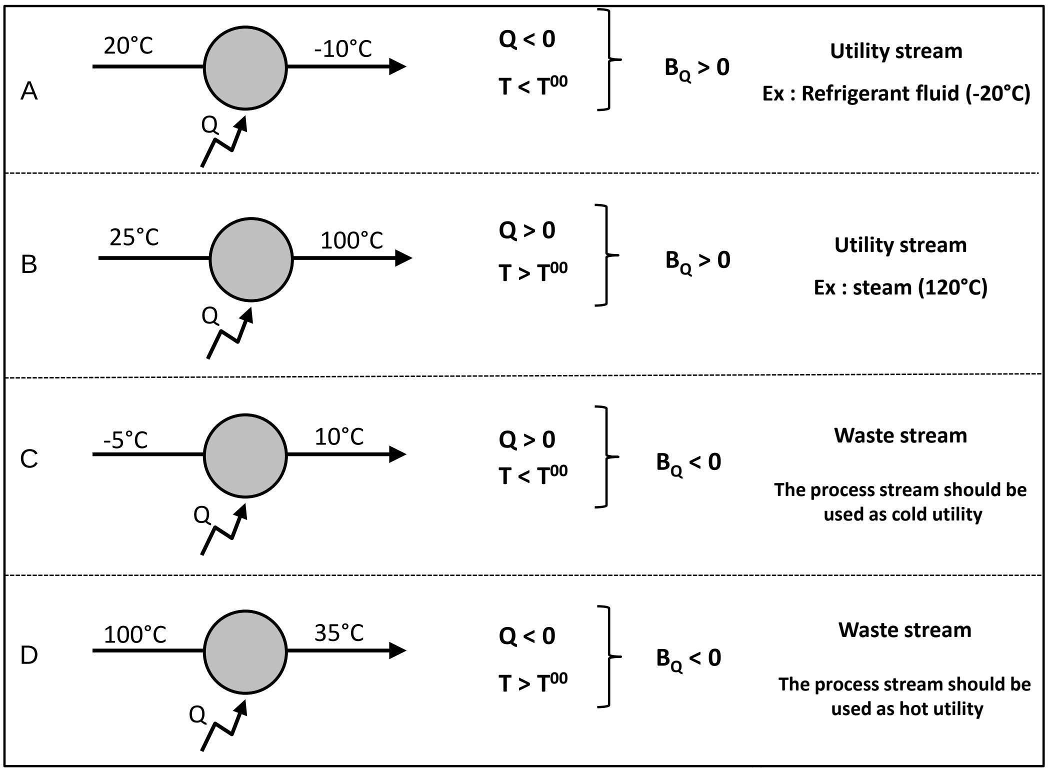


Figure 3.6. Utility vs output waste streams (here T^{00}*=25°C)*

The sign of B_Q determines the role of the heat stream. In Figure 3.6, case A and B respectively refer to cold and hot utilities consumed by the process; the exergy of these heat fluxes appear in B_Q^{in} terms. On the other hand, case C and D refer to waste streams. Case C concerns a situation where a sub-ambient process stream is wasted instead of being used in other part of the process as cold utility, whereas case D represents a situation where a process stream releases above-ambient heat that should be recycled in another part of the process as hot utility. In Figure 3.6, for the output heat streams (case C and D), as the recycling process of heat streams is not specified, these heat streams are systematically classified as waste heat streams. The exergy of these heat fluxes appears in $B_{Q,waste}^{out}$ term.

> *Instead of “waste stream” term usually found in the literature, we would prefer the term “recoverable stream” which refers to a stream that could be recycled in another part of the process to improve its performances.*

❖ *Conclusion: Grassmann diagram in the “design case’*

For new processes or part of processes, the resulting Grassmann diagram to be considered is represented in Figure 3.7.

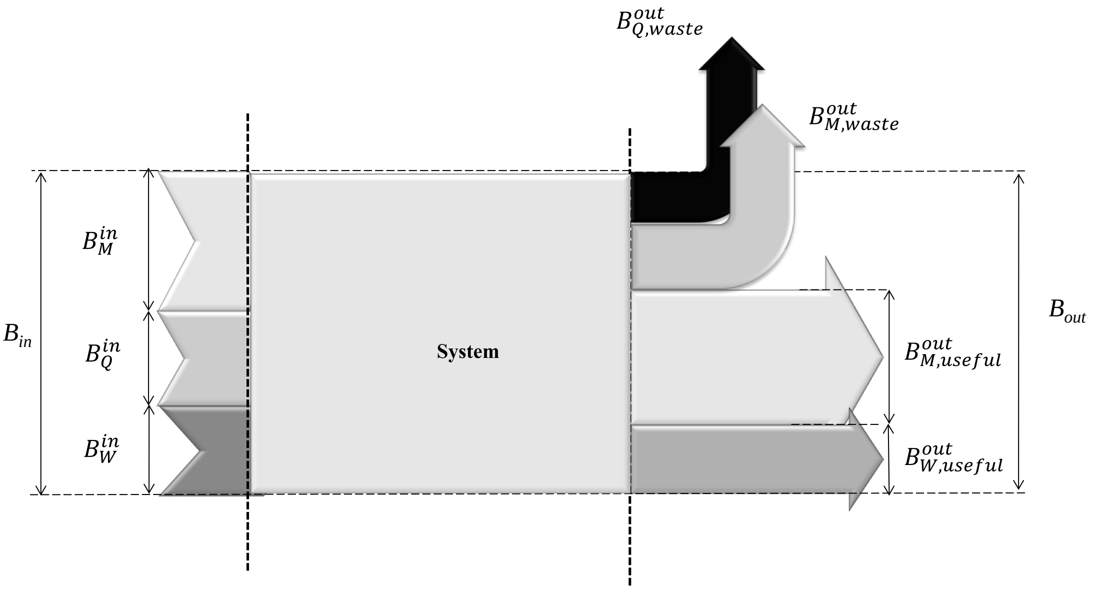


Figure 3.7. "Design case" Grassmann diagram

Furthermore, the hot streams are classified as described hereunder.

__Classification of heat streams:__

Given a heat stream i

- *If $B_{Q,i} > 0$, the heat stream is a utility stream. The term $B_{Q,i}$ must be included in* $B_{Q,}^{in} i$
- *If $B_{Q,i} < 0$, the heat stream is a waste heat stream. The term $B_{Q,i}$ must be included in* $B_{Q,waste,i}^{out}$
- *The term* $B_{Q,useful,i}^{out}$ *does not correspond to any physical situation. It can be removed from the Eq.(3.2).*

The general exergy balance equation can finally be written as follows:

$$\sum_{i=1}^{NS_M^{in}} B_{M,i}^{in} + \sum_{i=1}^{NS_Q^{in}} B_{Q,i}^{in} + \sum_{i=1}^{NS_W^{in}} B_{W,i}^{in} = \sum_{i=1}^{NS_{M,useful}^{out}} B_{M,useful,i}^{out} + \sum_{i=1}^{NS_{M,waste}^{out}} B_{M,waste,}^{out} i + \sum_{i=1}^{NS_{Q,waste}^{out}} B_{Q,waste,i}^{out} + \sum_{i=1}^{NS_W^{out}} B_{W,i}^{out} + I \qquad (3.19)$$

3.1.3.3 "Retrofitting case"

In the retrofitting situation, the external utilities located in the process are perfectly known. In this case, instead of modeling utilities as a set of heat flux, it would be preferable to represent all the utilities as a set of material flux. As an example, the equivalence between useful heat streams and input/output material streams for the case D formerly described is illustrated in Figure 3.6.

Here, the useful heat stream is recycled to heat another stream from 50°C up to 80°C. For exergy analysis, the configuration of Figure 3.8a must be replaced by the process represented in Figure 3.8b.

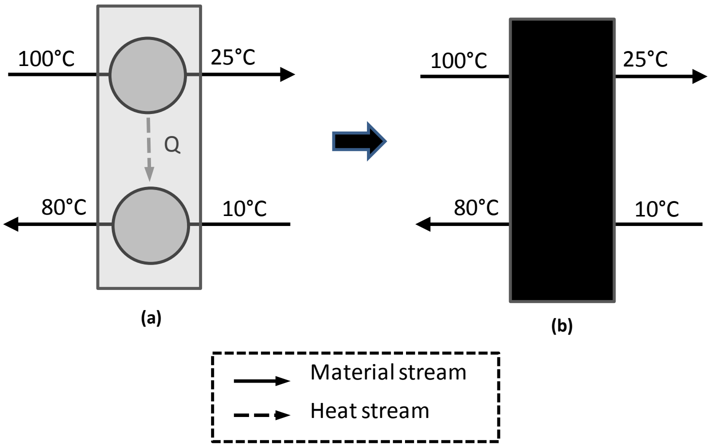


Figure 3.8. Equivalence between useful heat stream and input/output material streams

> *When retrofitting an existing process, the utility streams must be included in the set of material streams of the considered exergy balance region. In this case, as illustrated in Figure 3.9 the Grassmann diagram should not include any heat stream anymore.*

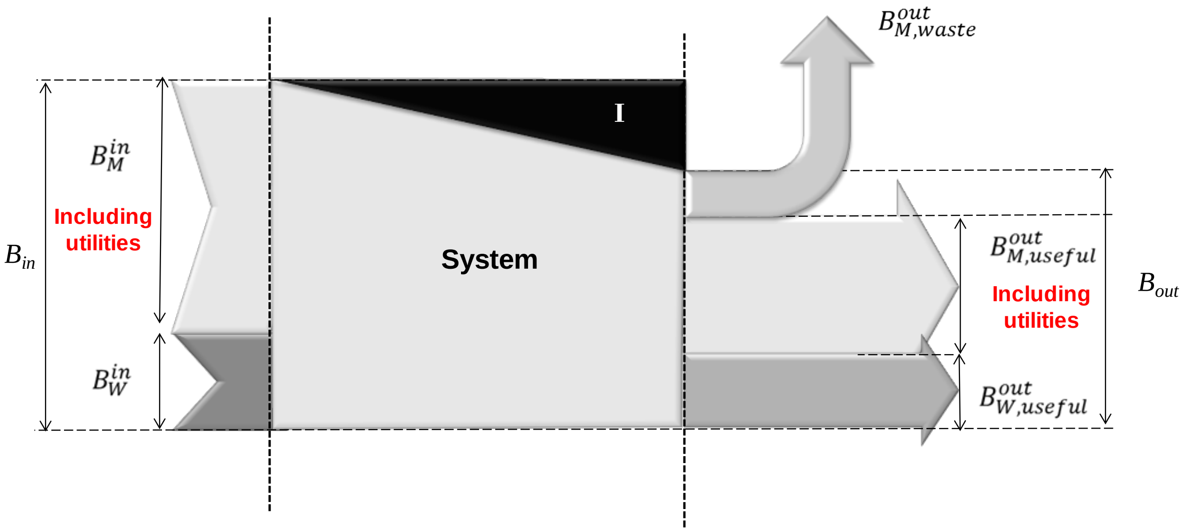


Figure 3.9. Grassmann diagrams considered in the retrofitting situation

3.2 INTERPRETATION OF EXERGY BALANCES

As highlighted previously, due to the introduction of second law of thermodynamics, the exergy balance is much more informative than the energy balance. In this section, some hints for the interpretation of exergy balances are given. More precisely, the principal reasons and improvements ways for irreversibilities and external losses are proposed.

3.2.1 Internal exergy loss

- Internal exergy losses, also called “irreversibility” or “exergy destruction” (Tsatsaronis 1993), is deduced from the entropy generation and depends on the environment temperature. According to the second law of thermodynamics (e.g. Eq. 2.2), irreversibility is always positive and is induced by the thermodynamic imperfection of process operations. According to Le Goff (1979), the irreversibility phenomena fall in three types:
- ***Non-homogeneities***: caused by mixing of two or more components with different temperature (T), pressure (P) or concentration ($\boldsymbol{z}$).
- ***Dissipative processes:*** due to mechanical frictions and pressure drop.
- ***Chemical reactions:*** the entropy generated in chemical reactors is proportional to the progress of the reaction and the affinity of the reaction itself defined using the stoichiometric coefficients and the chemical potentials

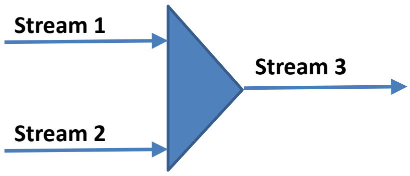
Each phenomenon will be described and illustrated in the following sections.

3.2.1.1 Non homogeneities

Non-homogeneities happen when substances are put into contact with each other. The most common unit operation where indirect contact occurs is heat exchanger. For direct contact, mixing is the most common process in thermal and chemical plants, for example open-type feed heater (a direct-contact heat exchanger in which extracted steam is allowed to mix with the feedwater), steam ejector, distillation column, etc. In a general mixing process, the irreversibilities are due to:

- Viscous dissipation during mixing which results in a pressure drop between the inlets, which are not in mechanical equilibrium.
- Heat transfer with finite temperature gradients between inlets, which are not in thermal equilibrium.
- Process of intermingling molecule of different species through molecular diffusion. A measure of this contribution to the process irreversibility is the work necessary (in a reversible process) to undo the mixing process, in other words, to separate the resultant components.

> *EXAMPLE: MIXING PROCESS*
>
> *Consider a steady-flow mixing process involving two streams of* CO_2 *at 100°C and 5atm and at 150°C and 15atm to be mixed and be sent to the storage as shown in Figure 3.10.*



Streams		Stream 1	Stream 2	Stream 3
Total flow	kg/s	0.03	0.14	0.17
Temperature	°C	100.00	150.00	141.81
Pressure	atm	5	15	5

Figure 3.10. A mixer

Physical exergy of a given material stream can be calculated from equations given in Chapter 2:

$$b^{ph} = \left[h(T,P,\mathbf{z}) - h(T^{00},P^{00},\mathbf{z})\right] - T^{00}\left[s(T,P,\mathbf{z}) - s(T^{00},P^{00},\mathbf{z})\right] \tag{3.20}$$

Assuming that the stream gas considered in this example behave like a perfect gas, we obtain

$$b^{ph} = c_P\left(T - T^{00}\right) - T^{00}\left(c_P \ln\frac{T}{T^{00}} - R\ln\frac{P}{P^{00}}\right) \tag{3.21}$$

Moreover, as explained earlier in Chapter 2, molar chemical exergy for the pure chemical reference substance such as CO_2 is available in the standard tables, calculated from partial pressure in atmosphere:

$$b^{0*}_{CO_2} = RT^{00}\ln\left(\frac{P^{0}_{CO_2}}{P^{00}}\right) \tag{3.22}$$

Table 3.1 reports the chemical and physical exergy of all the streams at the inlet and outlet.

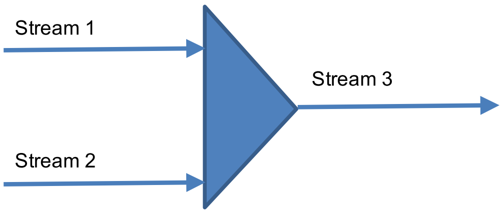
Table 3.1. Exergy of streams

Material Stream	*Stream 1*	*Stream 2*	*Stream 3*
Total Exergy Flow (kW)	*15.20*	*86.28*	*92.85*
Chemical Exergy Flow (kW)	*12.50*	*62.54*	*75.05*
Physical Exergy Flow (kW)	*2.69*	*23.73*	*17.79*

The difference between total exergy input and output results in irreversibility:

$$I = B^{in}_{stream\ 1} + B^{in}_{stream\ 2} - B^{out}_{stream\ 3} = 8.63\ \ kW \tag{3.23}$$

To reduce, exergy losses, these two streams have to be mixed as close as possible in terms of temperature and pressure. Let us take the mixer shown in Figure 3.11 where these two inlet streams are mixer at 5 atm.



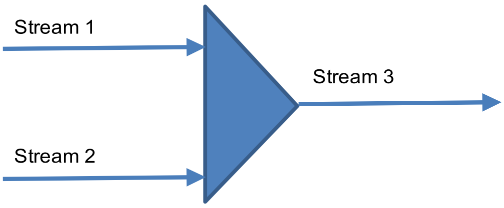
Streams		Stream 1	Stream 2	Stream 3
Total flow	kg/s	0.03	0.14	0.17
Temperature	°C	100.00	150.00	141.81
Pressure	atm	5	5	5

Figure 3.11. An isobar and non-isothermal mixer

Likewise the difference between total exergy input and output results in irreversibility:

$$I = B_{stream\,1}^{in} + B_{stream\,2}^{in} - B_{stream\,3}^{out} = 0.05 \;\; kW \tag{3.24}$$

Now, let us take the mixer shown in Figure 3.12 where these two inlet streams are mixed isothermally at 100°C.



Streams		Stream 1	Stream 2	Stream 3
Total flow	kg/s	0.03	0.14	0.17
Temperature	°C	100.00	100.00	100.00
Pressure	atm	5	15	5

Figure 3.12. Isothermal, non-isobar mixer

Likewise the difference between total exergy input and output results in irreversibility:

$$I = B_{stream\,1}^{in} + B_{stream\,2}^{in} - B_{stream\,3}^{out} = 8.59 \;\; kW \tag{3.25}$$

From comparison of these three cases, it can be concluded that the contribution of temperature and pressure in exergy loss does not have the same order of magnitude. For example, the isothermal, non-isobar mixer results in relative high exergy losses while the isobar, non-isothermal mixer causes a relative negligible exergy loss comparing the exergy input and output. By definitions given in Chapter 2, the higher exergy, the greater will be the potential for recuperations. When two streams with the same pressure are mixed together, the less work potential will be destroyed compared to the case where two streams with the same temperature are mixed.

3.2.1.2 Dissipative effect

Irreversibility of a process can be due to dissipative effects. In this case, the work performed on a system increases the molecular internal energy of the system (i.e. low grade energy). In other words, high grade energy (work) is transformed to low grade energy (internal energy). Consequently, this effect increases the temperature of the system. Dissipative effect may be due to viscosity, friction, inelasticity, electric resistance (Venkanna 2010).

EXAMPLE: COMPRESSION PROCESS

As an example, let us suppose the compression of a gas in a vessel(Pierre Le Goff 1979). There is a difference between the pressure outside the piston and the internal forces applied by the gas that corresponds to the force of friction. For a displacement Δl of the piston, there is heat release due to a work of f.Δl which results in entropy generation:

$$S_{gen} = \frac{Q}{T} = \frac{W_{\text{degraded}}}{T} = \frac{f.\Delta l}{T} \tag{3.26}$$

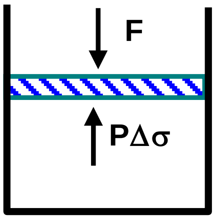


Figure 3.13. Mechanical friction

3.2.1.3 Chemical reaction

The entropy generated in chemical reactors is proportional to the progress of the reaction and the affinity of the reaction itself defined using the stoichiometric coefficients and the chemical potentials (Pierre Le Goff 1979). Entropy generated during chemical reaction will be given by:

$$\delta S_{gen} = \frac{A}{T} d\xi \tag{3.27}$$

where A is the affinity of reaction, ξ is the progress of reaction, ν is the stoichiometric coefficients and R is the chemical components.

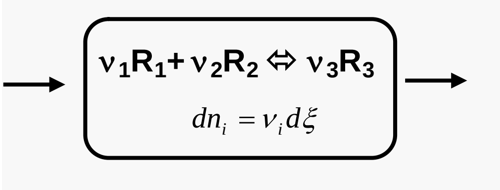


Figure 3.14. Chemical reaction

It can be shown that the entropy generation is zero at the chemical equilibrium. For certain values of pressure, temperature and concentration of products and reactants, A can be zero which corresponds to the reaction when it is on the equilibrium. When A is not zero, then the system is not in a chemical equilibrium; therefore, there will be entropy generation.

> *EXAMPLE: ESTERIFICATION REACTION*
>
> *Figure 3.15 is model of a reactor where the esterification is occurring. Esters are produced when carboxylic acids are heated with alcohols. The esterification reaction is slow, on equilibrium and quasi athermic. The equation for the reaction between an acetic acid and ethanol to produce ethyl acetate is:*
>
> $$CH_3COOH + CH_3CH_2OH \Leftrightarrow CH_3COOCH_2CH_3 + H_2O \tag{3.28}$$

The control region corresponds to the part of the reactor where the reaction takes place under constant temperature. The reactant consists of equimolar proportion of ethanoic acid and ethanol.

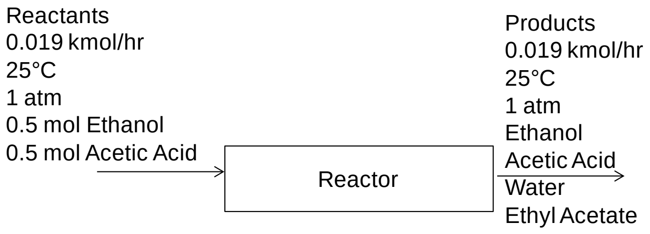


Figure 3.15. Reactor of esterification on vapor phase

To calculate the irreversibility, the exergy balance for this isothermal reactor has to be done.

$$I = B_{\text{Products}} - B_{\text{Reactants}} \tag{3.29}$$

The exergy of reactants and products is calculated by:

$$B^{in}_{\text{Reactant}} = n_{\text{Reactant}}\left(b^{ph}_{\text{Reactant}} + b^{ch}_{\text{Reactant}}\right) \tag{3.30}$$

$$B^{in}_{\text{Products}} = n_{\text{Products}}\left(b^{ph}_{\text{Products}} + b^{ch}_{\text{Products}}\right) \tag{3.31}$$

The molar standard chemical exergy for the reactants and products is calculated from:

$$b^{ch} = \sum_{i=1}^{NC} x_i b^{ch}_i + RT^{00} \sum x_i \ln x_i \tag{3.32}$$

In the case of the conversion of 0.1 for the reactants we have:

$$b^{ch}_{\text{Reactant}} = 1130.63\ kJ/mol \tag{3.33}$$

$$b^{ch}_{\text{Prodcuts}} = 1129.48\ kJ/mol \tag{3.34}$$

Assuming that the reactants and products behave like a perfect gas, their physical exergy can be calculated as follows:

$$b^{ph} = c_P\left(T - T^{00}\right) - T^{00}\left(c_P \ln\frac{T}{T^{00}} - R\ln\frac{P}{P^{00}}\right) \tag{3.35}$$

We obtain:

$$b^{ph}_{\text{Reactant}} = 15.44\ kJ/mol \tag{3.36}$$

$$b^{ph}_{\text{Prodcuts}} = 14.98\ kJ/mol \tag{3.37}$$

Substituting the calculated physical and chemical exergy component:

$$B_{\text{Reactant}} = 6.00 \;\; kW \tag{3.38}$$

$$B_{\text{Products}} = 5.99 \;\; kW \tag{3.39}$$

Substituting the calculated values of physical and chemical exergy:

$$I = 0.01 \, kW \tag{3.40}$$

This exergy loss is relatively small compared total exergy input and outputs. However, the small value of exergy loss is due to low conversion of reactant. Therefore to see the trend of irreversibility along the conversion a sensitivity analysis is performed as reported in Table 3.2. Obviously, the higher conversion, the higher will be the irreversibility.

Table 3.2. Irreversibility vs. conversion

Conversion	Irreversibility (kW)
0.1	*0.0084*
0.3	*0.0204*
0.5	*0.0299*
0.7	*0.0371*
0.9	*0.0416*
1	*0.0510*

3.2.1.4 Assessment of thermodynamic feasibility of processes

The notion of irreversibility can be useful to identify the thermodynamic feasibility of a process. Indeed, if irreversibility is negative, then the process is necessarily thermodynamically impossible.

Unfortunately, the reciprocal is not true! Indeed, a positive exergy balance does not necessarily means that the process is feasible.

To illustrate this, let us consider the simple heat transfer example illustrated in Figure 3.16. According to the exergy balance, the irreversibility of this unit operation is positive and equal to 3.07 kW. However, the hot and cold streams temperature profiles (Figure 3.16) clearly display a heat transfer cross pinch. In other words, although the total exergy loss is positive, the whole process is not feasible.

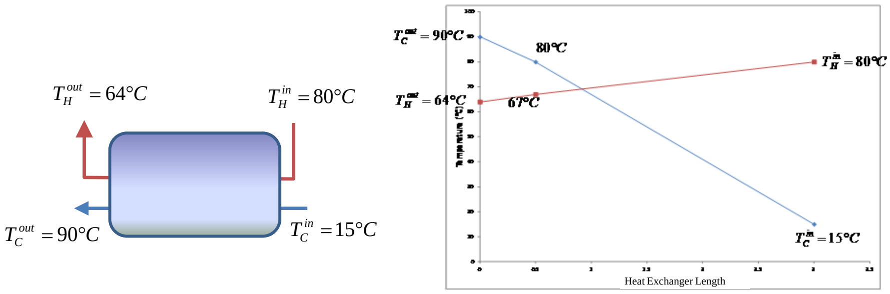


Figure 3.16. An unfeasible heat exchanger

To analyze this result, it is possible to split the heat exchanger in two parts: a "feasible heat transfer" and an "infeasible" part (rest of the heat exchange) as shown in Figure 3.17. For the feasible part, the temperature of cold stream is increased up to a temperature level equal or less than the temperature of hot stream. As the temperature of hot stream at the inlet is 80°C, the temperature of cold stream should be equal or less than 80°C. In this example, the temperature equal to 80°C is taken as the temperature of outlet of feasible part.

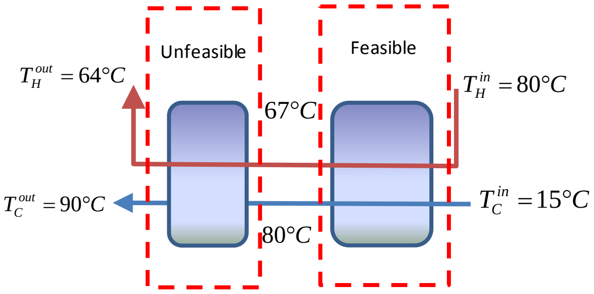


Figure 3.17. A combination of unfeasible and feasible heat exchangers

Like any real process, the "feasible" is accompanied by a degradation of exergy. An exergy balance on this part gives: *I* = 3.45 kW. On the other hand, the infeasible part is accompanied by a generation of exergy: *I* = -0.38 kW.

Moreover, we note that the sum of the irreversibilities of each part is equal to the total irreversibility. In this example, the irreversibility destroyed by the feasible part of the exchange is sufficient to compensate the exergy generated by the infeasible part of the exchange. That is the reason why the total exergy loss is positive, which might result in a misleading interpretation.

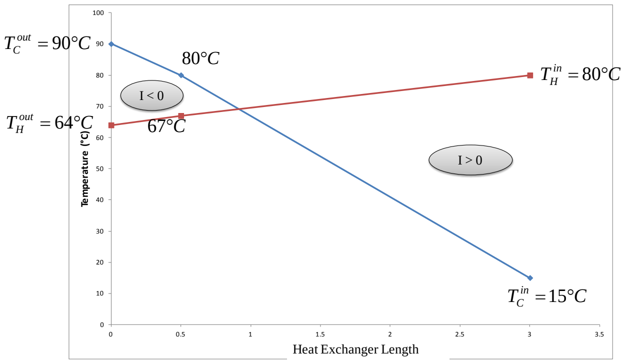


Figure 3.18. Temperature profile for an unfeasible heat exchanger

3.2.1.5 Improvement ways based on the sources of irreversibility

In the former section, the source of irreversibilities have been identified and explained. This section intends to propose the engineer a panel of technological solutions that could help him to reduce each kind of irreversibility.

To construct a preliminary database of solutions, the general commandments enounced by (Leites et al. 2003) have been exploited. Some of the most important commandments are reported as follows:

- *The driving force of a process must approach zero at all points in a reactor, at all times. Try to change the driving force to a uniform one.*
- *If the reaction is exothermic, it is necessary to raise (not to lower!) the temperature. If the reaction is endothermic, it is necessary to lower (not to raise!) the temperature. It is better to conduct the exothermic processes in a low flow-heat-capacity medium. It is better to remove reaction heat by phase change of the cooling medium, or by endothermic reactions, rather than by sensible heating of a cooling medium.*
- *If the reaction is conducted in the gas phase and the volume increases, it is necessary to raise (not to reduce!) the pressure. If the gas volume decreases, it is necessary to reduce (not to increase!) the pressure.*
- *It is not necessary to carry out chemical reactions up to their completion. It is better to recycle the unreacted streams.*
- *Do not mix streams of different temperatures, different compositions, or different pressures. If possible, don’t mix anything!*
- *Remember that the increase in the process rate often leads to an increase in energy resource consumption.*
- *Select the lowest temperature heat sources.*
- *The best chemical reactor is a counter-current one with plug flow.*
- *Investigate the conditions of quasi-static processes to discover methods for reducing energy resource consumption.*
- *The best process is the one in which energy and species enter and leave along the full length of the apparatus.*
- *A chemical process cannot be thermodynamically reversible if it has a stoichiometric excess; however, real processes can operate with minimal exergy expenditures at optimal stoichiometric excesses that are functions of the flowsheet.*

From detailed analysis of the above-mentioned rules and of the numerous publications existing in the literature (Kotas 1985; Szargut et a. 1988; Tarighaleslami et al. 2011; Smith 2005; Nadim 2010; Ray & Sengupta 1996), a table enumerating the major sources of irreversibility and giving us some clues for process improvement on each class of unit operations has been constructed (see Table 3.3).

As can be seen in this table, reduction of internal exergy losses does not necessarily require the modification of the unit operation itself, but can be obtained by simple modifications of the inlet streams characteristics, such as temperature using a preheating. This table is not exhaustive but can be proposed to an engineer as a preliminary database which will be gradually enriched during the analysis of different processes.

Table 3.3. Irreversibility, sources and improvement ways

Unit operation	Sources of irreversibility	Ways of Improvement
Reactor	Low conversion	Recycle the non-converted reactants Improve the conversion
	Exothermic reaction	Raise the temperature Recycle the heat of reaction
	Endothermic reaction	Reduce the temperature
	Temperature difference of cold feed and hot reaction medium	Pre-heat the feed
	Concentration gradients	Increase reaction stages as much as possible ⇨ prefer plug flow reactor
	Mixing of streams	Mixing reactant as uniformly as possible
Distillation column	Concentration gradients	Use intermediate reboiler or condenser Equal partition of driving force
	Improper separation sequence	Optimize distillation sequencing
	Pressure drop and mechanical friction	Optimize the hydraulic of the column
	Bubble-liquid mass transfer on the tray (Ray & Sengupta 1996)	Optimize the hydraulic of the column
	Thermal gradients	Introduce feed in a proper tray (Tarighaleslami et al. 2011) Split feed
Heat exchanger	Temperature difference	Use as low as possible driving force
	Non-uniform gradient	Use an uniform gradient ⇨ prefer counter current heat exchangers
	Pressure drop	Reduce the number of baffles (for shell and tube heat exchanger)
	Low heat transfer	Optimize the flow velocity (Szargut et al. 1988)
Cold utility	Refrigeration	Minimize use of sub-ambient system and replace it with cooling water (Smith 2005)
	Thermal difference	Use as high level as possible
	Use of external utilities	Maximize process steam generation
Throttling valve	Pressure drop	Replace by a steam turbine (for temperatures greater than the ambient)
Steam boiler	A chemical reaction for oxidation of the fuel (Nadim 2010)	Preheat the combustion air
	An internal heat transfer between high temperature product and the unburned reactant (Nadim 2010)	Use as low driving force as possible
	Physical mixing process (Nadim 2010)	Mix as uniform as possible
	Diffusion process where the fuel and oxygen molecules are drawn together (Nadim 2010)	Make as gradually as possible
	High heat capacity of combustion products	Oxygen enrichment (Kotas 1985)
	Isobar combustion	Move toward isochoric combustion (Kotas 1985)
Compressor	Hot inlet streams	Reduce the temperature of inlet streams or between the stages by intercooler
Steam turbine	Low temperature of steam	Use inter-heater (e.g. super-heater) between the stages
Pump	Hydraulic friction	Optimize the hydraulic of system
Mixer	Temperature difference	Mix as Isothermal as possible
	Pressure difference	Mix as Isobar as possible
	Composition difference	Mix as close as possible composition

Note also that the principles enounced in Table 3.3 do not take into account the profitability of the process. Certainly, as mentioned in literature (Leites et al. 2003), trade off between thermodynamic reversibility and capital cost of chemical processes must be found. Thermodynamic reversibility requires that all process driving forces, such as temperature, pressure and chemical potential differences should be zero at all points and times. On the other hand, a reversible chemical process operates at an infinitesimal rate, and requires an infinitely large plant. Furthermore, there is a conventional misconception which says that if we reduce driving force, capital cost will be raised. This is not always true. There are some ways to reduce driving force and capital cost simultaneously. Let us compare the simple examples of heat transfer with non-uniform ΔT driving force (Figure 3.19a), with the one with a uniform driving force (Figure 3.19b).

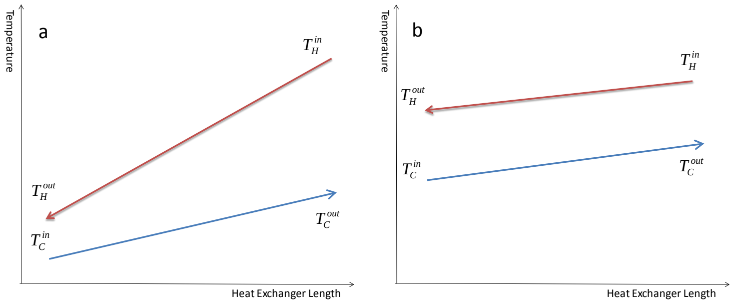


Figure 3.19. Non-uniform temperature profile vs. Uniform temperature profile

In Figure 3.19a, at the left end of the heat exchanger, the driving force is small. It means that the exergy losses are small. However, the heat exchange area must be very large. In Figure 3.19a, at the right end of the heat exchanger, the driving force is large. It means that the exergy loss is also large because it is proportional to the large area between the two temperature profile lines. However, the heat exchange area is small.

In Figure 3.19b, the use of a uniform driving force allows, however, a reduction in exergy losses as well as a reduction of heat exchanger area at the same time.

From this example, it can be concluded that changes in flowsheets that make driving forces more uniform can simultaneously reduce both exergy losses and capital investments (heat transfer area).

Another example is a throttling valve at the inlet of steam heater. In this case, as a result of the throttling of high-pressure steam, the temperature of steam is decreased. It means a decrease of the temperature difference in a heat exchanger happens. This would reduce the exergy loss in the heat exchanger itself. But the throttling process is used to achieve the required temperature and pressure of steam which is extremely irreversible. The result is an unnecessary increase of the required heat transfer area as the driving force between the streams is reduced.

These examples conclude that it is important to analyze the statement that "*the reduction in driving forces is the basis for energy saving methods*", because there are many examples where reduction in driving forces gave the opposite results (Leites et al. 2003). Only an overall system analysis could enable to observe this phenomenon.

3.2.2 External exergy loss

External exergy loss is usually associated with useless material or heat streams released into the environment. For example, a flue gas is emitted from a fired heater at a flame temperature which is much higher than the environment temperature (usually 25°C). If the energy contained in this flue gas is not recycled, the exergy associated with this effluent can be considered as an external exergy loss.

Concerning waste streams, several ways to exploit the exergy associated with them exist (Szargut et al. 1988). For example, if the temperature of the waste heat is high enough, waste heat recovery using heat exchanger networks can be an alternative. However, for the low-grade waste heat (Buchin & Ziegler 2011), heat pump (Roque Di-az et al. 2010) or absorption refrigerator (Bakhtiari et al. 2011) can be installed to exploit the physical exergy. To reduce external exergy losses associated with chemical exergy, combustible waste can be used as a fuel for combustion. Utilization of the non-combustible waste as a secondary raw material is an alternative, to recover the wasted chemical exergy (Szargut et al. 1988). To define the most adequate recycling strategy, the decomposition of exergy into thermal, mechanical and chemical terms, largely described in the Chapter 2, could be a very relevant tool.

Table 3.4 summarizes these solutions by listing the technological solution that should be used to recover the thermal, mechanical or chemical exergy contained in a waste heat flux and material streams. Certainly, this table is not exhaustive and should be enriched all along the studies of various processes.

Table 3.4. Improvement ways for external exergy losses recovery

Nature of exergy loss	Thermal recycling	Mechanical Recycling	Chemical Recycling
Heat stream (design case)			
Waste heat exergy output	- Recovery heat exchanger - Heat pump (Roque Di-az et al. 2010; Meggers & Leibundgut 2011) - Waste heat district heating network(Torío & Schmidt 2010)		
Material stream (design and retrofitting cases)			
Thermal Exergy	- Coupling of absorption-refrigerator with a cogeneration (P. Le Goff & Hornut 1999) - Recovery heat exchanger - Heat pump (Roque Di-az et al. 2010) - Absorption refrigerator (Bakhtiari et al. 2011) - Hot water cooled electronics (Zimmermann et al. 2012)		
Mechanical Exergy		- Turbine (Szargut et al. 1988)	
Chemical Exergy			- Combustible waste as a fuel for combustion (Szargut et al. 1988). - Non-combustible waste as a secondary raw material (Szargut et al. 1988)(M. Sorin et al. 1998)

EXAMPLE: HDA PROCESS

To illustrate these concepts, let us take an example of a reactor represented in Figure 3.20. The reactor feed is heated by the HP steam, whereas the reactor output is cooled by cooling water (CW) and sent to a liquid-vapor separator. The vapor at the outlet of the separator is purged to the environment. The product at the outlet of the separator is sent to the finishing section. An analysis of the external losses of this process will help the engineer to propose improvement solutions. Table 3.5 displays the exergy loss of each unit operation and Figure 3.21 represents the Grassmann diagram of the entire process. Note that the relative high exergy value of total exergy input and output, does not allow seeing clearly the irreversibilities in each unit operation.

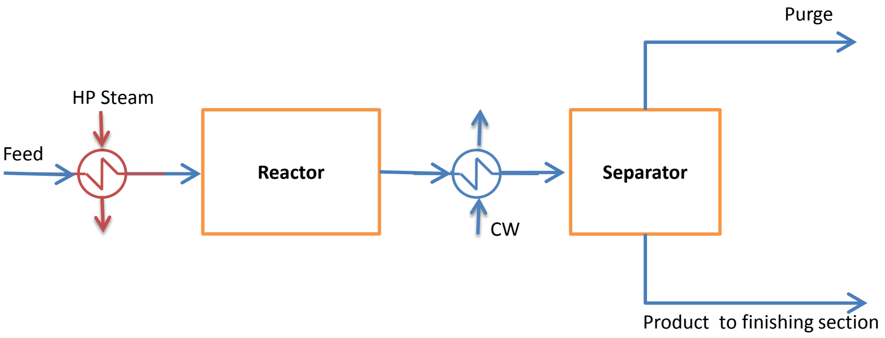


Figure 3.20. The base case

Table 3.5. Exergy losses of unit operations for the base case

Unit Operation	*Reactor*	*Separator*	*Steam Heater*	*CW Cooler*	*TOTAL*
Irreversibility (kW)	*605.64*	*226.14*	*1 455.94*	*1 130.08*	*3 417.80*
External Loss (kW)	*-*	*372 869.02*	*-*	*-*	*372 869.02*

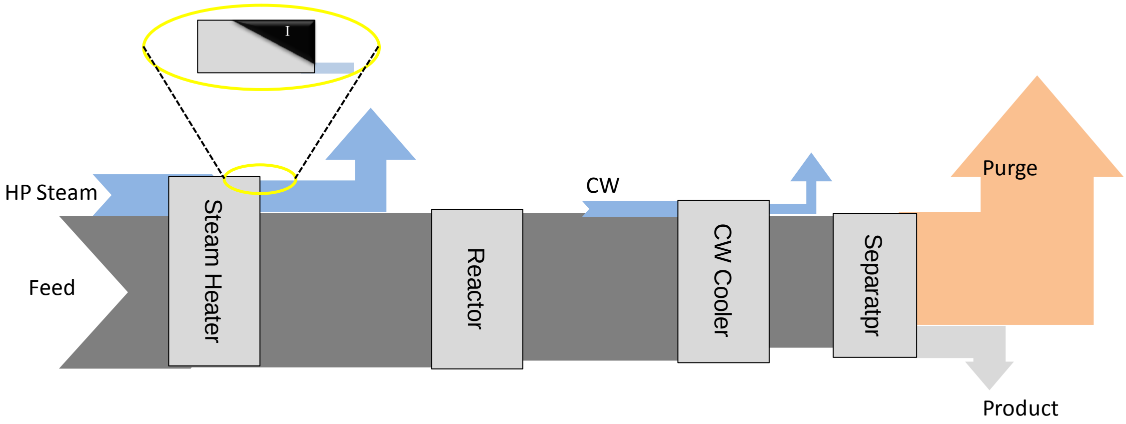


Figure 3.21. Grassmann diagram (base case)

In the base case, the vapor (i.e. purge) is simply emitted to environment. The vapor stream must be considered as a waste material and the absolute value of external exergy loss is equal to the exergy associated with purge rejected to the environment. From Figure 3.21, it can be seen that the purge stream accounts for high amount of exergy losses compared to total exergy input and output.

To improve the base case, Table 3.4 provides guidelines to reduce external exergy losses. As Table 3.4 proposes for the thermal exergy, recovery heat exchanger should be used. Thus, the thermal exergy associated with this effluent is recycled in the heat exchanger E-101 as a heat source to preheat the reactant (see Figure 3.22). In addition, based on Table 3.4, for chemical exergy losses, the stream should be used as a secondary raw material. Thus, the chemical exergy associated with purge is valorized in process B as a feed. In that case, the vapor at the outlet of separator can be considered as useful stream as its total exergy is valorized in process B. The integrated case is illustrated in Figure 3.22.

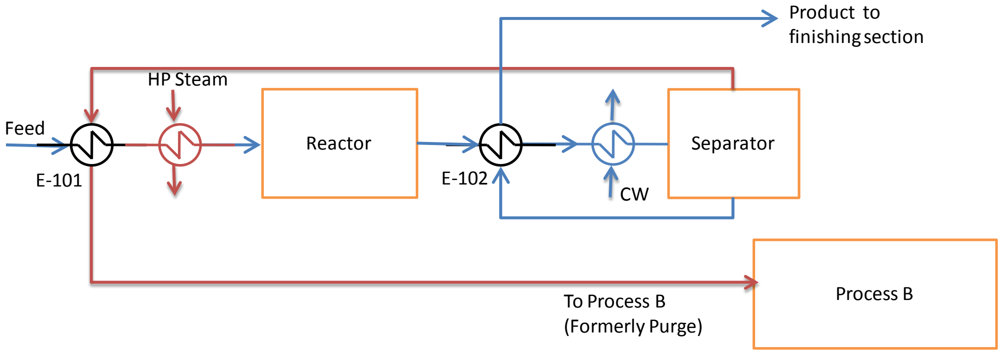


Figure 3.22. The integrated case

The new Grassmann diagram and the resulting external exergy loss after these modifications are reported in Figure 3.23 and Table 3.6.

Table 3.7 compares the utility consumption of the base case and the integrated case. As can be seen in these figures, an efficient use of exergy of streams clearly reduced the external exergy losses and leads to significant reduction of utility consumption.

The HP steam is reduced from 8.37 t/hr to 4.96 t/hr as a consequence of recovery of thermal exergy of purge by reduction of its temperature from 116°C to 36°C in order to preheat the reactor feed. Moreover, thanks to the use of reactor outlet as a heat source to heat the product up to 257 °C from 116 °C, the CW demand is reduced from 632.5 t/hr to 516.5 t/hr. Note in the base case the product stream is supposed to be heated up in the finishing section up to 300°C. It means heating of the product stream will not only save the CW demand but also reduce the heating demand of the finishing section.

Table 3.6. Exergy loss of unit operations for the integrated case

Unit Operation	Reactor	Separator	Waste Heater (Feed) E-101	Waste Heater (Prodcut) E-102	Steam Heater	CW Cooler	TOTAL
Irreversibility (kW)	605.64	226.14	537.89	104.95	466.36	843.65	2 784.62
External Loss (kW)	-	-	-	-			-

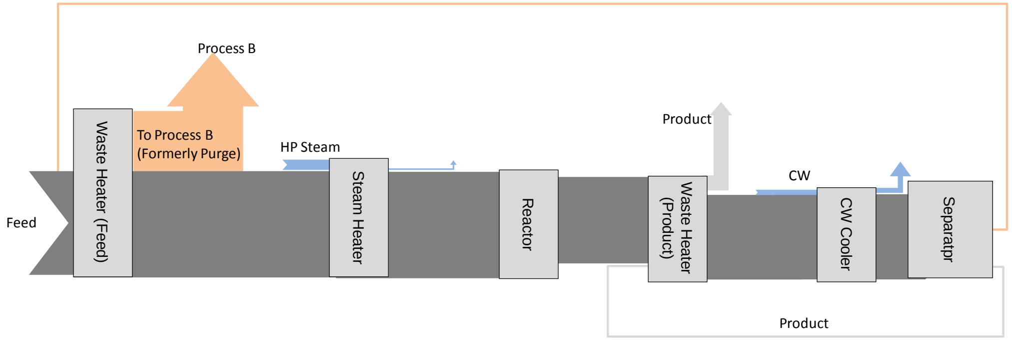


Figure 3.23. Grassmann diagram (integrated case)

Table 3.7. Utility data

Utility	Base case	*Integrated case*
CW flow (kg/h)	632 524.53	516 504.76
HP Steam(kg/h)	8 377.12	4 963.27
Steam cost (USD/yr)	443 241.60	262 610.40

According to this example, conclusions drawn from exergy balance are highly dependent on the utilization of the streams.

The analysis of external exergy losses requires the precise definition of the future utilization of the streams (waste streams rejected to environment or useful streams for another process). Then, this analysis enriched by the decomposition of material waste exergy into thermal, mechanical and chemical components could easily lead to pertinent proposal for the improvement of energy efficiency of the process.

3.3 PERFORMANCE CRITERIA FOR EXERGY ANALYSIS

The example described in the last section highlights the need for indicator which would enable to evaluate the energy efficiency - more precisely the exergetic performances of a process - and identify the unit operations that should be improved as a priority. In the literature, several formulations have been proposed. This section aims at comparing some of these formulations in order to find the most suitable one for a further implementation in a process simulator.

One of the most commonly used exergetic criteria is *exergy efficiency*. The exergetic efficiency evaluates the true performance of a process from the thermodynamic viewpoint. Based on the literature (Gong & Wall 1997), it is defined as ‘*utilized’ exergy* divided by ‘*used’ exergy*. Unfortunately, authors do not agree to define both terms ‘*utilized’* exergy and ‘*used*’ exergy.

3.3.1 Simple efficiency

As illustrated in Figure 3.24, the most simple definition of efficiency expresses all exergy input as *used* exergy, and all exergy output as *utilized* exergy (Cornelissen 1997). In these conditions, η_I is expressed as follows:

$$\eta_I = \frac{B^{out}}{B^{in}} = 1 - \frac{I}{B^{in}} \tag{3.41}$$

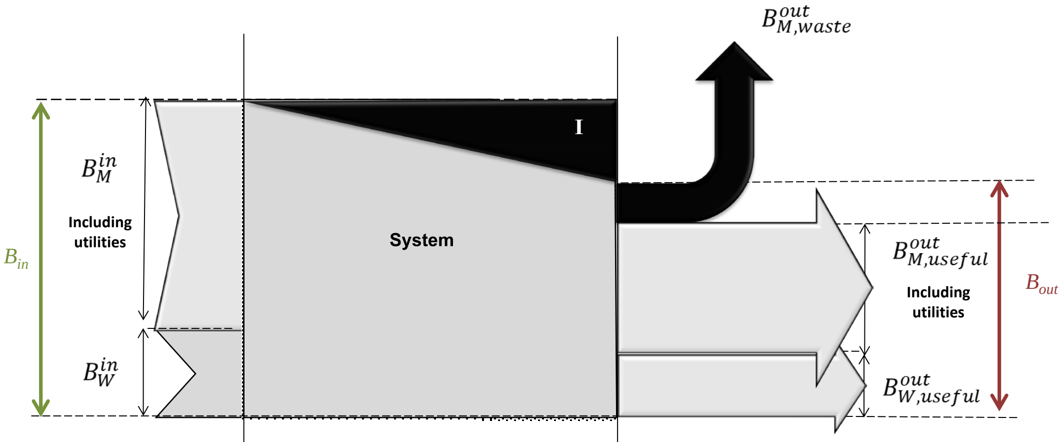
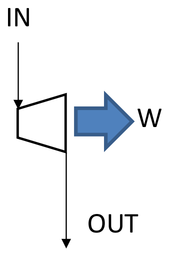


Figure 3.24. Simple exergy efficiency

Authors call this formulation of exergy efficiency, "*degree of thermodynamic perfection*" (Szargut et al. 1988; Torres & Gallo 1998) or "u*niversal efficiency"* (Woudstra 2004). As illustrated in Figure 3.24, only the irreversibility term is not included in the numerator. Moreover, it cannot differentiate between "*useful*" fluxes of exergy and "*waste*" ones. As a consequence, this exergy efficiency only permits to quantify the efficiency of the process relative to irreversibility and does not give any indicator about the external exergy loss.

EXAMPLE: TURBINE

To illustrate the use of simple efficiency, let us take an example of turbine shown in Figure 3.30*. As the first case, the working fluid is the steam which will be expanded from 10 atm and 400°C to 1 atm and 187.8°C to generated 84 kW shaft power.*



Material Stream		**IN**	**OUT**
Total Exergy Flow	**kW**	322.96	218.28
Chemical Exergy Flow	**kW**	108.28	108.28
Physical Exergy Flow	**kW**	214.67	110.00
Work Stream		**IN**	**OUT**
Work	**kW**	-	84
Total flow	**Kg.s^{-1}**	0.21	0.21
Temperature	**°C**	400.00	187.84
Pressure	**atm**	10.00	1

Figure 3.25. A typical expander

Applying this type of exergy efficiency gives 0.78 as calculated below:

$$\eta_I = \frac{B^{out}}{B^{in}} = \frac{B_M^{out} + B_W^{out}}{B_M^{in}} = 0.93 \qquad (3.42)$$

As expander only affects the physical exergy of the stream, there is no need to take into account the contribution of the chemical exergy when it is considerably greater than the contribution of physical exergy. However, as in this case chemical exergy of water has the same order of magnitude of physical exergy, this exergy efficiency gives quite right impression of process.

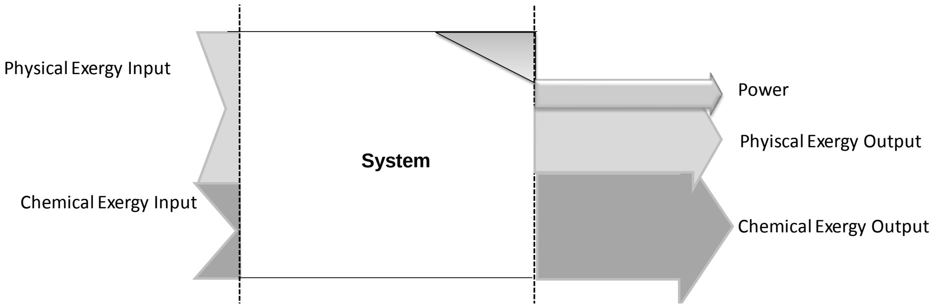


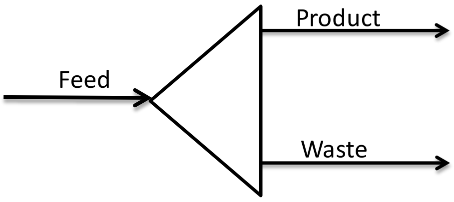
Figure 3.26. Grassmann diagram for expansion of water steam

EXAMPLE: SEPARATOR

To understand how using this efficiency gives the misleading results, let us take an example of a stream splitter shown in Figure 3.27. Applying this type of exergy efficiency gives 0.999 as calculated below:

$$\eta_I = \frac{B^{out}}{B^{in}} = \frac{B_{Waste}^{out} + B_{\mathrm{Product}}^{out}}{B_{Feed}^{in}} = 0.999 \qquad (3.43)$$

Although the splitter is operating to produce only the 'product stream' with 39263.32kW exergy, high exergy of waste (i.e. 262601.73kW) leads to efficiency close to unity which causes misleading result. Due to relative high value of exergy input and exergy output in Figure 3.28, the irreversibility cannot be clearly seen. In other words, the total exergy input and output have quite the same value.



Material Stream	Feed	Product	Waste
Total Exergy Flow (kW)	301897.24	39263.33	262601.73
Chemical Exergy Flow (kW)	301104.47	38962.13	262201.01
Physical Exergy Flow (kW)	792.77	301.20	400.73

Figure 3.27. A typical splitter

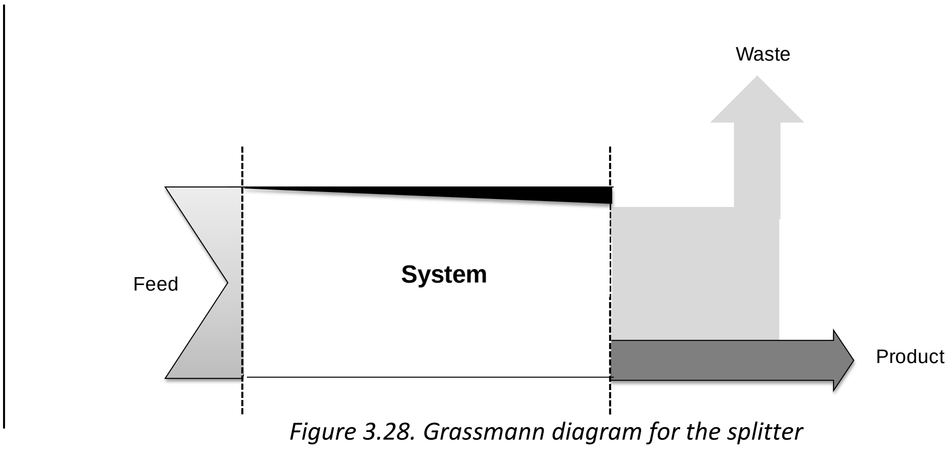


Figure 3.28. Grassmann diagram for the splitter

3.3.2 Coefficient of exergy efficiency taking into account external losses

To overcome one of the limitations highlighted for η_I, the *utilized* exergy can be given by the difference between the total exergy output and waste exergy output (Eq. 3.37) which we call the exergy of product $B_{product}$ (Wall & Gong 1997). In this case, according to (Brodyansky et al. 1994)the exergy efficiency η_{II} becomes:

$$\eta_{II} = \frac{B^{out} - B^{out}_{waste}}{B^{in}} = 1 - \frac{I}{B^{in}} - \frac{B^{out}_{waste}}{B^{in}} = \eta_I - \frac{B^{out}_{waste}}{B^{in}} \qquad (3.44)$$

This efficiency called “coefficient of exergy efficiency taking into account external losses” takes into account the “external exergy loss” and the irreversibility at the same time. In this manuscript, this formulation of exergetic efficiency will be called “Coefficient of Exergy Efficiency”.

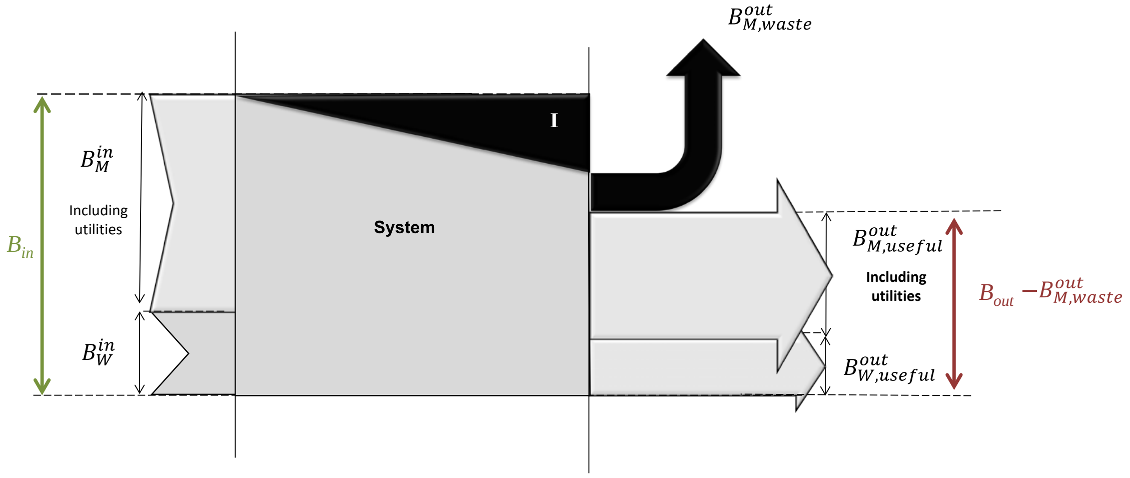


Figure 3.29. Coefficient of Exergy Efficiency

EXAMPLE: SEPARATOR

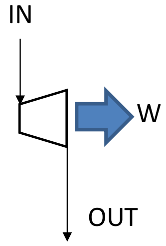
Calculating the coefficient of exergy efficiency for the splitter formerly presented, we obtain now:

$$\eta_{II} = \frac{B_{useful}^{out}}{B^{in}} = \frac{B_{\text{Product}}^{out}}{B_{Feed}^{in}} = 0.13 \qquad (3.45)$$

Consequently, compared to the first criteria, this exergy efficiency enables to estimate the part of input exergy that will be converted into useful one (either work or material). Moreover, as the first criteria, this coefficient is unambiguous and can be used for all process and plants. Unfortunately, as stated by Cornelissen (1997), this formulation can usually give the engineer the false impression of the thermodynamic perfection of a given process.

EXAMPLE: TURBINE

To illustrate the limitation of Coefficient of Exergy Efficiency, let us s take an example of turbine (Figure 3.30)



Material Stream		IN	OUT
Total Exergy Flow	**kW**	10124.64	10075.66
Chemical Exergy Flow	**kW**	10026.61	10026.61
Physical Exergy Flow	**kW**	98.03	49.04
Work Stream		**IN**	**OUT**
Work	**kW**	-	41.9
Total flow	**Kg.s^{-1}**	0.21	0.21
Temperature	**°C**	400.00	187.84
Pressure	**atm**	10.00	1

Figure 3.30. A typical turbine

The turbine reduces the pressure of propane from 10 atm and 400°C to 1 atm and 187.8°C to delivers 41.9 kW shaft power. The Coefficient of Exergy Efficiency of this process is given by

$$\eta_{II} = \frac{B^{out}}{B^{in}} = \frac{B_M^{out} + B_W^{out}}{B_M^{in}} = 0.99 \qquad (3.46)$$

According to this result the turbine seems to behave as a perfect process. However, the analysis of the Grassmann diagram represented in Figure 3.31 clearly shows that it is not true. As we can see, the input exergy is mainly composed of a chemical component which is not modified by the expansion processes. Only the physical component which is much smaller than the chemical one is reduced. As a consequence, the weight of the untransformed component is so high that the resulting Coefficient of Exergy Efficiency is very close to unity.

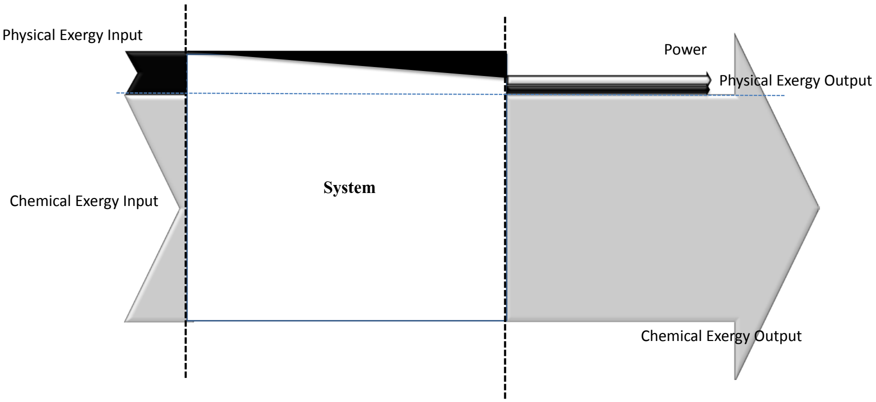
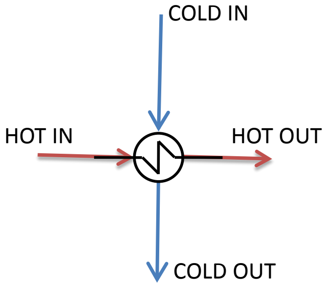


Figure 3.31. Grassmann diagram for expansion of propane

EXAMPLE: HEAT EXCHANGER

To illustrate other limitations of this exergy efficiency, let us take an example of heat exchanger in Figure 3.32. The analysis with help of Grassmann diagram will show this exergetic criterion can cause misleading results.



		COLD IN	COLD OUT	HOT IN	HOT OUT
Total flow	**mol.s^{-1}**	0.63	0.63	0.32	0.32
Temperature	**°C**	25.00	175.00	300.00	210.13
Pressure	**Atm**	2	2	10	10
Total Exergy Flow	**kW**	1356.01	1357.69	681.93	679.17
Chemical Exergy Flow	**kW**	1354.95	1354.95	677.46	677.47
Physical Exergy Flow	**kW**	1.06	2.75	4.45	1.75

Figure 3.32. Two-stream heat exchanger

The cold stream is the methane with high chemical exergy value. The hot stream is the steam with low chemical exergy value. As reported in Figure 3.32, the chemical exergy remains unchanged along the heat exchanger. On the other hand, the physical exergy changes. It means that inclusion of high chemical exergy input and output will not allow seeing the change of physical exergy as clearly shown in Figure 3.33. Therefore, Coefficient of Exergy Efficiency gives a value close to the unity:

$$\eta_{II} = \frac{B^{out}}{B^{in}} = 0.999 \qquad (3.47)$$

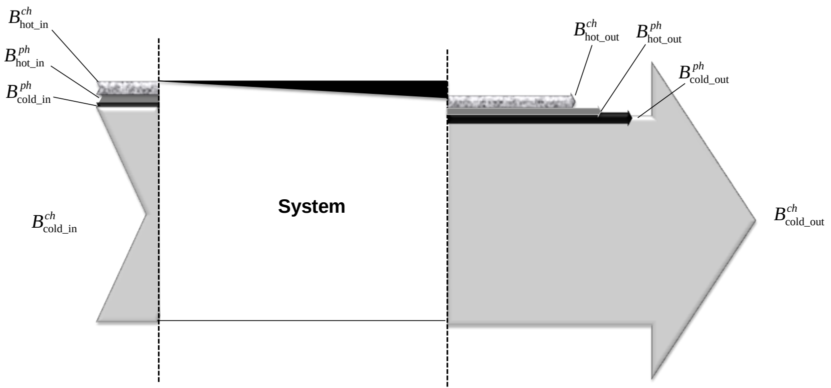


Figure 3.33. Grassmann diagram for heat exchanger

The coefficient of Exergy Efficiency gives a good impression of the thermodynamic perfection of a system only when all the component of incoming exergy flows (physical and chemical) are transformed to other components (e.g. for power stations). When it is not the case, the untransformed components give a false impression of the performance of the unit. In the case of chemical industry processes, unit operations such as the heat exchangers and expander only affect the physical exergy of the stream. Moreover, the sensitivity of the simple efficiency and of the coefficient of exergy efficiency reduces with increasing quantities of untransformed components which makes this kind of efficiency inefficient for process optimization.

Due to the limitations formerly mentioned, this efficiency does not provide an adequate characterization of the thermodynamic efficiency of processes. A solution might be to define precisely the purpose of the system and to include the “desired exergetic effect”.

3.3.3 Rational efficiency

The rational efficiency (Kotas 1985) permits to address the gaps highlighted for the previous formulation by defining the efficiency of a process as the ratio of the “desired exergy output” to the “exergy used”. Tsatsoronis (1993) prefers the terms “product” and “fuel”. The “desired exergy effect” represents the desired result produced in the system (“product”) whereas the “exergy used” represents the net resources which were spent to produce the desired effect (“fuel”).

$$\Psi = \frac{B_{\text{Desired Output}}}{B_{\text{Used}}} \tag{3.48}$$

$B_{\text{Desired Output}}$ is determined by examining the function of the system. After introducing the exergy used and the exergy of desired output, the overall exergy balance becomes:

$$B_{\text{Used}} = B_{\text{Desired Output}} + I + B_{waste}^{out} \tag{3.49}$$

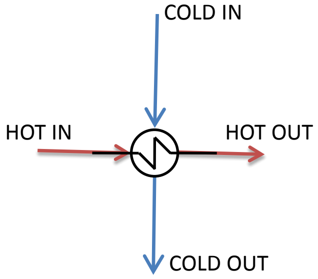
Then, combining these two last equations, the following alternative form of the rational efficiency can also be obtained.

$$\Psi = 1 - \frac{I + B_{waste}^{out}}{B_{\text{Used}}} \tag{3.50}$$

It results from these equations that the evaluation of this efficiency requires the definition of the term $B_{Desired\ Output}$ (i.e. the desired effect of the system). The term B_{Used} can then be deduced from Eq. (3.49).

EXAMPLE: HEAT EXCHANGER

The calculation of the rational efficiency is illustrated through the study of a two-stream heat exchanger shown in Figure 3.32. Basically the function of a heat exchanger is to change the thermal exergy of one stream at the expense of exergy change of the other stream.



		COLD IN	COLD OUT	HOT IN	HOT OUT
Total flow	**mol.s^{-1}**	0.63	0.63	0.32	0.32
Temperature	**°C**	25.00	175.00	300.00	210.13
Pressure	**Atm**	2	2	10	10
Total Exergy	**kJ.mol^{-1}**	2152.4	2155.06	2131.03	2122.41
Chemical Exergy	**kJ.mol^{-1}**	2150.71	2150.71	2117.06	2117.09
Physical Exergy	**kJ.mol^{-1}**	1.68	4.37	13.91	5.47
Total Exergy Flow	**kW**	1356.01	1357.69	681.93	679.17
Chemical Exergy Flow	**kW**	1354.95	1354.95	677.46	677.47
Physical Exergy Flow	**kW**	1.06	2.75	4.45	1.75
Mechanical Exergy Flow	**kW**	1.06	1.06	1.65	1.65
Thermal Exergy Flow	**kw**	0	1.69	2.80	0.05

Figure 3.34. Two-stream heat exchanger

Assuming that the function of the heat exchanger under consideration is to increase the thermal exergy of the cold stream, we have:

$$B_{\text{DesiredOutput}} = B^{\Delta T}_{\text{cold\_out}} - B^{\Delta T}_{\text{cold\_in}} = B_{cold\_out} - B_{cold\_in} \tag{3.51}$$

Because $B^{\Delta P}_{\text{cold\_out}} = B^{\Delta P}_{\text{cold\_in}}$ *and* $B^{ch}_{\text{cold\_out}} = B^{ch}_{\text{cold\_in}}$

As exergy balances are required to express the rational efficiency, the thermal contribution of exergy is used in this equation, and not the maximal potential for thermal exergy recovery.

Rewriting the exergy balance around the heat exchanger considering all component of exergy, we obtain:

$$\begin{aligned}\left(B^{\Delta T}_{\text{cold\_in}} + B^{\Delta P}_{\text{cold\_in}} + B^{ch}_{\text{cold\_in}}\right) + \left(B^{\Delta T}_{\text{hot\_in}} + B^{\Delta P}_{\text{hot\_in}} + B^{ch}_{\text{hot\_in}}\right) = {} & \left(B^{\Delta T}_{\text{cold\_out}} + B^{\Delta P}_{\text{cold\_out}} + B^{ch}_{\text{cold\_out}}\right) \\ & + \left(B^{\Delta T}_{\text{hot\_out}} + B^{\Delta P}_{\text{hot\_out}} + B^{ch}_{\text{hot\_out}}\right) \\ & + I\end{aligned} \tag{3.52}$$

Then, as we have $B^{\Delta P}_{\text{hot\_in}} = B^{\Delta P}_{\text{hot\_out}}$ *and* $B^{ch}_{\text{hot\_in}} = B^{ch}_{\text{hot\_out}}$, *we can deduce :*

$$B^{\Delta T}_{\text{cold\_in}} + B^{\Delta T}_{\text{hot\_in}} = B^{\Delta T}_{\text{cold\_out}} + B^{\Delta T}_{\text{hot\_out}} + I$$

Combining these two last equations, we obtain:

$$B_{DesiredOutput} = B^{\Delta T}_{\text{cold\_out}} - B^{\Delta T}_{\text{cold\_in}} = B^{\Delta T}_{\text{hot\_in}} - B^{\Delta T}_{\text{hot\_out}} - I = B_{\text{hot\_in}} - B_{\text{hot\_out}} - I \tag{3.53}$$

In a heat exchanger, the chemical exergy of hot and cold streams are not modified; Canceling out the chemical exergy at the inlet and outlet and identifying the term B_{Used} *based on Eq. (3.49), we obtain*

$$B_{\text{Used}} = B_{\text{Desired Output}} + I + B^{out}_{waste} = B_{\text{hot\_in}} - B_{\text{hot\_out}} \tag{3.54}$$

Then applying Eq. (3.55) rational exergy efficiency can be expressed as follows:

$$\Psi = \frac{B_{\text{cold\_out}} - B_{\text{cold\_in}}}{B_{\text{hot\_in}} - B_{\text{hot\_out}}} \tag{3.55}$$

Note that in this example, we have used the thermal and mechanical contributions of physical exergy not maximal ones as the aim was to calculate the exergy efficiency.

Coming back to the example of heat exchanger in Figure 3.32, the exclusion the chemical exergy input and output, allow seeing the evolution of physical exergy clearly as shown in Figure 3.35.

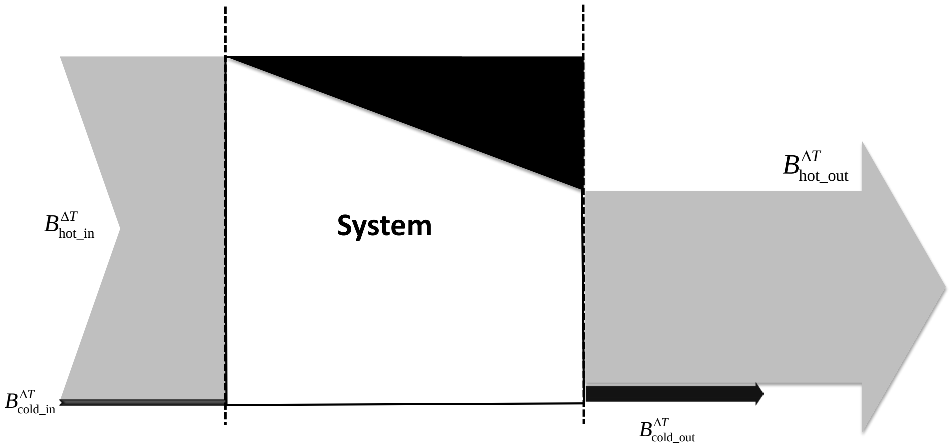


Figure 3.35. Grassmann diagram for heat exchanger excluding chemical and mechanical exergies

The application of rational efficiency based on Eq. (3.55) results in a value which shows thermodynamic imperfection is occurring in the heat exchanger, unlike the simple efficiency.

$$\Psi = 0.61 \tag{3.56}$$

In comparison with the simple exergy efficiency (0.98), the rational efficiency gives quite the right impression of the process, as it is not close to the unity. Note that the objective of this heat exchanger is supposed to be heating of cold stream. However, for the case where the objective is to cool the hot stream in this heat exchanger, a different value is obtained:

$$B_{\text{DesiredOutput}} = B_{\text{hot\_in}} - B_{\text{hot\_out}} \tag{3.57}$$

Then using the same approach explained above, the rational exergy efficiency can be expressed as follows:

$$\Psi = \frac{B_{\text{hot\_in}} - B_{\text{hot\_out}}}{B_{\text{cold\_out}} + B_{\text{cold\_in}}} = \underline{\underline{1.63 > 1}} \tag{3.58}$$

As the efficiency in this case is higher than unity, it means that for the heat exchanger only one objective MUST be defined where the exergy from the upper level is transferred to lower level in order to derive the process (e.g. heat transfer). In other words, for this example, it is not possible to define the second function as cooling the hot streams.

We can go further and define the desired effect as the heating of cold stream and cooling of hot stream:

$$B_{\mathrm{DesiredOutput}} = \left(B_{\mathrm{hot\_in}} - B_{\mathrm{hot\_out}}\right) + \left(B_{\mathrm{cold\_out}} - B_{\mathrm{cold\_in}}\right) \tag{3.59}$$

$$\Psi = \frac{\left(B^{\Delta T}_{\mathrm{hot\_in}} - B^{\Delta T}_{\mathrm{hot\_out}}\right) + \left(B^{\Delta T}_{\mathrm{cold\_out}} - B^{\Delta T}_{\mathrm{cold\_in}}\right)}{0} = \infty \tag{3.60}$$

As expected, an infinite efficiency is obtained.

By making the distinction between "*exergy used*" and "*exergy of desired output*", the rational efficiency permit to address the gaps identified for former formulations. However, the evaluation of this efficiency is a much trickier task as it requires the definition of the desired effect of a given system (process or unit operation).

For each unit operation, a function needs to be defined to evaluate the term $B_{DesiredOutput}$, then the term B_{Used} is deduced from the exergy balance. However, the function of a unit operation is not always easy to be determined. Consider for example the case of gas compression; the first objective is to increase the pressure of the gas. However, this question should be answer whether the desired effect is an increase of the temperature or not? A strong interaction of the user is required for the calculation of rational efficiencies and the user may not always answer to these complex questions. To highlight this complexity, Appendix C proposes the rational exergy efficiencies of various unit operations. Note that for most unit operations, different desired functions can be defined then resulting in different expressions for rational efficiencies. Moreover, extending the reasoning to global flowsheets, it may be really difficult to precisely define the "desired effect" of an entire process or of a process zone.

All these limitations prevents from automatic calculations of the efficiency of a process. As a consequence, this formulation does not appear as a good candidate for a further implementation in a process simulator

3.3.4 Exergy efficiencies with transiting exergy

3.3.4.1 Intrinsic efficiency and utilizable exergy coefficient

Another kind of efficiency was introduced to solve the problem addressed for previous expression of exergetic efficiency. Sorin et al. (1998) explained the strength of such a formulation. These explanations are reported below. It has been observed in the first sections that the simple exergy efficiency or the coefficient of exergy efficiency can be overestimated. In particular, these exergy 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 very small heat duty would produce such effect. The reason is the fact that only a part of the useful exergy is produced by the system in the accomplishment of all the physico-chemical phenomena which take place within its boundaries. The rest of exergy that leaves the system with the useful exergy is a part of the exergy input which has simply traversed the system without undergoing any transformation (see Figure 3.36). The name of transiting exergy (Kostenko, 1983) was given to this fraction of exergy supplied to the system. Typically, in a chemical reactor a part (but not all because of temperature and pressure changes) of the exergy associated with unreacted feed or inerts would constitute transiting exergy. Transiting exergy was further characterized by Brodyansky et al. (1994) who have developed algorithm for its computation. Because of the complicated calculation, there are not a lot of publications using the concept of transiting exergy in the literature.

As illustrated in Figure 3.36, only part of the input exergy B^{in} is consumed by the system to produce new form of useful exergy. On the basis of these observations, Sorin and Brodyansky (1985) have defined new exergetic efficiency later named by Sorin et al. (1994) the intrinsic exergy efficiency.

$$\eta_{\text{intrinsic}} = \frac{B^{\text{out}} - B^{tr}}{B^{in} - B^{tr}} = \frac{B^{\text{out}} - B^{tr}_{useful} - B^{tr}_{waste}}{B^{in} - B^{tr}_{useful} - B^{tr}_{waste}} = \frac{B^{p}}{B^{c}} \qquad (3.61)$$

The terms B^c, B^p and B^{tr} are the consumed, produced and total transiting exergies respectively. Intrinsic exergy efficiency is the measure of the true ability of the system to produce new exergy from a given amount of consumed exergy. However $\eta_{\text{intrinsic}}$ does not account for the fact that, because of the external exergy losses B^{out}_{waste} all of the exergy produced is not longer utilizable.

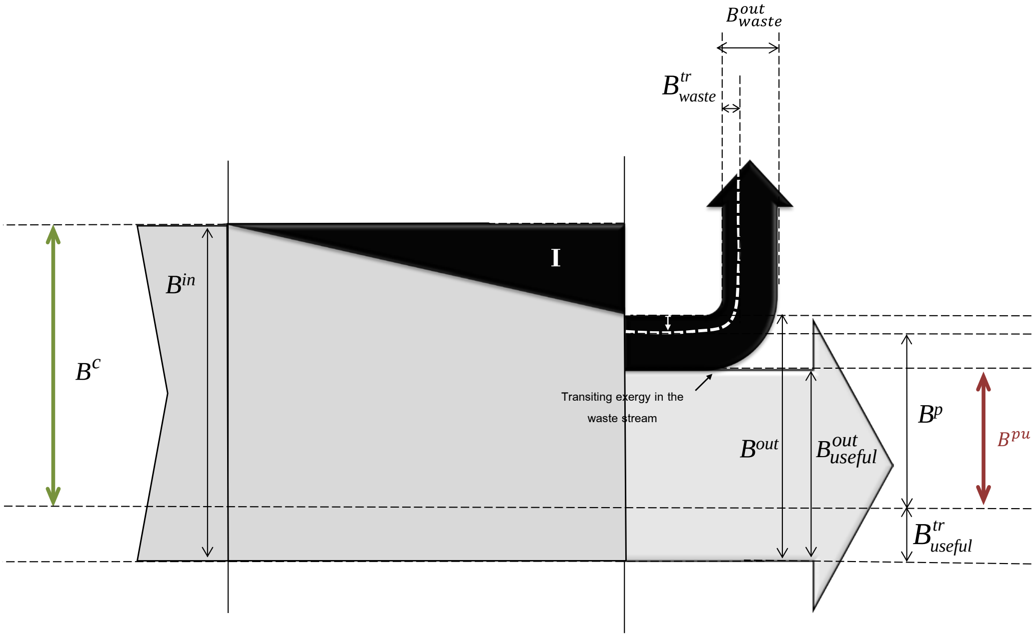


Figure 3.36. Exergy efficiencies with transiting exergy

To solve this problem, Sorin et al. (1998) introduced an alternative coefficient which is more pertinent to the evaluation of practical systems performance, the utilizable exergy coefficient $\eta_{\text{utilizable}}$. It is defined as:

$$\eta_{\text{utilizable}} = \frac{B_{\text{useful}}^{\text{out}} - B_{\text{useful}}^{tr}}{B^{\text{in}} - B_{\text{useful}}^{\text{tr}}} = \frac{B^{pu}}{B^{\text{c}}} \tag{3.62}$$

B^{pu} is the produced utilizable exergy; it constitutes part of B^{p}. B_{useful}^{tr} is only the part of transiting exergy which is included in the utilizable exergy stream. As illustrated in Figure 3.36 there may also be transiting exergy B_{waste}^{tr} in the external exergy losses stream B_{waste}; for example, exergy of the part of the initial feed traversing the system without transformation and lost into the environment. However, to compute $\eta_{utilizable}$ according to Eq. (3.62), there is no need to evaluate B_{waste}^{tr}.

3.3.4.2 Calculation of transiting exergies

As explained before, the transiting exergy concern the exergy that simply passes through the system without undergoing any transformation. As a consequence, when considering processes consisting in a single input material stream and a single output material stream, a simple definition of transiting exergy could be given by the following expressions:

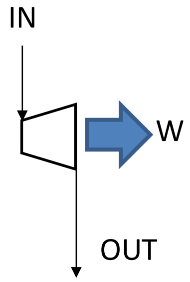
$$B^{ph,tr} = \min\left[b_{in}^{ph} ; b_{out}^{ph}\right] \tag{3.63}$$

$$B^{ch,tr} = \min\left[b_{in}^{ch} ; b_{out}^{ch}\right] \tag{3.64}$$

Note that no transiting exergy must be granted to work and heat flux. Indeed, we will consider that all the work (heat) brought to a given system is fully used to transform input forms of exergy into other forms; e.g. in a heat pump, input work is fully used to increase the physical exergy of the input material stream. In an endothermic reactor, input heat exergy flux permits to modify the chemical exergy of input reactants.

EXAMPLE: TURBINE

Considering the case of a turbine, after exergy balance on it, we obtain the results listed in Figure 3.37.



Material Stream		IN	OUT
Total Exergy Flow	**kW**	10124.64	10075.66
Chemical Exergy Flow	**kW**	10026.61	10026.61
Physical Exergy Flow	**kW**	98.03	49.04
Work Stream		**IN**	**OUT**
Work	**kW**	-	41.9
Total flow	**Kg.s^{-1}**	0.21	0.21
Temperature	**°C**	400.00	187.84
Pressure	**atm**	10.00	1

Figure 3.37. A turbine

The transiting exergy can be calculated as:

$$B^{ph,tr} = \min[98.0;49.0] \tag{3.65}$$

$$B^{ch,tr} = \min[10026.6;10026.6] \tag{3.66}$$

The total transiting exergy is the sum of chemical and physical ones:

$$B^{tr} = B^{ch,tr} + B^{ph,tr} = 10026.6 + 49.0 = 10075.6\ kW \tag{3.67}$$

Total exergy output is sum of shaft power and the expanded propane:

$$B^{out} = 10075.6 + 41.9 = 10116.9 \qquad kW \tag{3.68}$$

Then, intrinsic efficiency can be calculated as

$$\eta = \frac{10116.9 - 10075.6}{10124.6 - 10075.6} = 0.85 \tag{3.69}$$

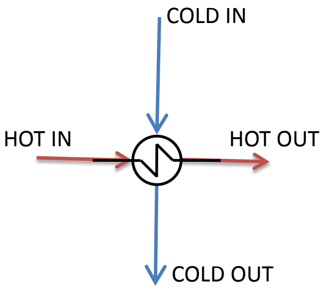
The efficiency provides a right impression as the transiting chemical exergy which remains unchanged are deduced from total exergy input and output. As the physical exergy and shaft power only play a role in the efficiency, the value of 0.85 accounts for the process which is actually occurring in the turbine.

3.3.4.3 Sub-streams concept

The former equations are consistent only for very simple operation with one input and one output material streams. The following heat exchanger example will permit to highlight the drawbacks of such formulations.

EXAMPLE: HEAT EXCHANGE

Let us consider again the case of a two-stream heat exchanger shown in Figure 3.38.



		COLD IN	COLD OUT	HOT IN	HOT OUT
Total Exergy Flow	**kW**	1356.01	1357.69	681.93	679.17
Chemical Exergy Flow	**kW**	1354.95	1354.95	677.47	677.47
Physical Exergy Flow	**kW**	1.06	2.75	4.45	1.70

Figure 3.38. Two-stream heat exchanger

When calculating the transiting exergy according to Eqs.(3.63) and (3.64) leads to

$$B^{tr} = \min[1.06 + 4.45; 2.75 + 1.70] + \min[1354.95 + 677.47; 1354.95 + 677.47] \quad (3.70)$$

$$B^{tr} = 5.51 + 2032.42 \quad (3.71)$$

$$B^{tr} = 2037.93 \quad (3.72)$$

Then, calculating the utilizable exergy coefficient, we obtain:

$$\eta_{utilizable} = \frac{1357.69 + 679.17 - 2037.93}{1356.01 + 681.93 - 2037.93} = \frac{-1{,}07}{0} = \infty \quad (3.73)$$

In the former example, all input streams on one hand and all output streams on the other hand are mixed together to calculate the transiting exergy. Then, this calculation leads to a not finite value for the utilizable exergy coefficient. Actually, hot streams and cold streams never mix themselves and are part of two distinct systems.

To solve this problem (Brodyansky 1994) has introduced a more complex definition for utilizable exergy efficiency. To illustrate this formulation, Figure 3.39 illustrates the calculation of the transiting exergy for the mixing of two material streams I and II. In this figure, streams are composed of 2 components: a component 1 (in black) and a component 2 (in white). The output stream III results from the mixing of streams I and II. As a consequence, a part of component 1 existing in stream III comes from input stream I whereas the other part comes from the input stream II. This observation leads to the definition of the sub-stream concept: in this case, two sub-streams can be defined: sub-stream I-III and the sub-stream II-III.

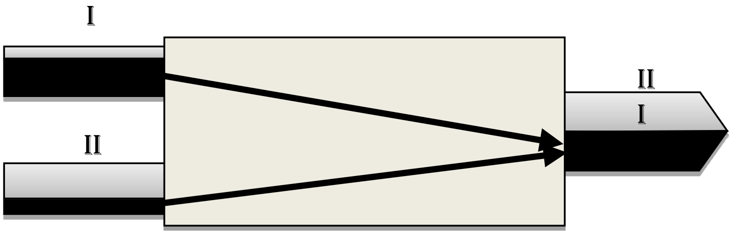


Figure 3.39. Adiabatic mixing of material streams

Starting from this sub-stream definition, (Brodyansky 1994) defined the physical and chemical transiting exergy by the following equations:

- *Physical transiting exergy*

$$B^{ph,tr} = B^{ph,tr}_{I-III} + B^{ph,tr}_{II-III} \tag{3.74}$$

$$B^{ph,tr} = min[n_I; n_{III}].min[b^{ph}_I; b^{ph}_{III}] + min[n_{II}; n_{III}].min[b^{ph}_{II}; b^{ph}_{III}] \tag{3.75}$$

$$B^{ph,tr} = n_I.min[b^{ph}_I; b^{ph}_{III}] + n_{II}.min[b^{ph}_{II}; b^{ph}_{III}] \tag{3.76}$$

- *Chemical transiting exergy*

$$B^{ch,tr} = B^{ch,tr}_{I-III} + B^{ch,tr}_{II-III} \tag{3.77}$$

$$B^{ch,tr} = min[n_{1,I}; n_{1,III}].min[b^{ch}_{1,I}; b^{ch}_{1,III}] + min[n_{2,I}; n_{2,III}].min[b^{ch}_{2,I}; b^{ch}_{2,III}] + min[n_{1,II}; n_{1,III}].min[b^{ch}_{1,II}; b^{ch}_{1,III}] + min[n_{2,II}; n_{2,III}].min[b^{ch}_{2,II}; b^{ch}_{2,III}] \tag{3.78}$$

$$B^{ch,tr} = n_{1,I}.min[b^{ch}_{1,I}; b^{ch}_{1,III}] + n_{2,I}.min[b^{ch}_{2,I}; b^{ch}_{2,III}] + n_{1,II}.min[b^{ch}_{1,II}; b^{ch}_{1,III}] + n_{2,II}.min[b^{ch}_{2,II}; b^{ch}_{2,III}] \tag{3.79}$$

where $n_{i,j}$ refers to the partial molar flowrate of component i in the stream j and $b^{ch}_{i,j}$ refers to the partial molar chemical exergy of component I in the stream j.

3.3.4.4 General formulation of transiting exergy

Considering a process composed of multiple input streams n and output streams m, the general formulation of the transiting physical and chemical exergy are given by the following equations:

- Physical transiting exergy

$$B^{ph,tr} = \sum_{m,n} B^{ph,tr}_{(m,n)} = \sum_{m,n} \min[n_m, n_n].\min[b^{ph}_m; b^{ph}_n] \tag{3.80}$$

- Chemical transiting exergy

$$B^{ch,tr} = \sum_{m,n} B^{ch,tr}_{(m,n)} = \sum_{m,n} \sum_{i}^{Nc} \min\left[n_{i,n}; n_{i,m}\right] \min\left[b^{ch}_{i,m}; b^{ch}_{i,n}\right] \tag{3.81}$$

where (m, n) is a combination of the input stream (i.e. m) and the output stream (i.e. n) which are physically connected:

Note that, to solve the problem highlighted when considering the heat exchanger example **physically connected input/output streams** have to be inventoried. In general, in any process simulator, the input streams of a unit operation are almost always physically connected to the output streams, except for a heat exchange module on which heat and cold streams are represented. In the example shown in Figure 3.40, there are two groups of physically connected streams groups I and II.

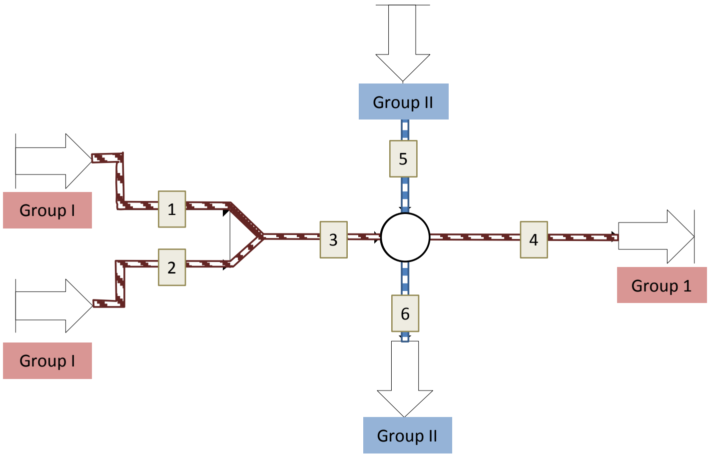


Figure 3.40. A group of material connected streams

EXAMPLE: HEAT EXCHANGE

Considering again the example of heat exchanger described in Figure 3.38 we can calculate the transiting exergies.

$$B^{ph,tr} = B_{(cold\_in,cold\_out)} + B_{(Hot\_in,Hot\_out)} \tag{3.82}$$

$$B^{ph,tr} = n_{cold\_in} \cdot \min\left[b^{ph}_{Cold\_in}; b^{ph}_{Cold\_out}\right] + n_{hot\_in} \cdot \min\left[b^{ph}_{hot\_in}; b^{ph}_{hot\_out}\right] = B^{ph}_{cold\_in} + B^{ph}_{hot\_out} \tag{3.83}$$

$$B^{ph,tr} = 1.06 + 1.75 = 2.81\,\mathrm{kW} \tag{3.84}$$

As the heat exchanger does not perform any chemical transformation, the chemical transiting exergy is equal the total input (output) chemical exergy:

$$B^{ch,tr} = 1354.95 + 677.46 = 2032.41 \tag{3.85}$$

Then, the resulting utilizable exergy coefficient is equal to:

$$\eta_{utilizable} = \frac{1357.69 + 679.17 - (2032.41 + 2.81)}{1356.01 + 681.93 - (2032.41 + 2.81)} = \frac{1.64}{2.72} = 0.61 \tag{3.86}$$

The heat exchanger example permits to demonstrate the qualities of the utilizable exergy coefficient. Indeed, in comparison with the simple exergy efficiency (0.99), this indicator gives the right impression of the process as it is not close to the unity. In addition, we can note that the utilizable exergy coefficient leads exactly to the same value as the rational efficiency without the need of user to define the function of unit operation. Moreover, Sorin et al. (1998) demonstrated the strength of this new utilizable exergy coefficient for the thermodynamic assessment of chemical reactors. Whereas the conventional coefficient of exergy efficiency decreases with the conversion of studied reactor, the utilizable exergy coefficient has a smooth maximum which establishes the thermodynamic compromise between energy consumption and conversion rate.

Contrary to the conventional coefficient of exergy efficiency which promotes solutions minimizing the exergy losses per unit of ***exergy output****, the utilizable exergy coefficient promotes solutions which minimize the exergy losses per unit of* ***produced exergy****.*

Thanks to these results, Sorin et al. (1998) concluded that the utilizable exergy coefficient is a more suitable criterion of a thermodynamic performance a chemical system. Therefore, the utilizable exergy coefficient seems to be the most promising exergy efficiency.

3.3.5 Conclusion on exergy efficiencies

Table 3.3 summarizes all of these exergy efficiencies by presenting the positive and negative points on them, in addition of implantation aspects of these criteria in process simulators. This table permits to draw some pertinent conclusions for the selection of the most appropriate exergy efficiency that could be implemented in a process simulator. The first expressions (simple exergy efficiency or coefficient of exergy efficiency) are very simple to implement but may lead to misleading conclusions and give a wrong impression of the process under study. However, they are really accurate formulation for process where all the component of incoming exergy flows (physical and chemical) are transformed to other components (e.g. for utility systems). This formulation should then be implemented in a process simulator but its utilization should be restricted to such processes. Rational efficiency, which intends to evaluate the performance of the system from given desired effect, was a promising solution. However, the definition of the desired effect of a unit operation and of the global flowsheet can sometimes be a hard task for the user and can also lead to ambiguous results. Finally, intrinsic efficiency and utilizable exergy coefficient not only eliminates the need for user interactions, but also makes it possible to calculate exergy efficiency of different unit operations together in a given zone. Certainly the utilizable exergy coefficient appears to be most promising, as it excludes from the numerator the waste streams.

Table 3.8. Comparison of exergy efficiencies

Name	Advantages	Shortcomings	Implementation in Process Simulators	Remarks on unit operation or processes
Simple Efficiency	Easy to calculate	- Insensitive to changes in process - Not good for diagnosis steps - not accurate when only physical exergy is modified	Very easy	- Adequate for energy systems - Fails for those with waste stream to environment
Coefficient of Exergy Efficiency (taking into account External Losses)	- Consideration of external exergy loss - Good for preliminary diagnostic steps	- Insensitive to changes in process - not accurate when only physical exergy is modified	Engineer needs to classify streams into “waste” streams and useful ones	- Adequate for energy systems
Rational Efficiency	- Specific for each unit operation - Sensitive to changes in processes-	- Undefined for some unit operations - Requires a clear definition of the desired output for each unit operation	- Engineer needs to classify streams into “waste” streams and useful ones. - Fully-automated calculation is impossible ⇨ Interaction of user is needed.	- Function of each unit operation in the particular process required. - Nothing to do with units like throttling valve, and all other fully- exergy-dissipative units
Intrinsic Efficiency	. Sensitive to changes in processes	- Manual calculation is cumbersome. ⇨ A process simulator is needed. - Not considering waste streams.	Fully-automated calculation is possible as the Interaction of user is not needed.	- Suitable for the process with a high transiting exergy (e.g. chemical reactor with conversion less that 100%
Utilizable Exergy Coefficient	- Consideration of external exergy loss	- Manual calculation is cumbersome. ⇨ A process simulator is needed.	Engineer needs to classify streams into “waste” streams and useful ones	- A comprehensive criterion for automated process synthesis (Sorin et al. 2000)

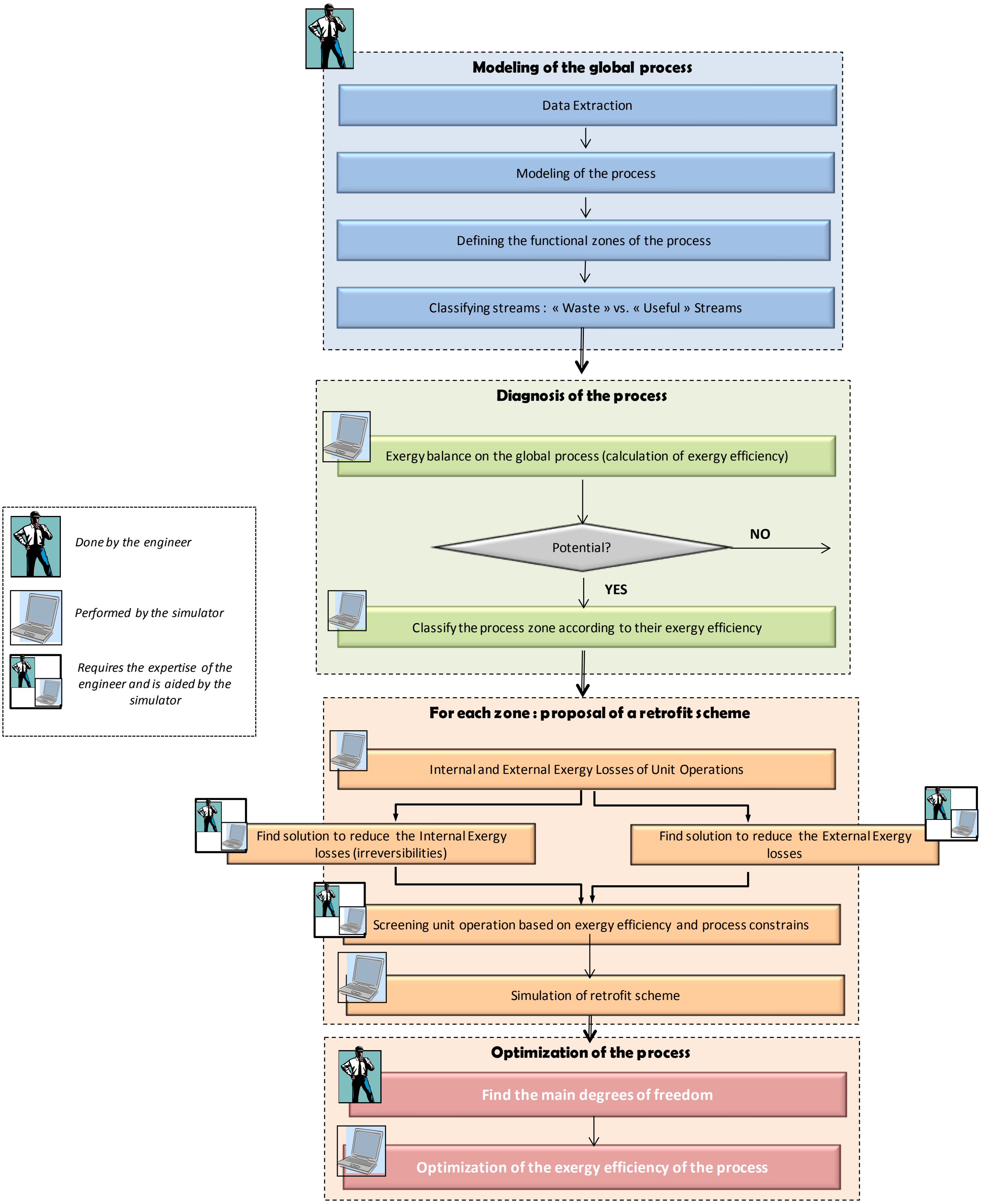


Figure 3.41 Exergy analysis methodology for retrofitting

3.4 METHODOLOGIES OF EXERGY ANALYSIS

As highlighted previously, when performing an exergy analysis, one must distinguish two cases: the exergy analysis for synthesis and design purposes and the exergy analysis for the diagnosis and retrofitting of existing processes.

In this section and in the case studies presented in the Chapter 5, we have chosen to limit ourselves to the exergy analysis dedicated to the retrofitting and optimization of existing processes. Concerning this aspect, a lot of case studies can be found in the literature (Doldersum 1998; Geuzebroek et al. 2004; Graveland & Gisolf 1998; Kim et al. 2001). Unfortunately, most of these analyses simply calculate the irreversibilities and external losses of each unit operation and sometimes exergy efficiencies but do not propose technological solutions to improve the global performance of the process. To fill this gap, this section introduces a systematic and sequential methodology starting from the modeling and the diagnosis of the existing process based upon exergetic criteria and resulting in a set of proposals for improvement and optimization of the process.

3.4.1 Detailed presentation of the methodology

The global flowchart of the methodology for retrofitting of processes based upon exergy analysis is represented in Figure 3.41. As highlighted in this figure, the methodology is composed of four stages: modeling of the process, diagnosis, proposal of a retrofit scheme and finally optimization of the final scheme. In this section, each stage will be detailed.

3.4.1.1 Modeling of the global process

This preliminary step intends to prepare the data for the further analysis of the process. This step is certainly the most delicate task of the methodology: indeed, extracting the data from a real process is a very time-consuming task; moreover, the relevance of the proposed solution given at the end of the procedure strongly depends on the accuracy of the model. This stage is composed of four steps:

Data Extraction: The energy analysis of an industrial site always requires performing a rigorous data extraction. This data extraction consists in collecting all the necessary data for mass and heat balances on the process and on the existing utility system. In this step, discussions with the site manager are essential in order to be able to classify the process data according to process specifications, degrees of freedom, process parameters. Furthermore, concerning the existing utility system, it is essential to answer the following question: *Can the process/utility system be completely replaced or is the purpose of the analysis just to improve the existing process/ utility system?*

Modeling of the process: The collected information is then capitalized by performing heat and mass balances which can either be performed on a simple spreadsheet or using more advanced tools such as process simulation software. In the proposed approach, ProSimPlus® simulator has been used.

Decomposition of the process into functional zones: The exergy analysis is intended to be applied to real industrial case studies; in this situation, the considered process may be very complex processes and composed of different functional zones. As an example, Figure 3.42represents the TAME (tertiary Amyl Methyl Ether) unit of a crude oil refinery process considered by Rivero et al. (2004) for exergy analysis. As illustrated in Figure 3.42, different functional sections have been considered: sections dedicated to the preparation of reactants (depentanizer section), reaction sections, by-products recovering sections (methanol recovering section) and product purification sections (raffinate washing section). This decomposition will permit to make the analysis easier by classifying the functional zones according to their exergy efficiency.

To generalize this approach, a generic decomposition of a given process is presented in Figure 3.43. It will always be possible to decompose any process according to this scheme: i.e. with reactant preparation sections, reaction sections, washing or recovery sections and support processes (wastewater sections, hot and cold utility production zones).

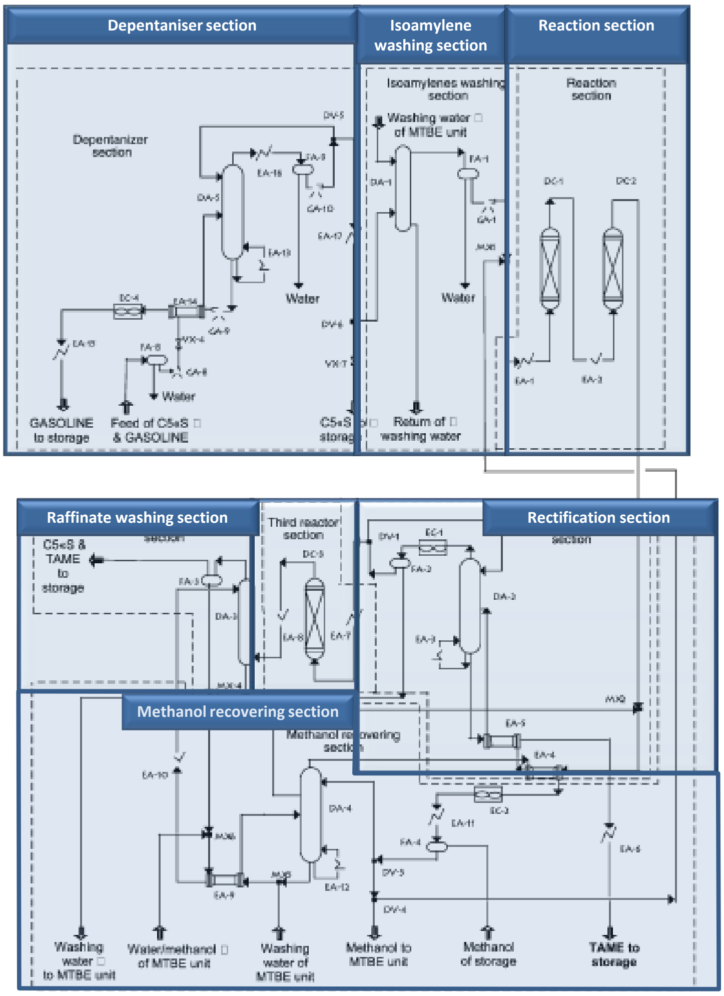


Figure 3.42. Decomposition of the process into functional zones

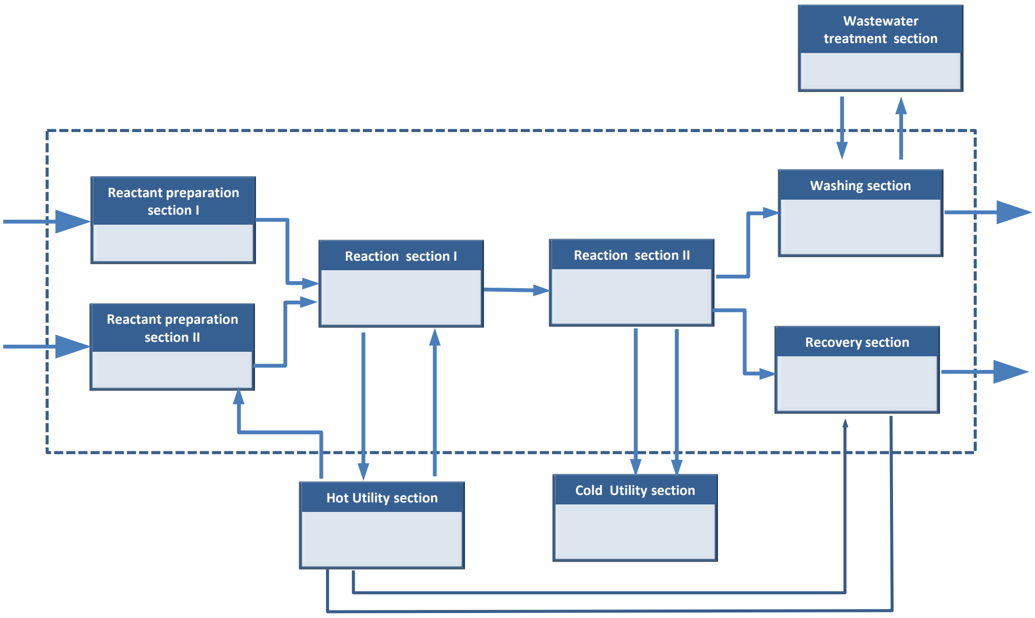


Figure 3.43. A generic decomposition of a process

Classification of the streams according to waste and useful streams: As highlighted in Section 3.2.2, the evaluation of exergy efficiencies requires a classification of outlet material streams of each functional zone as waste stream or useful streams. To make this step easy, by default, process simulator will consider all the outlet streams as useful streams. Depending on the considered process, the engineer will use his knowledge of the process to change the status of some outlet material streams from "useful" to "waste".

3.4.1.2 Diagnosis of the process

The second stage is performed using the process simulator and the model implemented in stage 1. This stage can be decomposed in 2 steps.

Exergy balance on the global process (calculation of exergy efficiency): The exergy coefficient less than η_{max} means the process under operation has potential for improvements. Note that this value is chosen by the user. In the case study presented in Chapter 5, the coefficient of utilizable exergy coefficient is chosen as the exergy efficiency and the value of 0.95 is taken for η_{max}.

Classify the process zone according to their exergy efficiency: The exergy efficiency makes it possible to determine the critical points of the system. It means that exergy efficiency makes a hierarchy of unit operation in such a way that measures can be applied in the units operations where they will be most effective. This stage aimes at classifying the functionnal zones according to their exergy efficiency in order to locate the major energy savings.

3.4.1.3 For each zone: proposal of a retrofit scheme

As mentioned before, most of the case studies in the literature stop at the end of the second stage. In the methodology we propose, the third stage used the results of the second one to identify and solve the main source of exergy losses. For that purpose, each functional zone is analyzed more precisely.

First, a graphical representation of the external and internal exergy losses occurring in each unit operation with bar and pie diagrams (Figure 3.44, Figure 3.45, Figure 3.46 and Figure 3.47) are proposed.

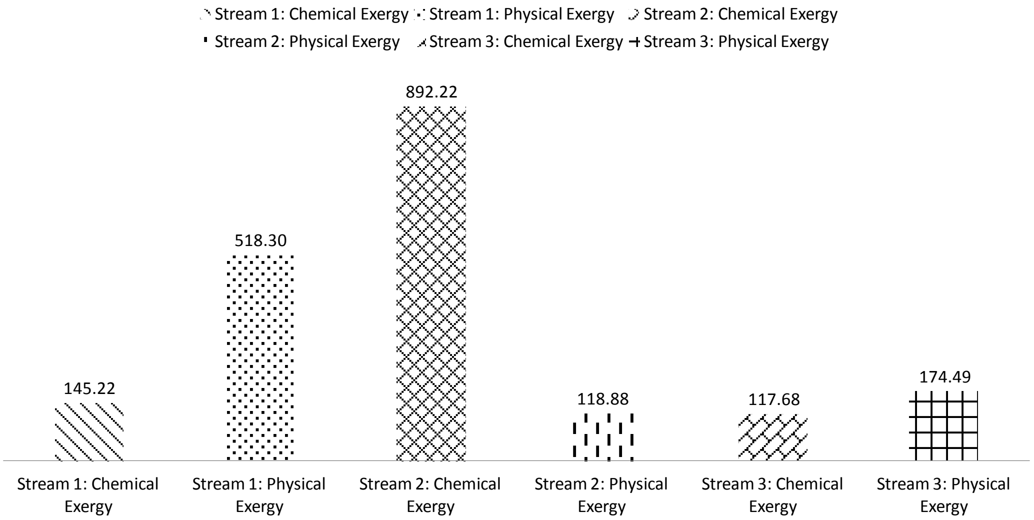


Figure 3.44. Bar diagram for external exergy losses

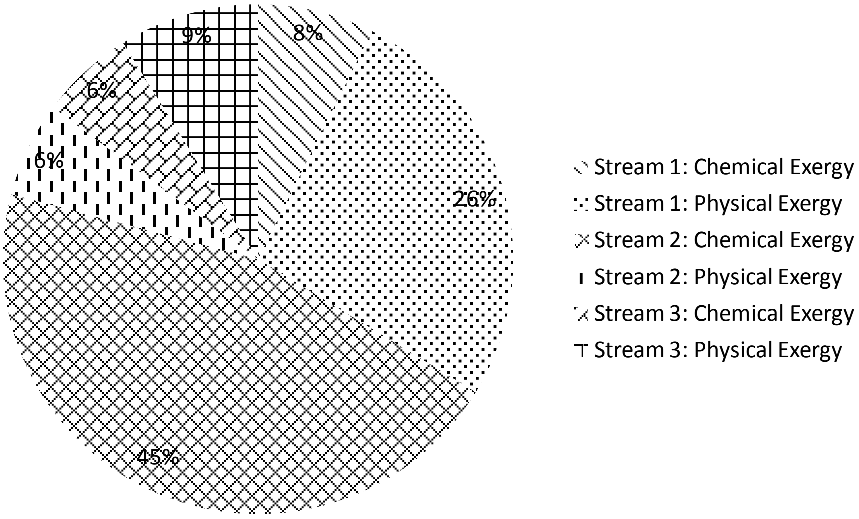


Figure 3.45. Pie diagram for external exergy losses

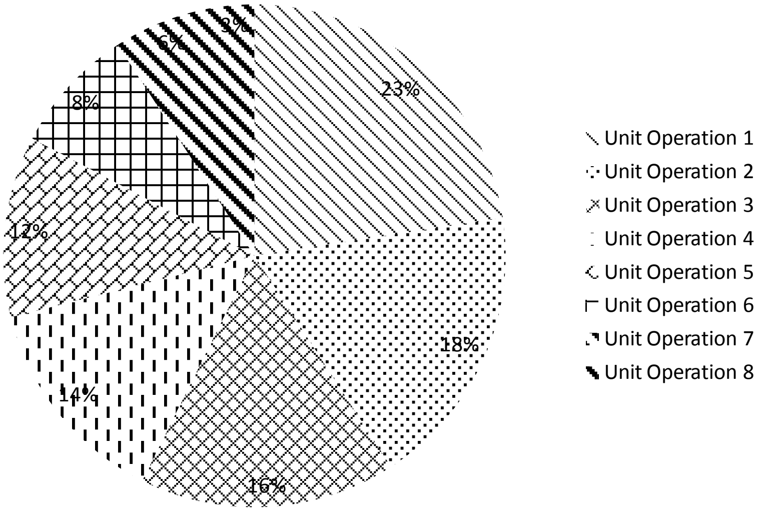


Figure 3.46. Pie diagram for internal exergy losses

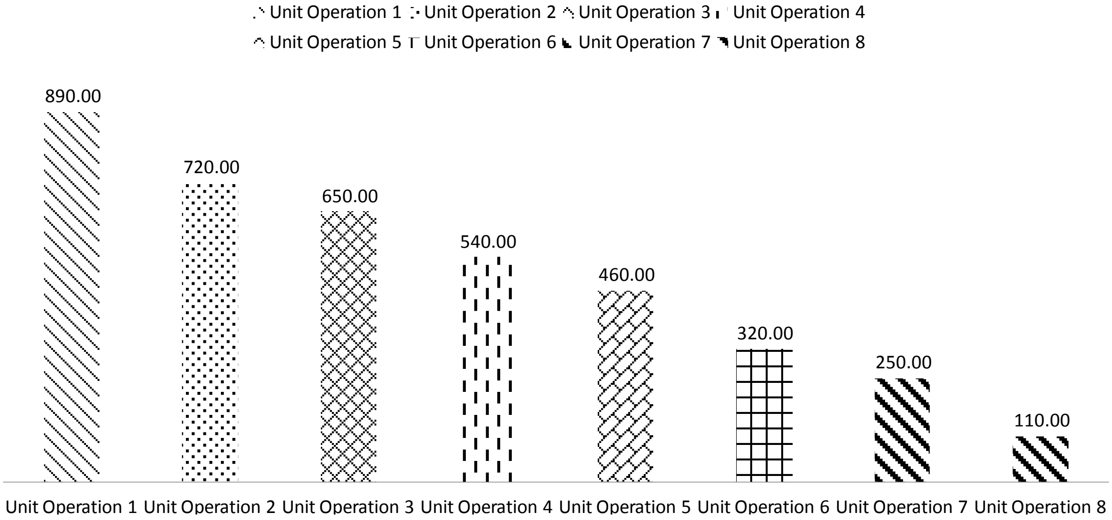


Figure 3.47. Bar diagram for internal exergy losses

Then, solutions are proposed. Generally speaking, the internal exergy losses can be reduced through development of the process or technology improvement. Based on the analysis made on the Section 3.2, one can identify technical solutions to improve the performances of the process to complete this task, Table 3.2 which enumerates the major sources of irreversibility and gives us the ways for process improvement on each class of unit operations can be used.

Concerning external exergy losses, they can be reduced by means of thermal, mechanical and chemical treatment of effluents. Section 3.2.2 shows several ways to exploit the exergy associated with them. One can identify technical solutions to improve the performances of the process based on Table 3.3 which enumerates the ways for process improvement on each type of external loss.

At the end of this step, all the technological solutions have been listed. Certainly all these solutions cannot be implemented either for economic reason or because of technical constraints inherent to the process. This third step aims at selecting the most relevant modifications. Finally, the simulation of the retrofit scheme is performed in order to check the accuracy of proposed solutions.

3.4.1.4 Optimization of the process

The former stage may have pointed out some degree of freedom such as operating parameters of some critical unit operation (e.g. operating pressure or temperature, reflux ratio). For that reason, the last stage of the methodology recommends an optimization step in order to determine the optimal values for these parameters. To find the optimum solution, a trade-off between exergy efficiency (e.g. utilizable exergy coefficient) and capital cost is performed.

3.5 CONCLUSION

This chapter presents the formulation of exergy balances on a real process. To do so, in addition of exergy of material stream calculated in Chapter 2, in this chapter, the exergy of work and heat are calculated. After exergy balance, its results are exploited in such a way to make modification on the process flowsheet to reduce exergy losses. Dividing exergy losses into two categories of internal and external, different solution are presented. For each category of exergy loss, the source of losses and the way for improvement are presented. These are tabulated to become as a guideline tool to serve engineers as a panel of solutions. To illustrate the application of these tables, different examples are presented as well.

In addition of exergy losses, to optimize the process properly, the exergy efficiencies are reviewed to find the most proper one to be implemented in a process simulator. It has been illustrated through a step-wise illustrative examples, that intrinsic efficiency and utilizable exergy coefficient not only eliminates the need for user interactions, but also makes it possible to calculate exergy efficiency of different unit operations together in a given zone. Ultimately, the utilizable exergy coefficient appears to be most promising as it excludes from the numerator the waste streams.

Furthermore, a complete methodology is presented starting from the diagnosis of the process according to exergetic criteria and resulting in a set of proposals for modification and improvement of the process. Moreover, our methodology is implemented in commercial process simulator to promote its utilization by any engineer. Although exergy analysis by definition aims to serve as a tool for conceptual process design, this approach is real engineering approach toward achieving this objective. Particularly, it is a rigorous approach for dealing with industrial flowsheets with several zones and also different process constraints.

PART III

IMPLEMENTATION AND APPLICATIONS

CHAPTER 4

Implementation of Exergy and Exergy Analysis in a Process Simulator

4.1 EXERGY ANALYSIS USING PROCESS SIMULATORS

As highlighted in Section 2.1.2, a lot of exergy analysis studies have been published in the literature since 1985. For example, Kotas (1985) carried out the exergy analysis based on the manual calculation without using any software. This means that in addition of need for competence of exergy experts, the procedure for exergy analysis was cumbersome. As shown in the Chapter 2 and 3 implementation of exergy analysis in process simulators, requires exergy calculation along with the traditional energy and mass balances. However, to facilitate this step of exergy analysis, during these last ten years, each case study usually gave rise to the development of dedicated exergy calculation tools. Some of these studies performed in Aspen Plus are reported in Table 4.1 and are classified according to the application fields (petrochemicals, utility systems, renewables). The tools used for exergy analysis for theses case studies only use the results of mass and energy balance from process simulator and then calculate exergy somewhere outside of the process simulator. Although these tools provided satisfactory results for the considered case study, they did not contribute to obtain a generic tool usable later for other case studies. To fill this gap, some authors have attempted to integrate exergy tools in the same commercial process simulators as presented in next section.

Table 4.1. List of some exergy analysis case studies in Aspen Plus

Type of process	*Reference*	*Description*
Petrochemicals	(Araújo et al., 2007)	Distillation processes
	(Wang & Zheng, 2008)	Natural Gas-based Acetylene Process
	(Hajjaji et al., 2012)	Hydrogen production via the steam methane reforming process
	(Tzanetis et al., 2012)	Sorption enhanced and conventional methane steam reforming
Renewables	(Ptasinski et al., 2002)	Methanol from the sewage sludge process
	(Panopoulos et al., 2006a)	High temperature solid oxide fuel cell integrated with novel thermal biomass gasification
	(Delsman et al., 2006)	Integrated fuel processor and fuel cell (FP–FC) system
	(Ojeda & Kafarov, 2009)	Enzymatic hydrolysis reactors for transformation of lignocellulosic biomass to bioethanol
	(Ojeda et al., 2011)	Ethanol production from lignocellulosic biomass
	(Vitasari et al., 2011)	Biomass-to-synthetic natural gas (SNG) process via indirect gasification of various biomass feedstock
	(Cohce et al., 2011)	Biomass-based hydrogen production system
	(Ofori-Boateng et al., 2012)	Microalgal and jatropha biodiesel production plant
	(van der Heijden & Ptasinski, 2012)	Thermochemical ethanol production via biomass gasification and catalytic synthesis
	(Peralta-Ruiz et al., 2012)	Microalgae oil extraction based on exergy analysis
Utilities	(Bram & De Ruyck, 1997)	Evaporative cycle

	(Vidal et al., 2006)	Refrigeration
	(Panopoulos et al., 2006a)	Hydrogen fired combined cycle with natural gas reforming and membrane assisted shift reactors for CO2 capture
	(Tirandazi et al., 2011)	C2+ recovery plants refrigeration cycles
	(Xie et al., 2012)	Fuel cell based micro combined heat and power cogeneration system
	(Gutiérrez Ortiz et al., 2012)	The supercritical water reforming of glycerol for power production
	(Ratlamwala & Dincer, 2012)	Cu-Cl cycle based integrated system for hydrogen production
	(Espirito Santo, 2012)	A building internal combustion engine trigeneration system
	(Mahabadipour & Ghaebi, 2013)	Development and comparison of two expander cycles used in refrigeration system of olefin plant based on exergy analysis

4.1.1 ExerCom: calculation of exergy for Aspen Plus and Pro/II [1](Scheihing, 2004)

ExerCom is a plug-in software routine to calculate exergy in Aspen and Pro/II (see Figure 4.1). It has been developed and is owned by Jacobs Consultancy in Leiden (The Netherlands). It aims at calculating the exergy of gases and liquids in a flowsheet modeled in Aspen or Pro/II. It calculates the chemical exergy according to Szargut's reference state, a mixing exergy and the physical exergy using the formulation described by (Hinderink et al., 1996). Additionally, it calculates a list of enthalpies relatives the reference conditions of Szargut. The database for the standard chemical exergy and enthalpy can be changed by the user. The result of the calculation is then added to the stream output and can be exported for further processing (Scheihing, 2004).

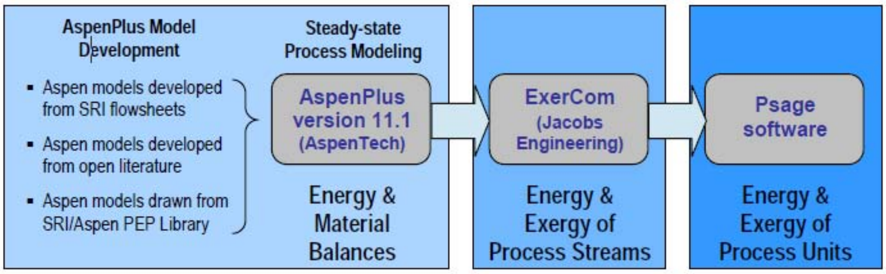


Figure 4.1. ExerCom for Aspen and Pro/II(Scheihing, 2004)

Moreover, the additional Psage-developed program interfaces directly with the Aspen Plus and ExerCom results to calculate exergies of heat, work, and solid streams around individual process units and the overall process model. Exergies of heat streams not calculated by ExerCom are computed from enthalpies using the Carnot quality factor. Exergy inflows not included within the model boundaries (mainly refrigeration and separation units) are estimated based on exergetic efficiencies of similar units.

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[1] http://www.cocos.nl/en/548/ccs/ccs_energieadvies.html

ExerCom was used for exergy analysis of advanced separation enhanced water-gas-shift membrane reactors (Carbo et al., 2006) and an oxy-combustion process for a supercritical pulverized coal power plant with CO_2 capture (Fu & Gundersen, 2010).The power efficiency penalty related CO_2 capture is 10.2 % points, where the air separation unit contributes 6.6 % points and the purification-compression unit contributes 3.6 % points. The main exergy losses related to CO_2 capture take place in the compressors in the air separation unit and the purification-compression unit. If the CO_2 recovery rate decreases from 95.1 % to 91.5 %, the power efficiency can be increased 0.3 % points. The net power efficiency can be increased 0.2 % points by heat integration between the air separation unit and the purification-compression unit. The power efficiency can be further improved by an optimal design of the sub-ambient heat exchanger network.

4.1.2 Open-source calculator for Sim42 (Montelongo-Luna et al., 2007)

Based on the method described (Hinderink et al., 1996), an open-source exergy calculator of material streams for the open-source chemical process simulator of Sim42 (Cota Elizondo, 2003) was developed (Montelongo-Luna et al., 2007). As Sim42 is an open source program, this permitted the seamless inclusion of the exergy calculations into the source code of the simulator without linking any external computer routines to the simulator. Unlike most chemical exergy calculators, its chemical exergy is calculated based on a uncommon reference environment (van Gool, 1998). This exergy calculator does not carry out the full exergy balance including heat and work stream. This open-source exergy calculator was recently used for development of the a new exergetic criterion (Montelongo-Luna et al. 2011) to measure the relative exergetic efficiency and the controllability of a process when a proposed process and control structure is postulated.

4.1.3 Excel and VB-based tools (Querol et al., 2011; Abdollahi-Demneh et al., 2011)

A Microsoft Excel-based exergy calculator for Aspen Plus® which facilitates the thermoeconomic analysis has been developed (Querol et al., 2011). It calculates exergy of heat, work and material streams where the mixing exergy is being considered to be a part of physical exergy. The reference environment is based on the most common one (Szargut et al., 1988). This tool presents some critical shortcomings as it requires very strict constraints concerning the Aspen model characteristics: the main one is associated with rules for the name of equipments and streams. For example, all the streams must be named with 5 digits; the first 3 are equal for all the streams with same composition. These rules make exergy analysis not user-friendly as expected when it is integrated in a commercial process simulator such as Aspen Plus.

Another tool based upon Visual Basic enables the calculation of exergy for of material streams in Aspen HYSYS has been developed where the chemical exergy is itself being considered to be composed of different components (Abdollahi-Demneh et al., 2011). The used reference environment (Szargut et al., 1988) can be adapted to the case under study by modifying of the reference temperature, pressure and composition but its database covers a limited number of chemical elements. Furthermore, proposed procedure for exergy calculation has been implemented by utilizing fifteen main user variables for material streams. For exergy analysis via process simulator softwares such as HYSYS, it is better to access the physical and chemical exergies of process streams within the flowsheet. This is not achievable unless user variables defined for process stream. For example, the required Visual Basic (VB) code for user variable named Ambient Temperature which is applicable to each of the user variables by changing the name of user variable within the VB code.

Although such computer-aided exergy calculations make exergy analysis more accessible, exergy analysis within process simulators is not still straightforward. When specifying the constraints of an implementation of exergy analysis in ProSimPlus, our main priority was to make the calculation of exergy as easy and straightforward as enthalpy calculations.

To achieve this goal, a first VBScript based prototype of the exergy calculation tool has been developed and validated through academic examples. Then based upon these tests, a complete specification draft for an integration of the exergy function in the Simulis Thermodynamic software has been prepared. This chapter presents the VBScript prototype and its results and summarizes the important specifications.

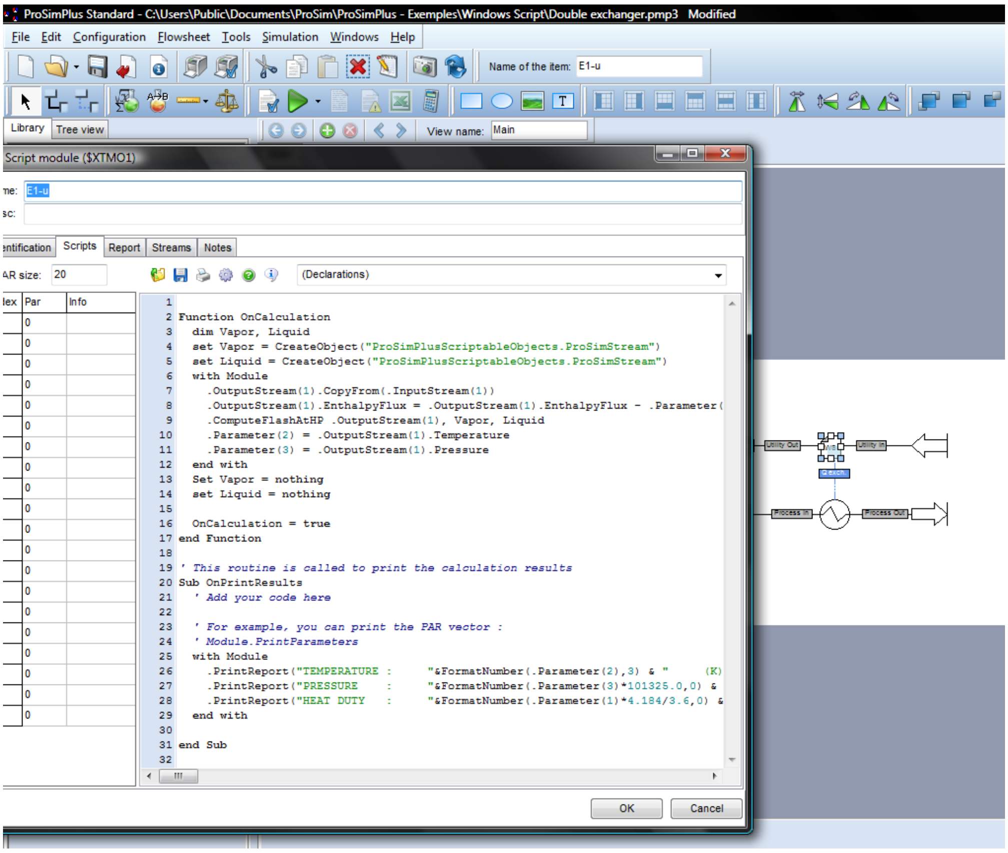
4.2 EXERGY CALCULATION OF MATERIAL STREAMS IN PROSIMPLUS

4.2.1 A VBScript library dedicated to material stream exergy calculation

4.2.1.1 Description of the scriptlet

In a first step, a prototype has been developed using the VBScript language in ProSimPlus to give different subroutines for calculating the components of the exergy of material streams. The Windows Script module (Figure 4.2) makes it possible to create quickly and simply your own modules of calculation in the ProSimPlus simulation environment. These modules, once created, can be used exactly in the same way as those which are provided with ProSimPlus. Their use is completely transparent and does not need any additional handling. Each Windows Script module is described (programmed) directly in the ProSimPlus graphical environment using a simple but powerful language. This language, Microsoft VBScript, is a simplified version of Microsoft Visual Basic. It allows writing simply the source code of a module.

This macro use the result of mass and enthalpy balance at the end of simulation by ProSimPlus and also use the accessible functions of the Simulis to calculate exergy of streams based on the equations given in Chapter 2.



ProSimPlus Standard - C:\Users\Public\Documents\ProSim\ProSimPlus - Exemples\Windows Script\Double exchanger.pmp3 Modified

Name of the item: E1-u

View name: Main

Script module ($XTMO1)

ne: E1-u

AR size: 20

(Declarations)

```
Function OnCalculation
  dim Vapor, Liquid
  set Vapor = CreateObject("ProSimPlusScriptableObjects.ProSimStream")
  set Liquid = CreateObject("ProSimPlusScriptableObjects.ProSimStream")
  with Module
    .OutputStream(1).CopyFrom(.InputStream(1))
    .OutputStream(1).EnthalpyFlux = .OutputStream(1).EnthalpyFlux - .Parameter(
    .ComputeFlashAtHP .OutputStream(1), Vapor, Liquid
    .Parameter(2) = .OutputStream(1).Temperature
    .Parameter(3) = .OutputStream(1).Pressure
  end with
  Set Vapor = nothing
  set Liquid = nothing

  OnCalculation = true
end Function

' This routine is called to print the calculation results
Sub OnPrintResults
  ' Add your code here

  ' For example, you can print the PAR vector :
  ' Module.PrintParameters
  with Module
    .PrintReport("TEMPERATURE :     "&FormatNumber(.Parameter(2),3) & "     (K)
    .PrintReport("PRESSURE    :     "&FormatNumber(.Parameter(3)*101325.0,0) &
    .PrintReport("HEAT DUTY   :     "&FormatNumber(.Parameter(1)*4.184/3.6,0) &
  end with

end Sub

```

Figure 4.2. Windows Script in ProSimPlus®

The calculation of the exergy is based on the procedures (Figure 4.3) which are described as follows:

- Definition of the reference environment (subroutine *DefinitionReferenceEnvironment)*

This procedure is used to define the conditions for the reference environment. The database of standard chemical exergy (Rivero& Garfias, 2006a) is used at the fixed temperature, pressure and composition as pointed out in Chapter 2. This procedure must be called before calculating of molar exergy of streams.

- Split multiphasic streams (subroutine SplitStream)

As mentioned in Section 2.2.1, the streams are supposed to be monophasic. This procedure is used to split multiphasic stream into several monophasic streams and then to calculate the exergy of each monophasic stream.

- Standard chemical exergy calculation for each cluster of components (subroutine StdChemExergyDataBank)

This procedure is used to build a data bank of standard chemical exergy of components existing in the flowsheet. To do so, first each component is broken down into its chemical elements using the DecompFormula. Then, for each stream to calculate the molar chemical exergy, the standard chemical exergy will be called by ChemExStd_Finder. The ElementStdChemEx (i.e. a database containing the chemical exergy of all elements including the standard database available with Simulis Thermodynamics) are matched with DecompFormula to calculate the chemical exergy.

- Molar physical exergy calculation for each material stream (subroutine *PhysExergyMaterialStream)*

This procedure calculates the physical exergy of the material stream. It uses procedure of CalcH&S to call enthalpy and entropy functions from Simulis Thermodynamics. As a part of PhysExergyMaterialStream, another procedure MecaThermEx (based on the procedure of CalcHAndS) calculates the contributions of mechanical and thermal exergy.

- Molar chemical exergy calculation for each material stream (subroutine *ChemExergyMaterialStream)*

This procedure calculates the chemical exergy of the material stream starting with calling StdChemExergyDataBank as a procedure to calculate the standard chemical exergy of the component found in the flowsheet based on the calculation methodology given in literature (Rivero& Garfias, 2006a).

- Chemical, physical and total exergy flow calculation for each material stream (subroutine *ExergyFlow)*

Having calculated molar exergy of streams, now the exergy flow in kW is computed to let the user for further exergetic criteria. As the exergy breakdown into chemical, thermal and mechanical are known in the mole basis, accordingly the exergy flow breakdown will be provided in thermal, mechanical, chemical components as well as total exergy flow.

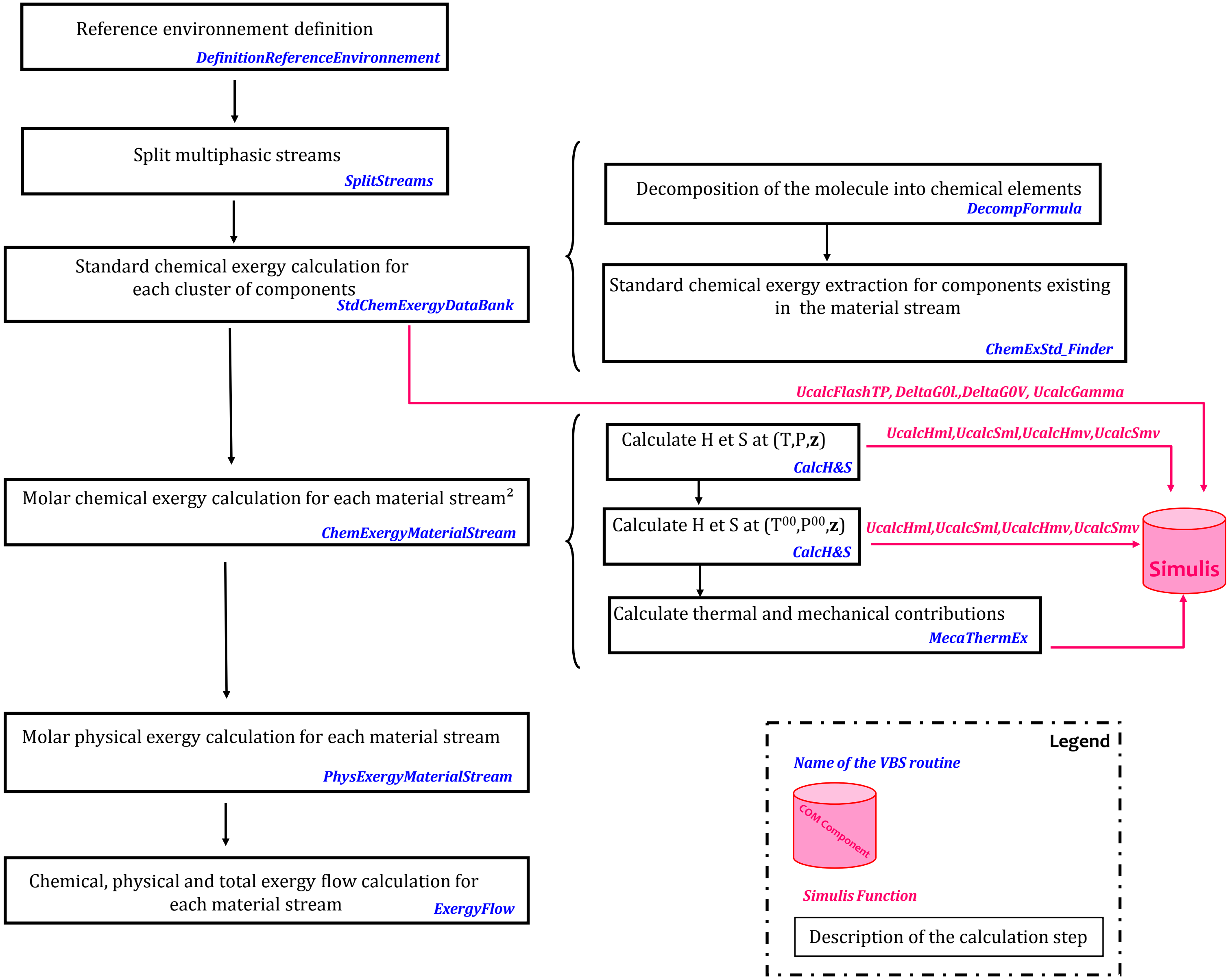


Figure 4.3. Calculation of exergy of material streams in ProSimPlus®

4.2.1.1 Integration in ProSimPlus as Scriptlets

ProSimPlus allows the user to easily develop calculation routines involving available thermodynamic functions. As a consequence, it has been decided to develop the preliminary exergy calculation tool using the ProSimPlus Scriptlets functions. As illustrated in Figure 4.4, by copying the VB Script code in ProSimPlus installation directory, the new function becomes available to any user of the software. The list of Scriptlets in the group of Exergy as a menu, appears by right-clicking on the project area.

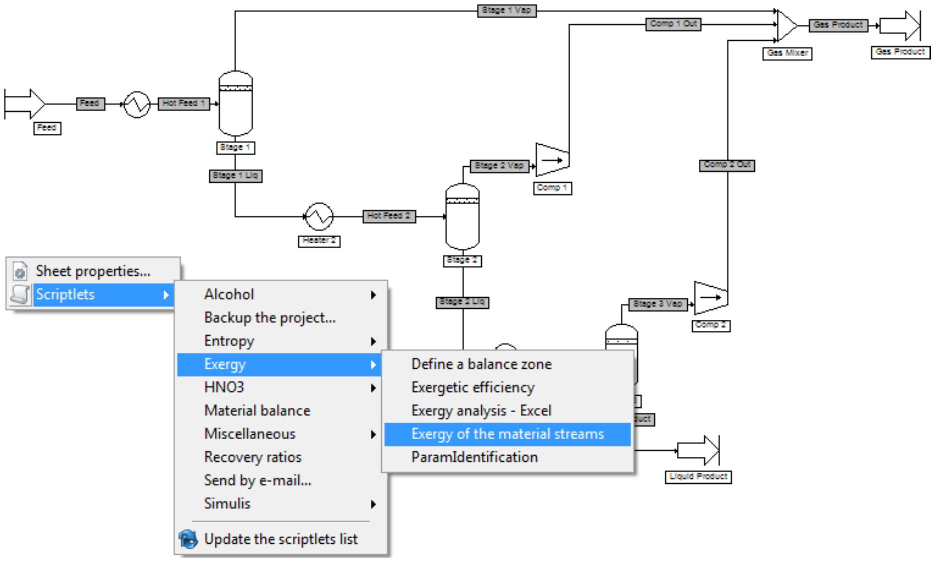
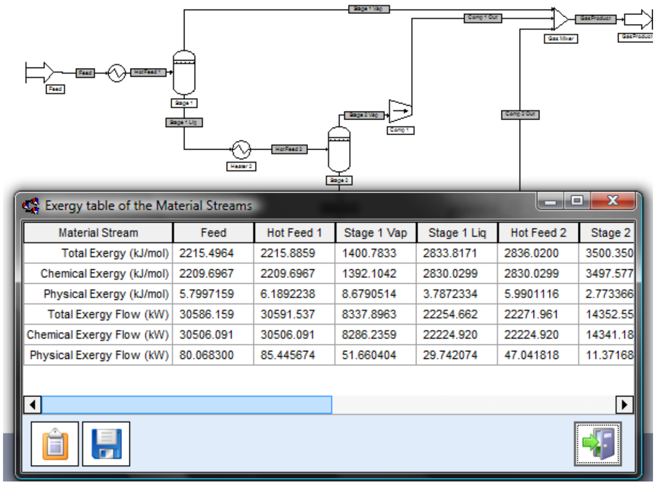


Figure 4.4. Calling the Scriptlet for material stream

4.2.2 Presentation of results

4.2.2.1 Exergy tables

By calling the scriptlet “Exergy of Material Streams” associated to the global flowsheet, the calculation of exergies for all the material streams contained in the flowsheet is performed and a table (Figure 4.5) containing the molar chemical and physical exergies and the exergy flux is displayed.

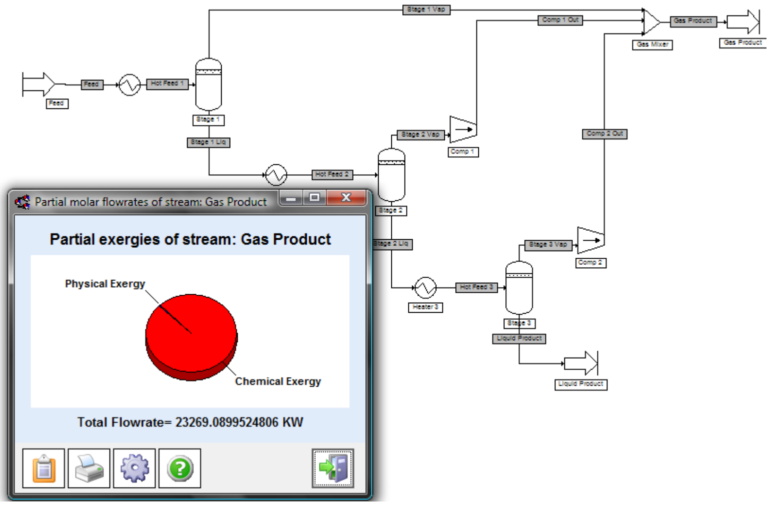


Material Stream	Feed	Hot Feed 1	Stage 1 Vap	Stage 1 Liq	Hot Feed 2	Stage 2
Total Exergy (kJ/mol)	2215.4964	2215.8859	1400.7833	2833.8171	2836.0200	3500.350
Chemical Exergy (kJ/mol)	2209.6967	2209.6967	1392.1042	2830.0299	2830.0299	3497.577
Physical Exergy (kJ/mol)	5.7997159	6.1892238	8.6790514	3.7872334	5.9901116	2.773366
Total Exergy Flow (kW)	30586.159	30591.537	8337.8963	22254.662	22271.961	14352.55
Chemical Exergy Flow (kW)	30506.091	30506.091	8286.2359	22224.920	22224.920	14341.18
Physical Exergy Flow (kW)	80.068300	85.445674	51.660404	29.742074	47.041818	11.37168

Figure 4.5. Table of exergy of material streams in ProSimPlus®

4.2.2.1 Exergy distribution of streams

Another Scriptlet has been developed to visualize the distribution of exergy of stream in form of pie diagrams. The menu of exergy appears by a right-click on a stream. It displays the exergy breakdown into chemical exergy and physical exergy. Note that except for streams encountered in utility systems mainly containing water, it is not surprising to observe a chemical exergy much greater than the physical exergy. An illustration of the results of this Scriptlets is given in Figure 4.6.



Partial exergies of stream: Gas Product

Total Flowrate= 23269.0899524806 KW

Figure 4.6. Distribution of exergy of material streams in ProSimPlus®

4.2.3 Validation

The proposed calculation methodology must now be validated through various case studies of the literature. Although the numerical examples of calculation of exergy flow are not numerous, we can rely on three numerical examples provided by literature (Kotas, 1985; Hinderink et al., 1996; Montelongo-Luna et al., 2007).

- *Example 1: Gaseous stream*

A numerical example from literature (Kotas, 1985) is taken to calculate exergy of a mixture of air and carbon monoxide at a temperature of 125°C and a pressure of 2.1 bar. This stream is gaseous both at the given temperature and pressure and also in the reference conditions. This makes possible to measure the deviation when there is no phase change. The simulation was performed by ProSimPlus using the ideal model. The simulation data are listed in Table 4.2.

Table 4.2. Data for simulation (Kotas, 1985)

Parameter	*Value*
Mass flowrate (kg/s)	0.5
Molar fraction of Air	0.85
Molar fraction of CO	0.15
T (°C)	125
P (bar)	2.1
Model	Ideal

The comparison between the results of literature (Kotas, 1985) and our calculator are given in Table 4.3. It can be seen that the values obtained are very close to those of the literature.

Table 4.3. Comparison of results

	ProSimPlus	(Kotas, 1985)	*Deviation (%)*
Chemical exergy (kW)	697.7	698.4	0.1
Physical exergy (kW)	38.3	38.9	1.5

The deviation in chemical exergy is due to different reasons. The main one is using different tables of standard chemical exergy. In our work, we have used the recent standard table (Rivero & Garfias, 2006a) compared to reference (Kotas, 1985). In addition, the deviation related to physical exergy is relatively higher. This is mainly due to the assumption where the mixture is taken to behave as an ideal mixture.

- *Example 2: Liquid / vapor stream at (T^{00}, P^{00})*

It is particularly difficult to find in the literature a detailed numerical example for liquid/vapor stream at (T^{00}, P^{00}). However, the example presented here are taken from the literature (Hinderink et al., 1996). This example allows measuring the deviation associated with phase transition. This stream is fully vapor at 150°C and partially liquid at T^{00} and P^{00} (vapor fraction: 0.8). The data required for the simulation of the stream are given in Table 4.4.

Table 4.4. Data for simulation (Hinderink et al., 1996)

Parameter	*Value*
Mass flowrate (mol/s)	1000
Molar fraction of H2O	0.22
Molar fraction of N2	0.75
Molar fraction of CO2	0.02
Molar fraction of NO	0.005
Molar fraction of CO	0.005
T (°C)	150
P (atm)	1
Model	SRK

The literature (Hinderink et al., 1996) defines a term corresponding to the exergy of mixing, which in our case is spread over the chemical and physical exergies. It is therefore impossible to validate the calculation of chemical and physical contributions. However, we can compare the value of the total exergy (Table 4.5). The low difference between the examples in the literature and our own calculation validates the calculation of exergy of streams. The deviation in total exergy might be due to different reasons. The first one is different vapor faction of the stream at T^{00}, P^{00} as two different simulators are used to flash the stream to T^{00}, P^{00}. As reported in Table 4.6, as a consequence of deviation of composition of vapor phase at T^{00}, P^{00}, there will be an obvious deviation in result of exergy. Second reason is use of different standard chemical exergy tables. In our work, we have used the recent standard table (Rivero & Garfias, 2006a) compared to reference (Szargut, 1988).

Table 4.5. Comparison of results

	ProSimPlus	(Hinderink et al., 1996)	*Deviation (%)*
Exergy (kW)	3746.8	3977	5.8

Table 4.6. Comparison of composition of streams in Aspen Plus and ProSimPlus at T^{00} and P^{00}

	ProSimPlus		(Hinderink et al., 1996)	
Phase	Liquid	Vapor	Liquid	Vapor
Mole fraction				
Water	1.00	0.0310	1.00	0.0227
Nitrogen	0.00	0.9317	0.00	0.9398
Carbon dioxide	0.00	0.0248	0.00	0.0251
Nitric oxide	0.00	0.0062	0.00	0.0063
Carbon monoxide	0.00	0.0062	0.00	0.0063

In summary, calculation of the molar exergy of a mixture by the equations given in Chapter 2, results in 1.5% and 5.8% deviation from the examples taken from literature (Kotas, 1985; Hinderink et al., 1996), respectively.

- *Example 3 : Global flowsheet*

The last validation example concerns a global process. The process is dedicated to the Natural Gas Liquid recovery (Montelongo-Luna et al., 2007). The exergy analysis of this process in the reference paper has some ideal assumptions which make the process far from real conditions. For example, the flash separation at stage 1, 2 and 3 were chosen to be isentropic in literature (Montelongo-Luna et al., 2007). However, in this step to have a comparable simulation file, only for the purpose of validation, the process conditions are taken as they were in the literature. But in Chapter 5, there have been some modifications on conditions of process to obtain more realistic conditions.

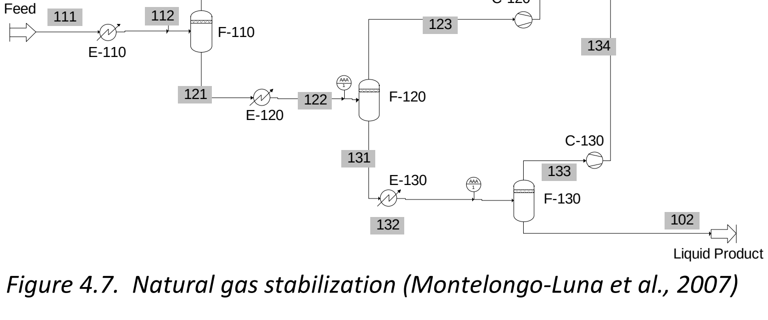


Figure 4.7. Natural gas stabilization (Montelongo-Luna et al., 2007)

The deviation in molar exergy might be due to different reasons. The first one is different composition of stream at T^{00}, P^{00} as two different simulators are used to flash the stream to T^{00}, P^{00}. Second reason is use of different standard chemical exergy tables. In our work, we have used the recent standard table (Rivero & Garfias, 2006a) compared to reference (van Gool, 1998).

Table 4.7 summarizes the results of validation by comparing the results obtained by (Montelongo-Luna et al., 2007) with the ones obtained using the macro we developed. Although in the reference work (Montelongo-Luna et al., 2007) different RE (van Gool, 1998) is chosen, it can be seen the maximum deviation for molar exergy flow is 2.35% which is acceptable. The deviation in molar exergy might be due to different reasons. The first one is different composition of stream at T^{00}, P^{00} as two different simulators are used to flash the stream to T^{00}, P^{00}. Second reason is use of different standard chemical exergy tables. In our work, we have used the recent standard table (Rivero & Garfias, 2006a) compared to reference (van Gool, 1998).

Table 4.7. Validation with the literature

Material Stream	*Total Exergy (kJ/mol)*		
	ProSimPlus	Literature	Deviation %
111	2215.50	2164.63	2.35
112	2215.89	2164.63	2.37
113	1400.78	1373.17	2.01
121	2833.82	2788.01	1.64
122	2836.02	2790.20	1.64
131	3500.35	3461.02	1.14
132	3502.46	3463.00	1.14
123	2108.40	2109.33	-0.04
124	2110.36	2111.30	-0.04
133	2852.35	2882.63	-1.05
134	2859.87	2889.87	-1.04
102	4466.14	4490.76	-0.55
101	1913.63	1905.28	0.44

4.3 CONCLUSION

For the purpose of exergy balance, all types of exergy associated with material, heat and work streams in a process and its related utilities, has to be calculated. In this chapter, implementation aspects of exergy calculations related to material streams in ProSimPlus are presented. Having reviewed different existing exergy tools in commercial process simulators, enable us to implement exergy in our process simulator in a more user friendly way. In the developed calculator, the exergy is now as accessible as enthalpy in ProSimPlus. This means after simulation, exergy of streams can be seen for each single stream. However, the calculation type of exergy is limited to retrofit case. Further implementation aspects of exergy analysis in ProSimPlus will be carried out in a project funded by ANR.

CHAPITRE

5

Application: NGL Recovery Process

5.1 INTRODUCTION

As demonstrated in Chapters 2 and 3, exergy analysis is an efficient tool dedicated to the diagnosis and retrofitting of existing processes. It enables to pinpoint the major source of inefficiencies of a given process and suggest guidelines for improving and optimizing its performances. In Chapter 3, the implementation of exergy calculation in ProSimPlus simulator has been validated with different examples from literature. In this chapter, the value of the developed tool is demonstrated and the concepts discussed in the previous chapters are illustrated through a simple example.

The case study concerns the Natural Gas Liquid recovery process already analyzed by Montelongo-Luna et al. 2007. The exergy analysis of this process in the reference paper has several shortcomings which need to be overcome. First, with an estimated value close to one, the use of simple exergy efficiency is not adequate to promote the exergy. Then, the case study only considers the NGL process excluding the utility system, which is not relevant when trying to optimize the energy efficiency of an integrated process. Finally, the presented analysis was limited to internal exergy losses without taking into account external exergy losses. Above all, no step-wise approach was presented to show how we can use exergy analysis as a diagnostic tool for improvement of the existing process.

All these above-mentioned limitations become an incentive to take this sample flowsheet and enrich it considerably for analysis with use of a generic step-wise exergy analysis which could be general and applicable for any flowsheet.

5.2 DESCRIPTION OF THE PROCESS

Natural Gas Liquid (NGL) is a term for the mixtures of methane, ethane, propane, butane, and natural gasoline extracted from natural gas. Natural gas liquids recovery consists in removing and gathering propane, butane and other heavier hydrocarbon products from natural gas. The process is often used to reduce a gas stream's heating value to meet pipeline tariff requirements while removing excess liquids that may condense and cause problems in transmission. The liquids are accumulated in an on-site tank and later trucked to a refinery for fractionation into its saleable hydrocarbon components. The end results is a gas stream that meets pipeline quality standards with the benefit of a by-product which provides additional revenue for the producer (Tuckergas 2012).

Figure 5.1 represents the block flow diagram for a stabilization train of natural gas containing traces of oil. To satisfy the specifications of marketing, natural gas needs to be stabilized. In this process, the natural gas (C1 to C9 hydrocarbons) is separated into a stabilized condensate (C4 to C9 hydrocarbons) and a saleable gas (C1 to C4 hydrocarbons). In our case, as the amount of natural gas is not so high, a full Natural Gas Liquid (NGL) recovery train is not economically justifiable and a simple stabilization scheme is chosen (Montelongo-Luna et al. 2007).

Along this process, a rich gas is heated in three heaters followed by separators where the inlet gas streams are flashed. At each step, the outlet liquid stream is sent to the next flash where the pressure is reduced further. The liquid stream from the last flash is the stabilized condensate. On the other hand, the outlet gas streams from all of the separators are mixed together with same pressure to obtain a stabilized gas product stream with the desired specifications as reported in Table 5.1 (Montelongo-Luna et al. 2007).

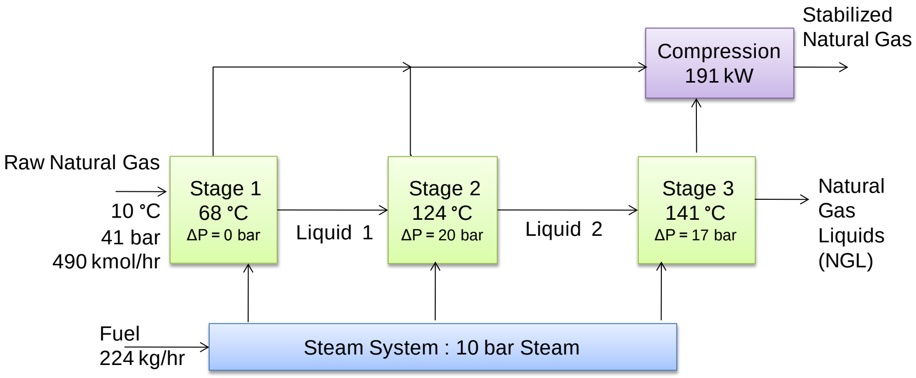


Figure 5.1. Block diagram of the NGL recovery process

Table 5.1. Specification of the NGL process

Components	*Recovery ratio (%) in gas product*	*Recovery ratio (%) in liquid product*
Methane	99.96	0.04
Ethane	99.59	0.41
Propane	98.17	1.83
Isobutane	95.40	4.60
n-Butane	93.79	6.21
Isopentane	86.90	13.10
n-Pentane	84.46	15.54
n-Hexane	69.76	30.24
n-Heptane	52.44	47.56
n-Octane	36.04	63.96
n-Nonane	23.29	76.71

To meet the heating requirements of the process, a relative high pressure steam at 10 bar with 80°C degree of superheat for all three separation stages is used (see Figure 5.1). As well as steam heating, electricity is required to drive the compressors at the second and third stages of stabilization where pressure drop causes the flash separation. The required electricity for the base case is imported from the external electricity grid.

Process Constraints: Ahead of simulation, a set of assumptions and process constraints should be taken into account. In this study, due to the constraints imposed by process side, the process conditions should be maintained as it is in the existing flowsheet. On the contrary, conditions of utility can be modified to obtain optimum conditions.

5.3 SIMULATION

5.3.1 Thermodynamic model

To represent the systems involved in different process zones as accurately as possible, ProSimPlus simulator allows the definition of different thermodynamic models. For the process under study, the following models are used:

- In the NGL process and the fuel gas combustion sections: Peng–Robinson equation of state is chosen because of the following reasons:
  - The mixture is not a liquid strongly non-ideal as it is made of hydrocarbons.
  - It has hydrocarbons lighter than C5 such as methane, ethane, propane, isobutane, n-butane and isopentane.
  - It does not have hydrogen as it is made of hydrocarbons.
  - Operating temperature is not less than -30°C as it is in the range of 10-141°C.
- The utility system exclusively contains water: a water specific thermodynamic model embedded in ProSimPlus has been chosen. This model is applicable for both water and steam as it consists of pure water.

5.3.2 Process Simulation

Figure 5.2 presents the ProSimPlus flowsheet of the process. The flowsheet is divided into two zones: the zone 1 refers to process whereas zone 2 concerns the utility system. To name the equipments, the first letter indicates the equipment type, the first number represents the process zone and the second number represents the stage if there is, e.g., F-210 is a flash in zone 2 and for the first stage. For the streams, a three-digit number is used where the first digit represents the zone, the second digit represents the stage, and the third digit represents the sequence in the flowsheet (e.g. 1 for inlet and 2 for outlet).

All the required data and specifications for the simulation of the process and the utility system are given in Table 5.2, Table 5.3, Table 5.4 and Table 5.5. The operating parameters of utility system (i.e. splitting ratio of stream 211 and 221 in the S-202, water make-up flowrate steam 251) are adjusted to obtain the desired outlet temperatures of heaters E-210, E-220 and E-230 reported in Table 5.3. In addition, the fuel flowrate (stream 261) is adjusted to keep the flue gas (stream 263) temperature equal to 300°C which is much higher than the acid dew point (140°C). As listed in Table 5.2, the feed (stream 111) (C1 to C9 hydrocarbons) has to be separated into a stabilized condensate (stream 102) (C4 to C9 hydrocarbons) and a stabilized gas (stream 101) (C1 to C4 hydrocarbons). For that purpose, a rich gas is heated in three heaters followed by separators where the inlet gas streams are flashed. As well as heating for the gas stream (streams 111, 121 and 131) at the inlet of each stage, a pressure drop is done to vaporize the volatile component into the vapor phase. The stage 1 does not have pressure drop and the separation made by heating of stream up to 68°C by low-pressure steam (stream 211). The inlet stream (stream 121) of stage 2 (F-120) is first heated up to 124°C and then it goes through a pressure drop of 2075 kPa. The inlet stream (stream 131) of stage 3 (F-130) is first heated up to 134°C and then it undergoes a pressure drop of 1700 kPa as listed in Table 5.3.

Table 5.2. Composition of the feed

	Compound	***Mole fraction***
Composition of the feed	Methane	0.316
	Ethane	0.158
	Propane	0.105
	i -Butane	0.105
	n-Butane	0.105
	i -Pentane	0.053
	n-Pentane	0.053
	n-Hexane	0.027
	n-Heptane	0.026
	n-Octane	0.026
	n-Nonane	0.026
Flowrate	490 kmol/hr	
Temperature	10 °C	
Pressure	4125 kPa	

The outlet gas streams (101) from all of the separators (F-110, F-120, F-130) should be mixed together to be sent into the pipeline. Therefore, they should be mixed with same pressure (4125 kPa) to avoid any deviation of stream which can cause the gas from one pipe goes to another pipe. To do so, the stabilized gas product from each stage is pressurized by compressors (C-120, C-130) with isentropic efficiency of 75% (see Table 5.3).

Table 5.3. Input data for process simulation

Parameter	***Value***
Outlet temperature of heater E-210 (°C)	68
Outlet temperature of heater E-220 (°C)	124
Outlet temperature of heater E-230 (°C)	134
Stage 1 (F-110) pressure drop (kPa)	0
Stage 2 (F-110) pressure drop (kPa)	2075
Stage 3 (F-110) pressure drop (kPa)	1700
Gas Product (101) pressure (kPa)	4125
C-120 isentropic efficiency	75%
C-130 isentropic efficiency	75%

To meet the heating requirements of the process, a relative high-pressure steam (stream 256) at 10 bar is used (see Table 5.4). As this steam should be hot enough to heat all three separation stages, 80°C degree of superheat is taken. The process streams (streams 111, 121, 131) are heated up by the steam condensation in heat exchangers (E-210, E-220, E-230) and condensate is throttled down to 3 bar. The condensate (stream 241) is returned at 3 bar and is mixed with the boiler water makeup (stream 251) to feed the steam boiler. Note that a small portion of steam at 10 bar (stream 254) is used in the deaerator (D-201) to separate air from return-condensate (stream 243).

Table 5.4. Input data for simulation of the utility system

Parameter	***Value***
Stack temperature (°C)	200
Degree of superheat of HP/MP steam (°C)	80
Temperature of return condensate (°C)	134
Pressure of return condensate (bar)	3

As well as steam heating, electricity is required to drive the compressors (C-120, C-130) at the second (F-120) and third (F-130) stages of stabilization where pressure drop causes the flash separation. The required electricity for the base case is imported from the external electricity grid.

The operating parameters of utility system (i.e. splitting ratio of stream 211 and 221 in the S-202, water make-up flowrate steam 251) are adjusted to obtain the desired outlet temperatures of heaters E-210, E-220 and E-230 reported in Table 5.3. In addition, the fuel flowrate (stream 261)is adjusted to keep the flue gas (stream 263) temperature equal to 300°C which is much higher than the acid dew point (140°C).

Table 5.5. Setpoints and variables for the base case

Setpoints	**Variables**
Outlet temperature of heater E-210 = 68°C	Splitting ratio of the splitter S-201
Outlet temperature of heater E-220 = 124°C	Splitting ratio of the splitter S-201
Outlet temperature of heater E-230 = 134°C	Water make-up flowrate
Flue gas temperature = 300°C	Fuel flowrate

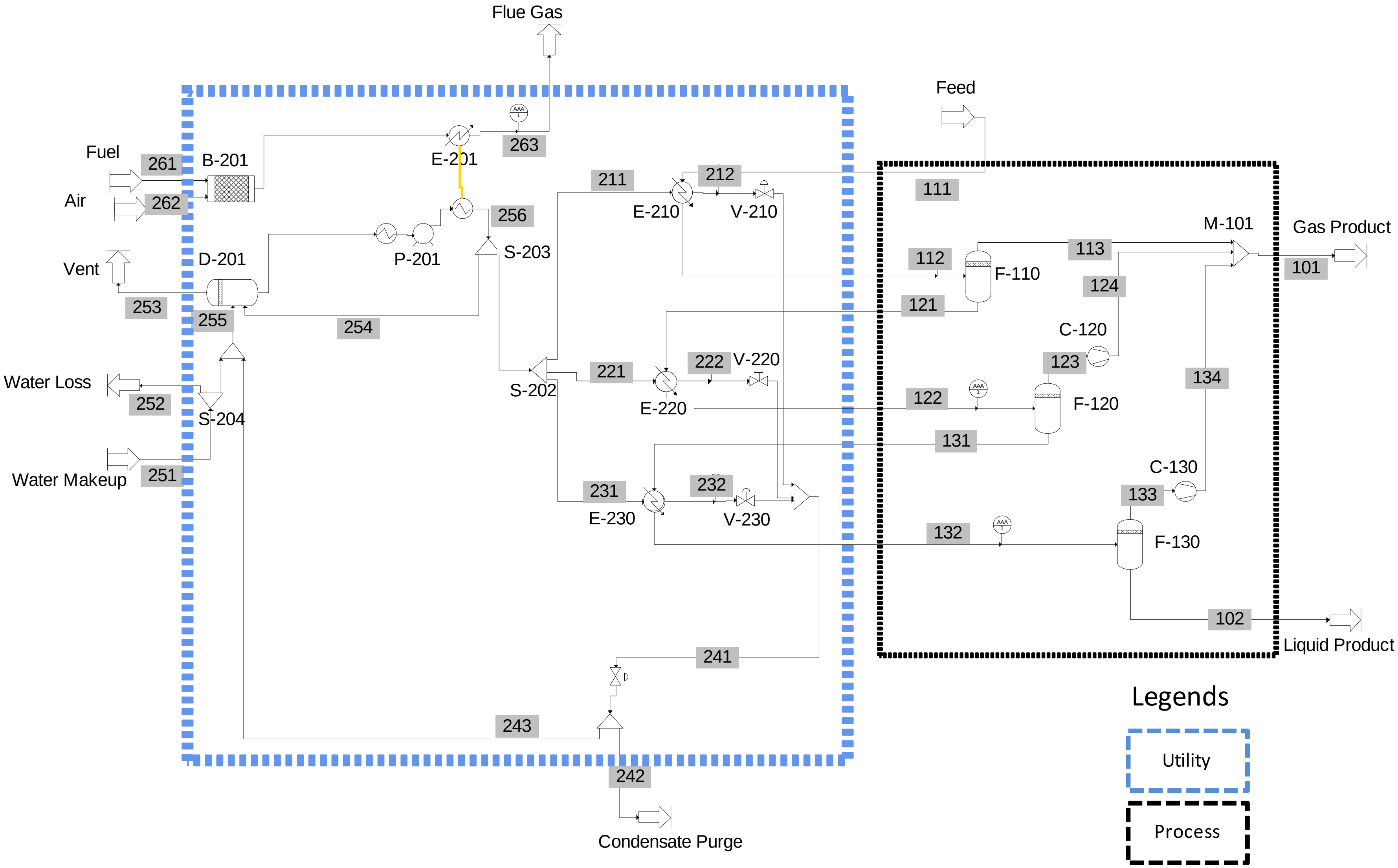


Figure 5.2. Natural gas stabilization

5.3.3 Nominal heat exchanger network

As shown in Figure 5.3, the HP steam (stream 256) in S-202 is divided into three portions. The process streams 111, 121 and 131 are heated up by the steam condensation in heat exchangers E-210, E-220 and E-230 in parallel.

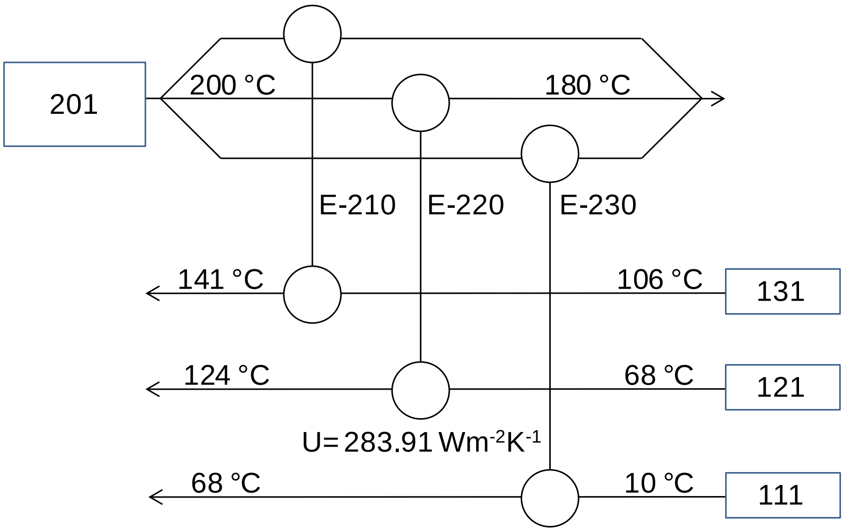


Figure 5.3. Grid diagram of heat exchanger network for the base case

Although many types of heat transfer equipment are used in the industries, the most commonly used type (the shell-and-tube heat exchanger) is taken for our case study. In the conceptual design of heat exchanger, the overall heat transfer coefficient can be taken from tables in literature (Ludwig 2001) as a guide to the order of magnitude. For our case, 283.91 $Wm^{-2}K^{-1}$ is taken for overall heat transfer coefficient (U) as the steam is used as a hot fluid and hydrocarbon is on the cold side. Then required effective outside heat transfer surface area based on net exposed tube area can be calculated as explained in Appendix F and are reported in Table 5.6.

Table 5.6. Heat transfer Area

Heat Exchanger	***Q (MW)***	***U (W m-2 K1)***	***T1***	***T2***	***t1***	***t2***	***LMTD (°C)***	***A (m2)***
E-210	1.170	283.9	200	179	10	68	149.7	27.5
E-220	0.879	283.9	200	179	68	124	92.4	33.5
E-230	0.135	283.9	200	179	124	141	57.0	8.4

5.4 EXERGY ANALYSIS

The exergy analysis tools introduced in the Chapter 4 offers the possibility to perform automatic calculations of exergy of material and heat streams and to present the result of exergy balances in different forms such as pie or bar diagram (Ghannadzadeh et al. 2011a). In addition, Chapter 3 presents the exergy analysis through step-wise methodologies. The application of the retrofitting methodology is presented in the following section by step-by-step analysis of the case study.

5.4.1 Modeling of the global process

Data extraction and modeling of the process: This stage has been explained in Section5.3.

Defining the functional zones of the process: This task for our case study has already been done in the Section 5.3. The flowsheet is divided in two main zones (process zone and utility system) as shown in Figure 4.

Classifying streams: « Waste » vs. « Useful » Streams: As demonstrated earlier, the exergy analysis requires the definition of the utilization of the streams (i.e. waste or useful) by the user. In this case study all the material streams leaving the process are useful whereas all the material output streams in the utilities system are considered as waste streams as they are directly rejected into the environment. As a consequence, in this specific case study, external exergy loss will only be associated with the utility system.

Table 5.7. Useful and waste streams definition

Zone	*Material Stream*	*Useful / Waste*
1	101	*Useful*
	102	*Useful*
2	263	Waste
	253	Waste
	252	Waste
	242	Waste

5.4.2 Diagnosis of the process

5.4.2.1 Exergy balance on the global process

The main task is exergy calculation of streams. Table 5.8 summarizes the total exergy and the exergy flows for each material streams. The exergy flow of the most streams in zone 1 is approximately 10 times higher than zone 2. This is because of use of hydrocarbons in this zone unlike zone 2 where the water is the main component. This difference can be clearly seen in the Grassmann diagram shown in Figure 5.4.

Table 5.8. Exergy calculation of streams

Zone	*Material Stream*	*Total Exergy (kJ/mol)*	*Total Exergy Flow (kW)*
Zone 1	111	2215.50	30586.16
	112	2215.89	30591.54
	113	1400.78	8337.90
	121	2833.82	22254.66
	122	2836.02	22271.96
	131	3500.35	14352.56
	132	3502.46	14361.22
	123	2108.40	7912.65
	124	2110.36	7920.03
	133	2852.35	7000.88
	134	2859.87	7019.33
	102	4466.14	7350.80
	101	1913.63	23269.09
Zone 2	261	78.51	2813.20
	251	9.50	134.50
	263	4.94	177.29
	256	25.16	1452.06
	254	25.16	14.52
	241	34.03	1749.70
	242	34.03	194.41
	252	9.50	26.90
	211	25.16	769.85
	221	25.16	578.47
	222	12.06	277.26
	232	12.06	42.76
	231	25.16	89.22
	212	12.06	368.99

5.4.2.2 Calculation of exergy efficiency

As listed in Table 5.9, performance improvement of the process can be evaluated based on several criteria which make analysis of the process very complex. To fill this gap and facilitate further optimization of the process, the utilizable exergy coefficient proposes an aggregated criterion including all the aspects listed in Table 5.9.

Table 5.9. Performance of the base case

Parameter	*Base case*
Fuel demand (kg/hr)	224.6
Water makeup (t/hr)	1.03
Electricity demand (MW)	0.191
Internal exergy losses (MW)	2.764
External exergy losses (MW)	0.292
Total exergy loss (kW)	3.056
Utilizable exergy coefficient	0.89

The utilizable exergy coefficient of 0.89 means the process which is under operation has potential for improvements. However, the Grassmann diagram shows the relative small irreversibility as the exergy of hydrocarbons (e.g. 30.586 MW exergy of stream 111) are relatively high and do not let us to see the contribution of each unit operation which make total irreversibility of 2.764 MW.

Table 5.9 reports that exergy loss is more due to internal rather than external exergy losses. It means that the improvement of the energy efficiency of the process requires adjustments on the process configuration rather than recycling of effluent streams. To find the main source of exergy losses, a detailed exergy analysis of each unit operation has to be carried out. This analysis will be presented in the next section.

5.4.2.3 Capital cost of the heat exchanger network

The stream pressure has a relation with minimum temperature approach and certainly the required surface area of heat exchangers E-210, E-220 and E-230. To complete the analysis of the process, estimation the capital cost of heat exchangers as a function of surface area needs to be performed. For that study, the costing law (Hall et al. 1990) has been adopted:

$$\mathit{Cost}\ (USD) = 30800 + 750A^{0.81} \tag{5.1}$$

where 30800 represents a fixed cost of installation independent of the area, and A represents the surface area. To use this costing law, it is assumed that plant life is 6 years and capital interest is 10% per year. The heat exchangers are assumed to be made of carbon steel and operate under 10 bar in both sides of shell and tube.

Note that use of ProSimPlus simulator permits to implement very easily the cost calculation. The use of another law more relevant for the considered case study would not be difficult to be implemented.

Assuming 283.91 $Wm^{-2}K^{-1}$ as the overall heat transfer coefficient, investment cost of HEN will be 120,241.9 USD.

5.4.2.4 Classify the process zone according to their exergy efficiency

For each zone, exergy efficiency is calculated and is reported respectively in Table 5.10 and Table 5.11.As expected, the utility system displays much lower exergy efficiency. This means that the higher potential for improvement relies on this zone.

Table 5.10. Exergetic criteria for zone 1 (process)

Exergetic criteria	
External exergy loss (kW)	0
Internal exergy loss (kW)	686.50
Total exergy loss (kW)	686.50
Utilizable exergy coefficient	0.99

Table 5.11. Exergetic criteria for zone 2 (utility system)

Exergetic criteria	
External exergy loss (kW)	292.13
Internal exergy loss (kW)	2 077.64
Total exergy loss (kW)	2 369.77
Utilizable exergy coefficient	0.09

The high utilizable exergy coefficient of zone 1 is because of use of high efficient equipments in this zone such as compressors (0.75) and flash. In addition, zone 1 does not discharge any effluent streams as all the streams are useful as shown in Grassmann diagram (Figure 5.4). Consequently, the external exergy losses are zero.

On the other hand, zone 2 has very low utilizable exergy coefficient. This is due to the several reasons such as no power generation in addition of discharge of flue gas, vent and condensate losses into the environment as shown in Grassmann diagram (Figure 5.4). Therefore, instead of throttling of steam through the valves a more efficient system such as cogeneration can be used.

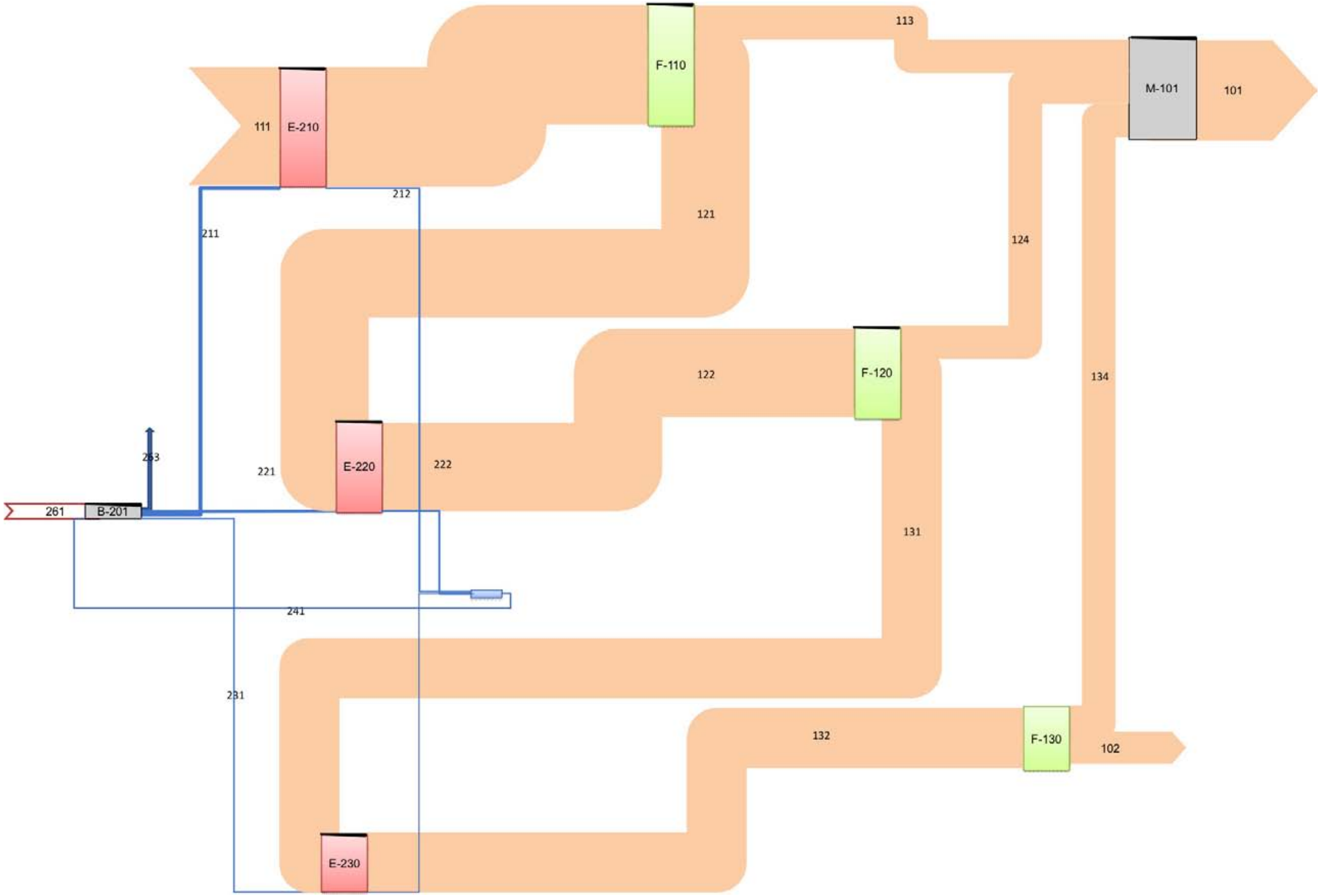


Figure 5.4. Grassmann diagram

5.4.3 Proposal of a retrofit scheme

5.4.3.1 Zone 1 - Internal and external *exergy losses of unit operations*

By representing the external and internal exergy losses occurring in each unit operation with bar diagram (see Figure 5.5), one can identify technical solutions to improve the performances of the process. In this zone, external exergy losses are null whereas some unit operations have high internal exergy losses (or irreversibilities); these losses can be reduced through development of the process or technology improvement.

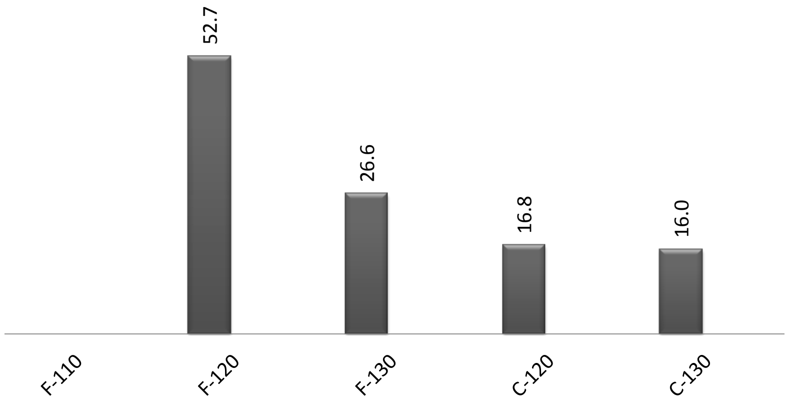


Figure 5.5. Internal and external exergy losses (kW) for the base case (zone 1)

Flash separator (F-110, F-120, F-130): Unlike F-110 which is only heated up, F-120 and F-130 are both heated up and undergo pressure drop (i.e. throttling process). That is the reason why the exergy loss in F-110 is zero. The throttling process is main cause to have a relative high exergy loss for F-120 and F-130. The throttling process is a part of the separation process. It means that it is intrinsic of the flash separation. Therefore keeping this technology will not allow us to reduce the exergy losses. Although based on Table 3.3 expanders can be solutions to reduce exergy losses, the process streams unlike utility streams are not possible to be expanded through turbines.

Compressor (C-120, C-130): Thanks to a relative high isentropic efficiency (75%), theses compressors do not cause high exergy losses. Although the temperature reduction of inlet stream can reduce exergy losses based on Table 3.3, there is a risk of condensation of natural gas liquids in the compressor. Therefore, the temperature of inlet stream has to be kept as it is in the base case.

Gas mixer (M-101): The gas mixer causes relative exergy losses. As reported in Table 3.3 its exergy loss is due to mixing of stream with different conditions. In this case, the exergy losses are due to the temperature and composition difference. As the operating conditions of separators cannot be changed, the compositions cannot be consequently changed. However, the streams can be mixed isothermally to reduce the exergy losses associated with non-isothermal mixing.

5.4.3.2 Zone 2 - Internal and external *exergy losses of unit operations*

- Internal losses

The same analysis is performed for the utility system. Figure 5.6 displays the internal and external exergy losses of each unit operation.

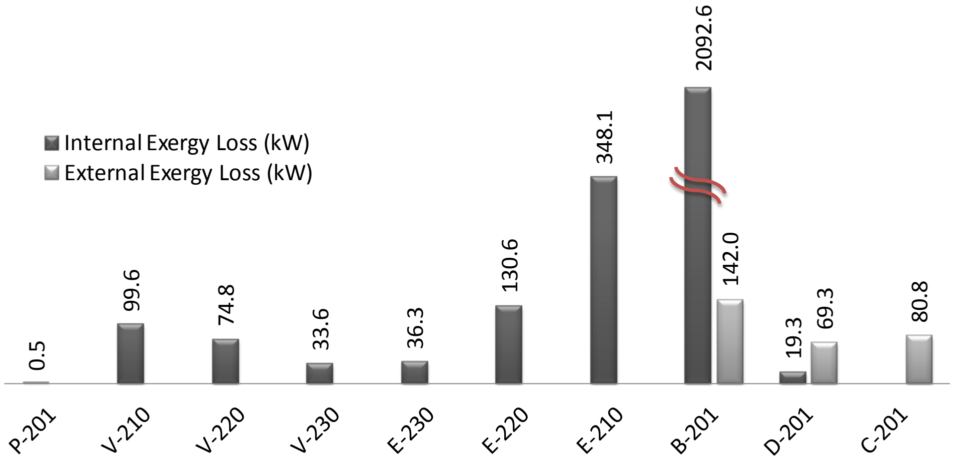


Figure 5.6. Internal and external exergy losses (kW) for the base case (zone 2)

Steam boiler (B-201): As can be seen in Figure 5.6, the largest irreversibilities occur in the steam boiler (B-201). Intrinsic irreversibility due to the combustion is unavoidable; however, according to Table 3.3 solutions exist to reduce the internal exergy loss such as preheating of combustion air through an economizer.

Heat exchanger (E-210, E-220, E-230): The second-largest irreversibility occurs in the heat exchanger network and mostly in the heat exchanger E-210 because of the large temperature difference between hot and cold streams. This point reveals that the utility system is poorly integrated with the process. To improve the process, a temperature difference as small as possible but higher than ΔT min (i.e. 10°C) must be used.

Throttling valve (V-210, V-220, V-230): Due to pressure drop, V-210, V-220 and V-230 display a high exergy loss. According to Table 3.3, replace these valves by steam turbines can be a solution.

Deaerator (D-201): Its exergy loss is due to mixing of high-pressure steam with the condensate. This is the principle of deaeration process to separate air from condensate. As there is no other technology available to do this, we have to bear the exergy losses caused by deaerator.

- External losses

Contrary to zone 1, utility system displays non-negligible external losses. To reduce these external losses, Figure 5.7 presents in a pie diagram the external losses for each unit operation and gives the contribution of chemical and physical exergy losses.

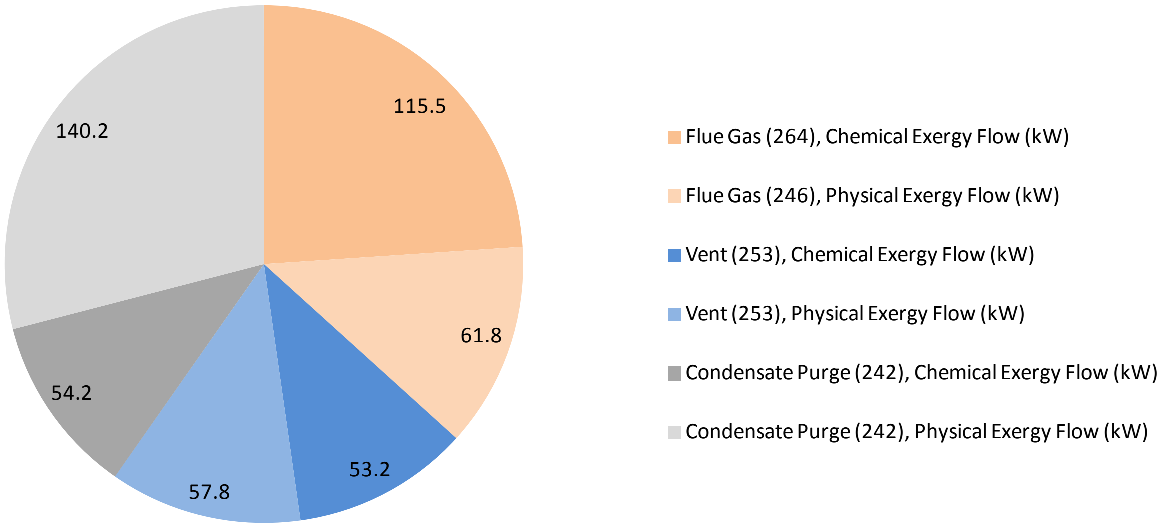


Figure 5.7 External exergy losses

Flue gas (stream 264) - steam boiler (B-201): The external exergy losses associated with the steam boiler is due to its flue gas. To reduce this external loss chemical and thermal recuperation of flue gas can be applied. Although the recovery of its chemical exergy needs a system such as solvent based capture of CO_2 from flue gases (Cousins et al. 2011), the physical exergy can be recovered by a simple waste heat exchanger. As shown in Figure 5.7 up to 61.8 kW exergy can be recovered by a reduction of temperature of flue gas (stream 263) into the ambient temperature.

Vent (stream 253) – deaerator (D-201): The exergy losses of deaerator are due to both physical and chemical exergy losses as shown in Figure 5.7. To exploit the thermal component of exergy of the hot vent stream of deaerator (stream 253), a waste heat exchanger might be a solution. Its condensation in a recovery heat exchanger till ambient condition can save up to 57.8 kW exergy.

Condensate purge (stream 242) - condensate system (C-201): As shown in Figure 5.7, the exergy losses of condensate system are more due to physical exergy rather than chemical exergy losses. To exploit the thermal component of exergy of the condensate purge (stream 242) up to 140.2 kW, a waste heat exchanger can be installed to recover its heat down to 25°C.

5.4.4 Screening unit operation based on exergy efficiency and process constrains

The simple exergy efficiencies are very easy to calculate and have been given by Montelongo et al. (2007). However, in the NGL process, where the major part of exergy input consists in the chemical exergy which remains unchanged, the simple exergy efficiency is quite restrictive. It is not surprising to obtain the simple exergy efficiency close to one for all the unit operations except for the steam system as shown in Montelongo et al. (2007). In such a process, it would be better to calculate the utilizable exergy efficiency as reported in Figure 5.8.

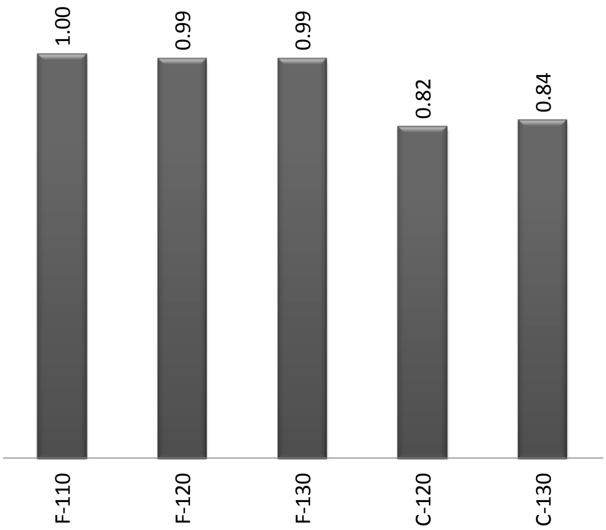


Figure 5.8. Utilizable exergy coefficient for unit operations (zone 1)

As pointed out in Section 5.4.2.4and can also be seen in Figure 5.8, the zone 1 is relatively high efficient. Therefore, zone 2 should be chosen as a zone which is a promising zone to yield high potential for improvement. The utilizable exergy coefficient for zone 2 is calculated as reported in Figure 5.9.

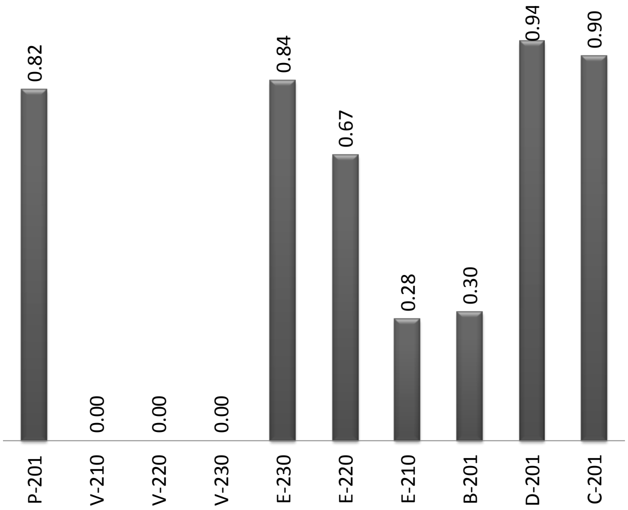


Figure 5.9. Utilizable exergy coefficient for unit operations (zone 2)

The efficiency equal to zero for V-210, V-220 and V-230 pinpoint the focus where it is likely to yield the greatest potential. Note that it is not surprising to find exergy efficiency of zero as these three valves do not have any useful function rather than depressurizing the steam.

The exergy efficiency of each unit operation and the process constraints must then be analyzed together to prioritize the feasible process modifications. Although the steam boiler (B-201) has the largest potential, its intrinsic irreversibility due to the combustion needs chemical modifications (e.g. solvent based capture of CO_2 from flue gases, (Cousins et al. 2011) which needs further investigation. This process constraint limits us to the thermal and mechanical modifications. Therefore, only retrofit options related to physical exergy (such as installation of an economizer) will be taken into account.

In addition, heat exchanger E-210 with the second-largest potential will be revamped as far as the process constraints allow. As mentioned earlier, to reduce the irreversibilities in heat exchangers, it is necessary to reduce the driving force between hot and cold streams. As the process streams cannot be modified, it is decided to reduce the inlet temperatures of the steam by expansion through turbines. For that purpose, steam turbines are preferred over the simple expanding valves as the steam turbines can provide the required shaft power for stages 2 and 3. Based on this analysis, a modified flowsheet is created which is presented in the next section.

5.4.5 The retrofit scheme

5.4.5.1 Description of the retrofit scheme

As we have pinpointed the sources of exergy losses and screened the unit operation to be modified, we are in the position to propose a retrofit scheme based on the analysis of sources of irreversibilities.

Steam boiler (B-201): As mentioned earlier to reduce the internal exergy loss, combustion air is preheated through an economizer (E-202) where flue gas is used for heating. In addition, this will contribute to reduce the external losses as the physical exergy of flue gas will be recovered by the economizer.

Heat exchanger (E-210, E-220, E-230): To reduce the driving force between hot and cold streams and to keep the steam hot enough to meet the heating demand of the process, the steam is expanded to 4.5 bar for the last stage and 3 bar for the first and second stages. Note that compared to the base case, the degree of superheat of steam generated by the boiler, is fixed to be 80°C to avoid the steam condensation in the steam turbine which can damage the machine. It means for the values less than 80°C, there will be condensation in the steam turbine. In other words, 80°C is the minimum degree of superheat of steam generated in the steam boiler.

Throttling valve (V-210, V-220, V-230): According to Table 3.3, as these valves are operating in temperature above ambient, therefore their replacement by a steam turbine can be solutions. The operating conditions of the steam turbines are based on the process side as pointed out above for heat exchangers (E-210, E-220 and E-230).

Dearator (D-201): To exploit the thermal component of exergy of the hot vent stream of deaerator, a waste heat exchanger (E-253) is proposed. The temperature of vent is reducing down to 25°C to exploit its total thermal exergy.

Condensate system (C-201): To exploit the thermal component of exergy of the condensate purge a waste heat exchanger (E-242) is installed. The temperature of condensate loss is reducing down to 25°C.

The improved configuration of the process and its grid diagram are presented in Figure 5.10 and Figure 5.11. To simulate the modified flowsheet, the outlet temperature of process streams in heater E-210, E-220 and E-230 has to be fixed to 68, 124 and 134 °C, respectively. To reach these specifications, splitting ratio of the S-201 and S-202 distributing the steam among the heaters, and water make-up flowrate are modified by the simulator. In addition to keep the flue gas temperature equal to 200°C (which is still higher than the acid dew point, 140°C), the fuel flowrate is also modified by the simulator (see Table 5.13).

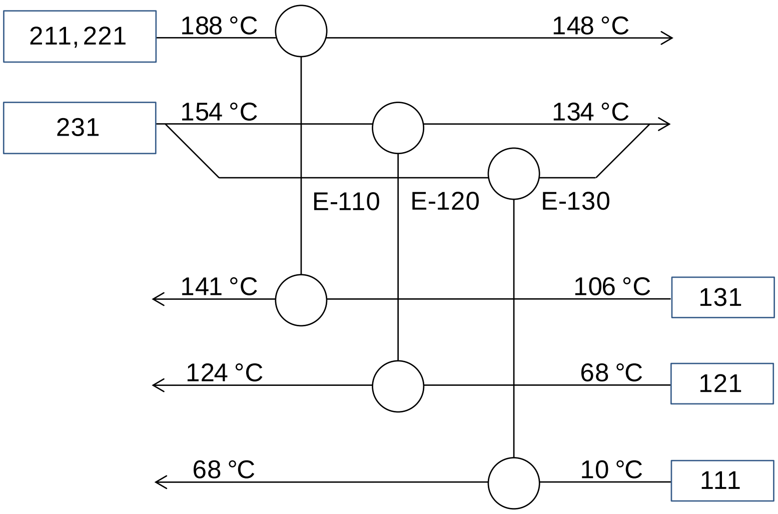


Figure 5.10. Grid diagram of heat exchanger network for the retrofit

Table 5.12. Setpoints and variables for the revamped flowsheet

Setpoints	*Variables*
Outlet temperature of heater E-210 = 68°C	Splitting ratio of S-201
Outlet temperature of heater E-220 = 124°C	Splitting ratio of S-202
Outlet temperature of heater E-230 = 134°C	Water make-up flowrate
Flue gas temperature = 200°C	Fuel flowrate

Table 5.13. Input data for simulation of utility for revamped flowsheet

Parameter	*Value*
Stack temperature (°C)	200
Degree of superheat of HP steam (°C)	80
Temperature of return condensate (°C)	134
Pressure of return condensate (bar)	3
Steam turbine isentropic efficiency	75%

5.4.5.2 Performance of the retrofit scheme

Table 5.14 compares the performance of the base case and the retrofit one. As highlighted in this table, the use of low-pressure steam for heating reduces both fuel and water demand while increases cogeneration potential as more latent heat can be taken from the condensation of steam in the lower pressure. As the process cannot undergo any modification, it is left out of the optimization where the exergy efficiency will be defined only for the utility system.

Table 5.14. Comparison of performance of the base case and integrated retrofit configurations

Parameter	*Base case*	*Retrofit*
Fuel demand (kg/hr)	224.6	220.1
Water makeup (t/hr)	1.03	0.63
Electricity demand (MW)	0.191	0
Internal exergy losses (MW)	3.007	2.628
External exergy losses (MW)	0.292	0.17
Utilizable exergy coefficient of utilities	0.09	0.17

As listed in Table 5.14, performance improvement of the integrated process is noticeable based on several criteria which makes analysis of the process very complex. To fill this gap and facilitate further optimization of the process, the utilizable exergy coefficient proposes an aggregated criterion including all the aspects listed in Table 5.14.

5.4.5.3 Capital cost of the retrofit scheme

Reducing the provided stream pressure necessarily results in a reduction of the minimum temperature approach and certainly increasing of the required surface area of heat exchangers E-210, E-220 and E-230. Estimation the capital cost of heat exchangers as a function of surface area, based on the costing law (Hall et al. 1990) is performed. Assuming 283.91 $Wm^{-2}K^{-1}$ as the overall heat transfer coefficient, investment cost of retrofitted HEN is 150,754.4 USD.

Table 5.15. Comparison of CAPEX of the base case and integrated retrofit configurations

	HEN CAPEX (USD)
Base case	120,241.9
Retrofit	150,754.4

Compared to the base case, an economizer is added in retrofit flowsheet. This economizer results in fuel saving. Assuming 0.015 $/kWh as a fuel cost (Varbanov et al. 2004), the fuel cost for base case and retrofit are calculated as listed in Table 5.16. Taking into account a profit from fuel saving, the installation of economizer results in 22% return on investment.

Table 5.16. Fuel cost for base case vs. retrofit

	Fuel demand (kg/hr)	*Heating value (MWh)*	*Fuel cost (USD)*
Base case	224.6	24436480	366547.2
Retrofit	220.1	23946880	359203.2

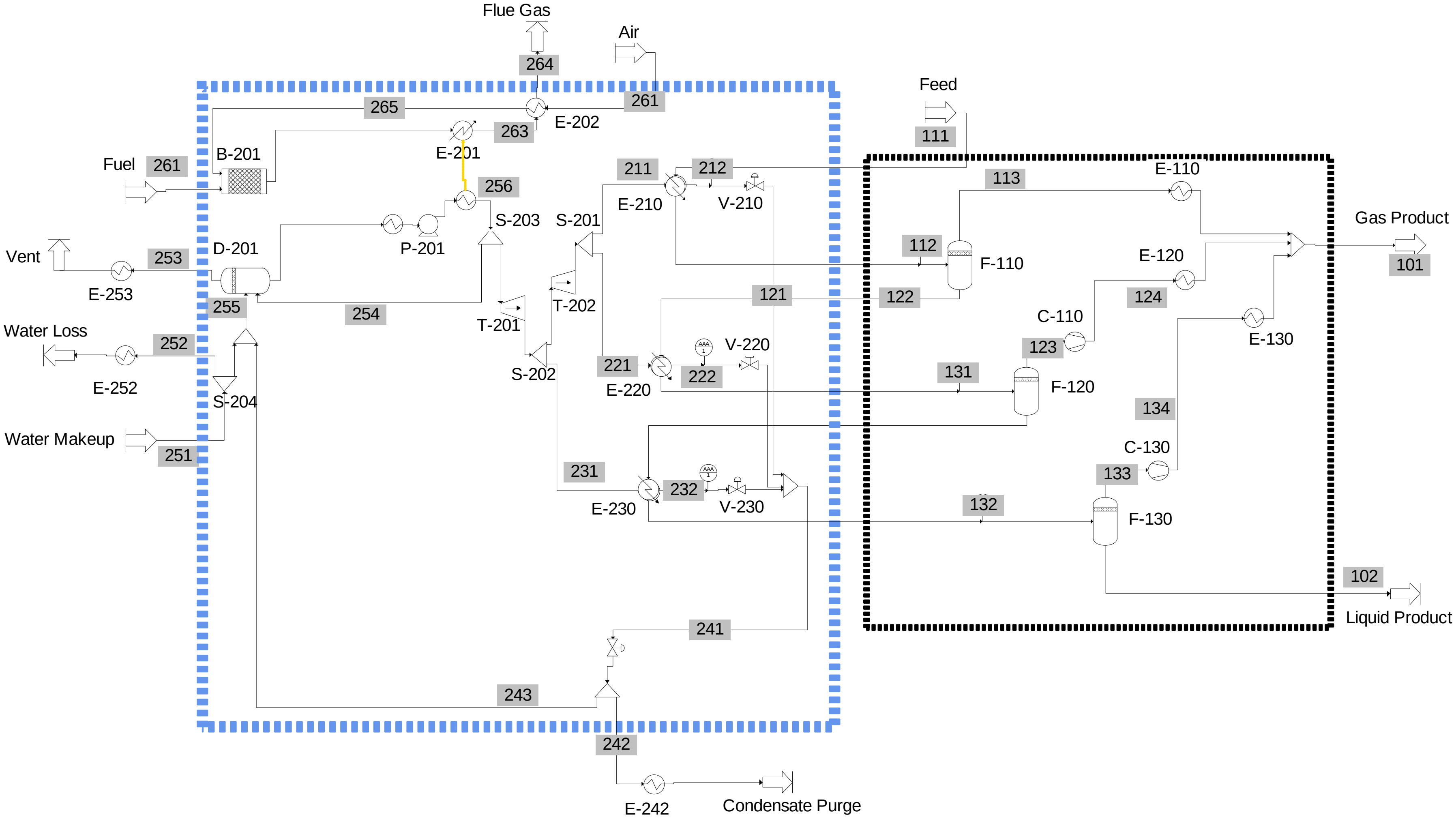


Figure 5.11. Improved process & utility flowsheet

5.5 BI-CRITERIA OPTIMIZATION

In order to offer a decision support in retrofitting step, we propose to perform a bi-criteria optimization.

5.5.1 Optimization framework

In this study, optimization tool of ProSimPlus® is used to perform a bi-criteria (exergetic efficiency/ investment cost) optimization. The details of the optimization model are as follows.

The optimization method chosen to solve the flowsheet optimization problem is based upon the feasible path method. In this approach, the equality constraints of problem are satisfied for every intermediate estimate of the decision variables along the path towards the optimal solution (Kisala et al. 1987). This method combines optimization module with a specification module (see Figure 5.12).

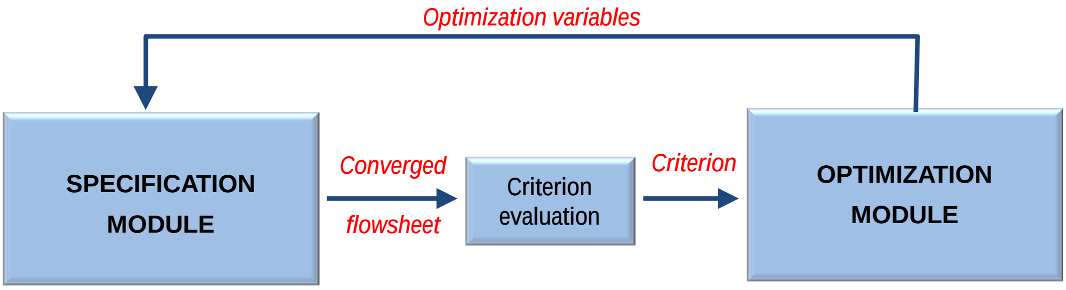


Figure 5.12. A method combines optimization module with a specification module

The specification module unit can be used to handle the constraints related to recycles in order to discharge the optimization module unit with these process constraints. In this case, the user must supply the calculation sequence and the optimization module which is necessarily the master block. It means the optimization module unit encloses the convergence loop managed by the specification module.

5.5.1.1 Formulation of the optimization problem

- *Objective function*

Two criteria must be optimized:

- Maximize the exergetic efficiency
- Minimize the HEN cost (Hall et al. 1990)

To perform this optimization problem, an ε-constraint procedure (Lim et al. 1999) is carried out and a Pareto front is build for support of decisions making.

$$Maximize\ \ \eta = \frac{B^{out} - B^{out}_{waste} - B^{tr}_{useful}}{B^{in} - B^{tr}_{useful}} \tag{5.2}$$

$$Minimize\ HEN\ Cost\ (USD) = 30800 + 750A^{0.81} \tag{5.3}$$

One of the most popular methods for multiobjective optimization is to minimize a convex combination of objectives and thus to convert the multiobjective problem to a parametric single objective problem (Lim et al. 1999):

$$\text{Objective Function : Min}\left\{-\omega.(\text{efficiency}) + (1-\omega).\frac{CAPEX}{10^6}\right\} \tag{5.4}$$

where, $0.0 \le \omega \le 1.0$ and the utility functions (i.e. exergetic efficiency and HEN CAPEX) are linearly combined with the objective functions and the parametric weighting factors (ω) under the constraint set. Note that as the efficiency and CAPEX do not have the same order of magnitude, the CAPEX is divided by 10^6. To achieve this objective function, the pressure of two steam mains (i. e. MP and LP) are chosen as the variables for the reasons provided earlier.

It should be noted that this approach is acceptable when all of the objective functions and the constraints are convex. In this case, the Pareto curve is also convex. Though computationally more expensive, this approach gives an idea of the shape of a non-inferior solution surface and provides the user with a trade-off among the various objectives (Lim et al. 1999).

- *Decision variables*

Decision variables are as follows:

- LP pressure
- MP pressure
- Water flowrate
- Fuel flowrate

To define the bonds for LP and MP, in addition of constrains such as Eq. 5.11, the operating conditions of LP and MP should be taken into account.

In the case of minimum pressure of LP, the condensate system plays the role. As the condensate system is operating at 3 bar, the minimum pressure of LP is 3 bar as well. In the case of the maximum pressure of MP, the steam boiler plays the role. As the steam boiler is operating at 10 bar, the maximum pressure of MP is 10 bar as well. According to the constraints given in Eq. 5.11, the maximum pressure of LP steam should be 1 bar less than the MP pressure. As the maximum pressure of MP is 10 bar, the maximum pressure of LP becomes 9 bar. Likewise, the minimum pressure of LP is 4 bar.

For fuel and water flowrate the bonds are listed in Table 5.17. They are based on the sensitivity analysis where it is observed that the fuel flowrate is changing in the range of 4003-4011 kg/hr (Figure 5.13b and Figure 5.13d). To be on the safe side, the bonds for fuel flowrate is chosen to be 3000-5000 kg/hr as reported in Table 5.17. Likewise, the water flowrate is changing in the range of 740-800 kg/hr (Figure 5.13a and Figure 5.13c). To be on the safe side, the bonds for water flowrate is chosen to be 100-1000 as reported in Table 5.17

Table 5.17. Bonds for action variables

Name of module	*Variable*	*Bonds*	
		Min	Max
Specification module	LP pressure (bar)	3	9
	MP pressure (bar)	4	10
Optimization module	Water flowrate (kg/hr)	100	1000
	Fuel flowrate (kg/hr)	3000	5000

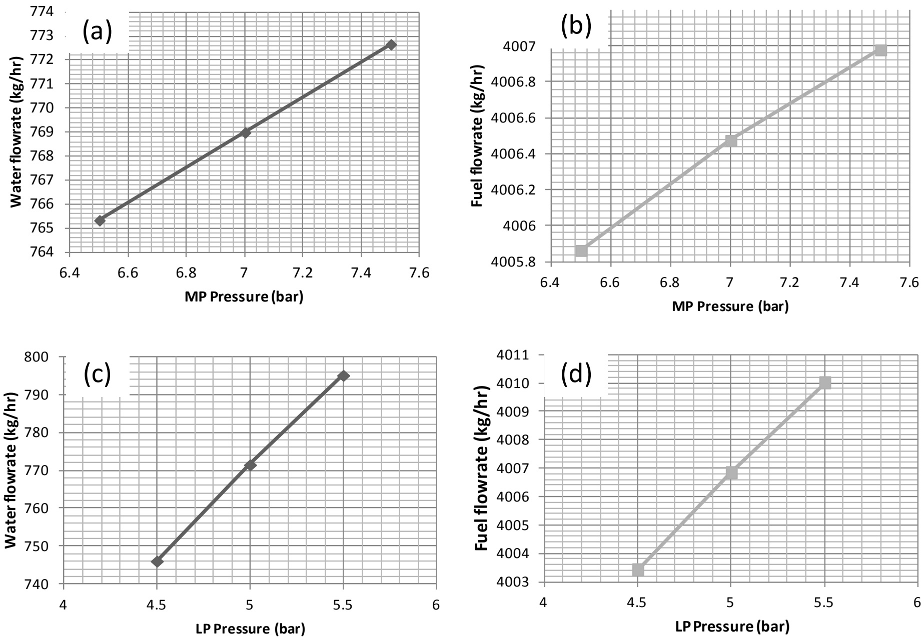


Figure 5.13. a) Sensitivity analysis on water flowrate as a function of MP pressure, b) Sensitivity analysis on fuel flowrate as a function of MP pressure, c)Sensitivity analysis on water flowrate as a function of LP pressure, d) Sensitivity analysis on fuel flowrate as a function of LP pressure

- *Model constraints*

For a feasible heat transfer from steam levels to process section, a set of constraints is needed. Temperature of all hot streams (steam) should be always greater than temperature of all cold streams (process) as follows:

$$T_{211} - T_{112} \geq 10 \tag{5.5}$$

$$T_{221} - T_{122} \geq 10 \tag{5.6}$$

$$T_{231} - T_{132} \geq 10 \tag{5.7}$$

$$T_{212} - T_{111} \geq 10 \tag{5.8}$$

$$T_{222} - T_{121} \geq 10 \tag{5.9}$$

$$T_{232} - T_{131} \geq 10 \tag{5.10}$$

Obviously, the exhaust pressure of second stage of turbine should be lower than the first stage. A difference of 1 bar is chosen between the two stages of turbines:

$$P_{231} - P_{211} > 1 \tag{5.11}$$

The single equality constraints concerning utility system consists in fixing the flue gas temperature to acid dew point (473 K).

$$T_{264} = 473 \tag{5.12}$$

The process streams have to be heated enough to make separation of NGL possible form the natural gas. The feed, the stabilized gas coming from first and second separators have to be heated up to 341, 397 and 414 K, respectively.

$$T_{112} = 341 \tag{5.13}$$

$$T_{122} = 397 \tag{5.14}$$

$$T_{132} = 414 \tag{5.15}$$

5.5.2 Numerical method

The Successive Quadratic Programming (SQP) method is an available method implemented in ProSimPlus. SQP is an iterative method for nonlinear optimization which is used on problems for which the objective function and the constraints are twice continuously differentiable. SQP methods solve a sequence of optimization sub-problems, each which optimizes a quadratic model of the objective, subject to a linearization of the constraints. The optimization problem is solved when the optimality conditions (Karush-Kuhn-Tucked) are satisfied. The Appendix G presents the numerical parameters chosen for the optimization step.

5.5.3 Results

The Pareto front shown in Figure 5.14 is constructed from the optimum points given by ProSimPlus and reported in Table 5.18. It exhibits the non-dominated points, i.e. the points where the exergy efficiency cannot increase without an increase in capital cost.

Given this Pareto front, the decision maker is able to choose the “best solution”. A maximum value of capital cost can be put and then the maximum expected utilizable exergy coefficient can be deduced. Alternatively, efficiency can be targeted and then the minimum available capital cost to achieve the target can be deduced. For example, as listed in Table 5.18, for available capital cost of 136,502 USD, maximum exergy efficiency that can be achieved is 0.1658 which corresponds to 7.0 and 3.8 bar for pressure of MP and LP steam main, respectively. Therefore, this kind of representation based on cost and exergy calculations in the process simulator constitutes the first steps of a decision support system for plant retrofitting. Other key data such as fuel demand and water makeup are listed in Table 5.18.

Table 5.18. The optimum points given by ProSimPlus

Weighting Factor	*Water Flow (kg/hr)*	*Fuel Flow (kg/hr)*	*T-201 Pressure (atm)*	*T-202 Pressure (atm)*	*CAPEX*	*Exergy Efficiency*
0	963.8	4076.3	10.0	9.0	120995.91	0.1231
0.1	963.8	4076.3	10.0	9.0	120995.81	0.1231
0.2	894.3	4068.0	10.0	7.0	123636.61	0.1353
0.3	790.6	4055.6	7.9	4.8	130034.74	0.1539
0.4	725.2	4048.3	7.0	3.8	136502.64	0.1658
0.5	693.1	4045.1	6.8	3.3	141388.95	0.1718
0.6	674.2	4043.4	6.7	3.0	145459.84	0.1754
0.7	673.9	4043.3	6.6	3.0	145509.60	0.1754
0.8	649.4	4036.4	4.0	3.0	152340.79	0.1791
1.0	649.4	4036.4	4.0	3.0	152340.83	0.1791

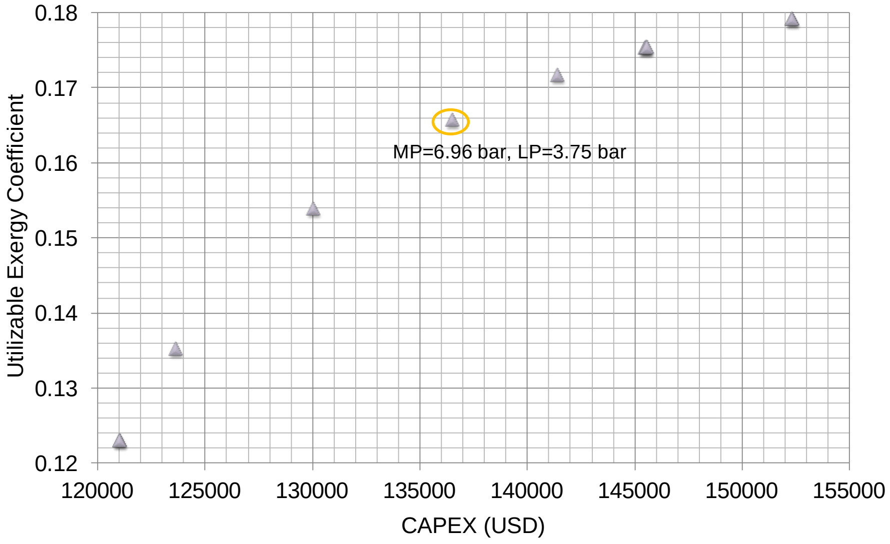


Figure 5.14. Pareto front

5.6 CONCLUSION

Through the case study discussed in this chapter, it was demonstrated that the exergy calculation tool developed and implemented into ProSimPlus process simulator allows for quick and easy exergy analysis. When performing a simulation in ProSimPlus simulator, the exergy flow of each stream is available without any extra effort. Then, an exergy balance on a given system (unit operation, process zone or global flowsheet) can enable to estimate the irreversibility and external exergy losses. Finally, unlike most approaches and case studies in the literature, the analysis goes further by proposing a structured methodology based on the calculation of exergy flow to identify areas to be revamped and suggest the ways for improving of the process performance.

More precisely for our case study, the exergy analysis has permitted to highlight an irrelevant destruction of exergy in throttling valves. Starting from this observation, the expertise of the user and exergy assistant made up of synthetic tables can come together to find a way to exploit the mechanical component of exergy. In the considered example, the throttling valves have been replaced by the steam turbines. This is not certainly the case for all the ways of improvement on the flowsheet where several alternatives can be taken into account. Moreover, given the technological solution, exergy analysis can also be a helpful tool to fix the optimal operating parameter. In our case study, the, exhaust pressure of steam turbine can be fixed with trading-off between the capital cost of heat exchanger and utilizable exergy coefficient.

Moreover, through this case study it has been shown that the exergy efficiency appears as a comprehensive meaningful indicator aggregating various criteria relative to both process and utility system performance. The exergy efficiency does not only include operating cost but also environmental aspects included in the external exergy losses (waste streams including emitted CO_2 as well as fuel and fresh water). Finally, this criterion can be considered as a universal indicator which contrary to a traditional operating cost does not depend on the actual market prices.

PART IV

TO GO FURTHER

CHAPITRE 6

Conclusions and Perspectives

The energy issue is a crucial problem and will become increasingly important in the coming decades. Higher energy cost and progressively stringent environmental laws are forcing the industrial sector to streamline its energy consumption. On industrial sites, the promotion of best practices to enable an efficient utilization of energy has emerged as one of the major points of focus. To tackle this challenge, process integration appears to be one of the most promising solutions. Instead of placing the emphasis solely on production, the current tendency on industrial site consists in optimizing at the same time the production (manufacturing unit) and the utility system which usually represents the largest consumer of energy (manufacturing unit), thus giving equal importance to both units.

Among the different approaches existing to optimize the integration of site utility systems, the **exergy analysis** appears as one of the most promising one, as it enables to:

- Evaluate the inefficiencies of the process,
- Translate all kinds of inefficiencies to the primary fuel consumption and
- Propose hints to reduce these inefficiencies.

Unfortunately this approach, which relies on complex thermodynamic concept, remains difficult to understand and is not well mastered by chemical engineers. One solution to promote this kind of analysis would be to implement exergy analysis in a process simulator in order to provide engineer with a computer aided tool dedicated to this very meaningful analysis.

The significance of this dissertation lies in its contribution both in theoretical and practical terms.

In theoretical terms, this work has contributed to:

- Propose a **generic formulation for exergy of material streams that does not depend on the thermodynamic model,** so that it could be easily be implemented in a process simulator. The different contributions of exergy (thermal, mechanical and chemical) have been developed and new concept such as the maximal thermal and mechanical recovery potential has been introduced in order to pave the way for exergy analysis.
- Develop a **systematic methodology for exergy analysis**. To introduce exergy balances in a process simulator, it was essential to deal with the different situations that can be encountered when modeling a system in a process simulator: the "*design situation*" in which the process model does not include all the details concerning the utilities and the "*retrofit situation*" which aims at improving an existing process. The formulation of the exergy balances has been introduced for both situations and some hints for the interpretation of this exergy balances have been given. Synthetic tables providing solutions to reduce irreversibilities or external losses have been introduced. Moreover, different kinds of exergy efficiency have been defined to provide a new criterion for the optimization of the process.

In practical terms,

- A first **VBScript prototype has been developed to implement the calculation of exergy for the material streams** in a process flowsheet modeled in ProSimPlus. Thanks to this VBScript program, exergy of each material stream appears in a synthesis table next to the traditional thermodynamical values such as the enthalpy. This prototype has already been used to redact the business requirement document that will be the basis for the integration of the “exergy function” in Simulis Thermodynamics (Stroesser et al. 2012).

- The case study permitted to demonstrate **the benefit of the exergy analysis for the improvement of existing processes**. First, the exergy analysis permits to make an energy diagnosis of the process: it pinpoints the inefficiencies of the process which relies not only on irreversibilities but also on external exergy losses. Then, based upon respective values of internal and external losses and also thanks to the breaking down of exergy into it thermal, mechanical and chemical contributions, some technological solutions are suggested to propose a retrofit process; finally, the exergy efficiency criteria enables to optimize the operating parameters of the process in order to improve its energy efficiency.

However, the work presented in this dissertation is only the first step towards a global methodology that will contribute to a more rational use of exergy in industrial units. The following recommendations were identified during the study, which need to be investigated in greater details. These recommendations are directed towards the improvement of the **exergy analysis** methodology, introduction of new concepts, further implementations in ProSimPlus software but also towards future extensions a more comprehensive methodology including other approaches such as **pinch analysis**.

Concerning the exergy analysis, potential improvement of the methodology mostly concerns the improvement of the interpretation of exergy balances process. This step is essential as it permits to propose technological solutions for the improvement of the unit operations or for a better utilization of external exergy loss (Figure 6.1).

To interpret the results concerning the irreversibilities of a process, it could be interesting to **break down the exergy losses into unavoidable and avoidable exergy losses**. Exergy analysis can only indicate the potential or possibilities of improving processes performance, but cannot state whether or not the possible improvement is practicable and economic. Exergy analysis is a thermodynamic study that compares real performances of a process to the reversible one; in the ideal process, the driving force for heat and mass transfer must be equal to 0. However, any practical process needs a certain driving force for the process to take place. Some of the irreversibilities estimated during the exergy analysis are necessary and cannot be suppressed. Then, in order to identify potentials for improvements which are practical and economic, the method proposed based on the analysis of unavoidable and avoidable exergy loss of a system (Feng et al. 1996) can be used. This will allow integrating technological constraints into the exergy analysis and proposing more realistic improvement solutions.

Moreover, currently the determination of relevant technological solutions only relies on the engineer’s expertise. To help engineer, tables have been proposed and should be completed at each time a new study is concluded. To improve this process and systematically propose more innovative solutions, the use of problem-solving, analysis and forecasting tool such as TRIZ (Sushkov et al. 1995) or case-based reasoning (Kocsis, 2012) could be imagined. The Laboratoire de Génie Chimique has built a skill in this area for the last ten years: it should be employed to improve the Exergy Analysis Methodology (Negny, 2012).

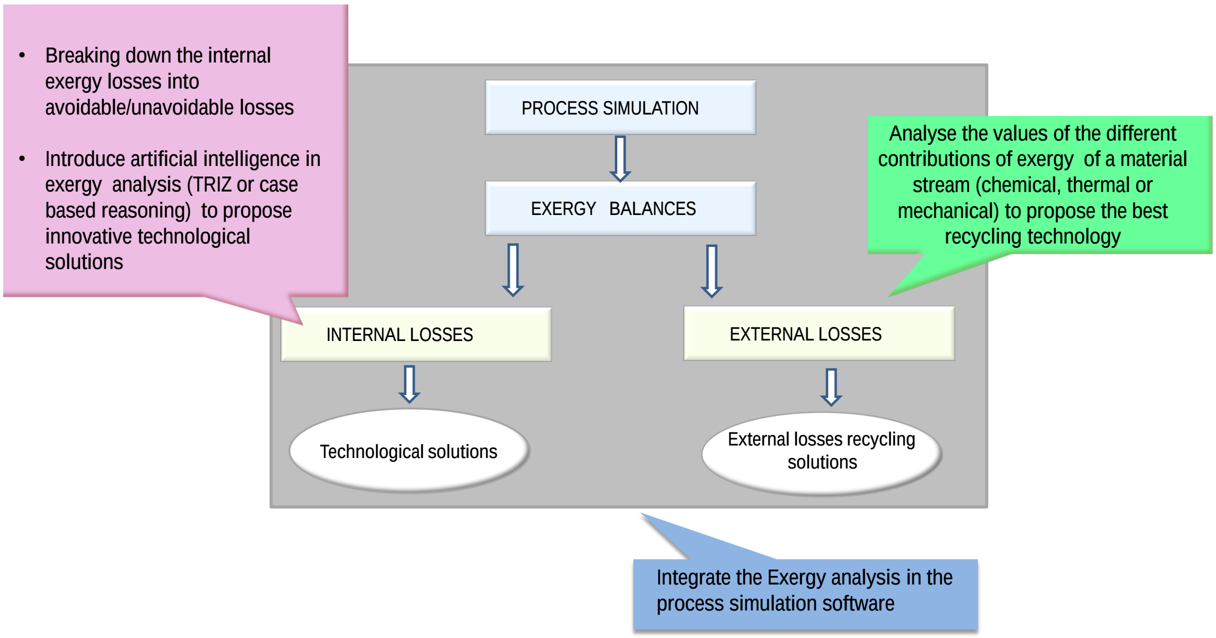


Figure 6.1. Future extensions concerning exergy analysis

Concerning the reduction of external losses, some efforts must be made to develop a **decision making tool enabling to find the best external losses recycling technological solution** according to the respective values of chemical and maximal potential for thermal and mechanical recovery.

Finally, the **full integration of exergy calculations and exergy analysis in the process Simulator ProSimPlus** is currently under study (Stroesser et al. 2012a) (Stroesser et al. 2012b).

On another level, it is important to remind that another approach exists and is usually used to improve the energy efficiency of process: the pinch analysis (Linnhoff, 1994). This approach is a well-known screening and scoping tool that enables to set the "targets" on minimum energy consumption and to identify the type of required utility prior to the detailed design of heat exchanger network. It has been demonstrated in the literature that it seems appropriate to implement a **methodology combining exergy analysis and pinch analysis** (Feng& Zhu, 1997; Staine & Favrat, 1996). First studies initiated during this PhD work permitted to prepare the groundwork for a methodology combining pinch analysis and exergy analysis (see Figure 6.2). At first, Exergy Analysis permits to obtain a diagnosis of the existing process as it evaluates the irreversibilities of each unit operation and suggests technical ways to reduce these internal exergy losses. Then, it pinpoints and calculates external exergy losses. As exergy is decomposed into thermal, mechanical and chemical component, it allows determining the best valorization process. In the case of chemical exergy loss, some recycling solutions could be considered. In the case of mechanical exergy, cogeneration or heat pump could be implemented. Finally, in the case of thermal exergy, the concerned streams can become hot or cold streams for Pinch Analysis. Then, starting from the list of hot and cold streams, Pinch Analysis proposes different solutions to optimize both process and the utility system and also to reduce the energy consumption of the global system. Finally, calculation of the exergetic efficiency of the different configurations can help the process manager to make a choice among several solutions. The study of an industrial case study (pulp and paper production) which has been presented during the last SFGP (Ghannadzadeh et al., 2011b) and reported in Appendix H permits to highlight the strengths of each approach and to propose a first way of combining Exergy Analysis and Pinch Analysis in a sequential strategy.

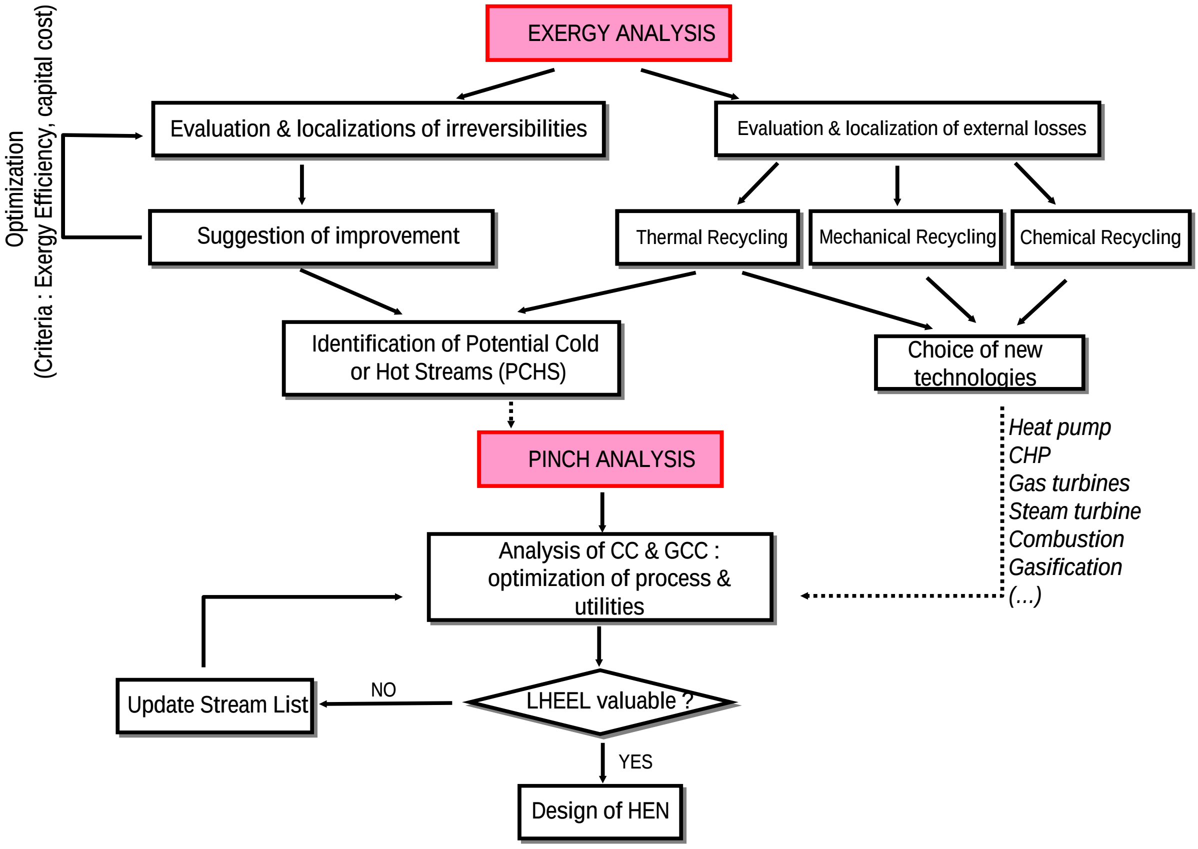


Figure 6.2. A methodology combining pinch analysis and exergy analysis

Certainly, this methodology is not fully accomplished and should be improved mainly in the choice of utilities after the evaluation of external exergy losses. Furthermore, to the development and the promotion of such approach in the industrial sites will necessarily require a more robust implementation of pinch analysis in ProSimPlus process simulator.

Most of these recommendations will be dealt with in the context of a three-year ANR project called COOPERE (*Combining Process Optimization, Energy recovery and Exergy analysis for a better energy efficiency of industrial processes*) and initiated in March 2012.This project whose academic partners are the Laboratoire de Génie Chimique et AgroParistech and industrial partners are ProSim SA and VEOLIA will precisely focus on the recycling of streams that increase the external exergy losses on currents processes. Emblematic case studies can be found in the food industry where by-products are numerous and where we can find some high energy consuming unit operations (dryers for example). To improve such processes and increase their exergy efficiency, the project will:

- Develop a systematic decision making tool to define the most promising recycling technology according to the recovery exergy potential of by-products (gasification, combustion, heat pump, gas turbine …),
- Propose a methodology combining pinch analysis and exergy analysis,
- Develop a software coupled to ProSimPlus that would implement this methodology,

- And finally test this methodology and the software through various industrial case studies extracted from the food industry.

At the end, it can be concluded that exergy analysis as a powerful tool for increasing efficiency of processes but also sustainability of process by reducing environmental impact. There is no doubt that in the near future, this methodology and exergy balances will eventually supplant the traditional enthalpy balance and that any chemical engineer will have to be trained and familiar with this new kind of analysis.

APPENDICES

APPENDIX A

Standard Chemical Exergy

Table A.1 Standard chemical exergy table (Rivero & Garfias, 2006a)

Chemical Element	*State*	*Chemical Formula*	*Mole Fraction*	*Standard Chemical Exergy (kJ/gmol)*
Ag	(s)	AgCl	1.00E-09	99.30
Al	(s)	Al2SiO5	2.07E-03	795.70
Ar	(g)	Ar	9.13E-03	11.64
As-	(s)	HAsO4	3.87E-08	492.60
Au	(s)	Au	1.36E-09	50.60
B	(s)	B(OH)3	3.42E-04	628.10
Ba	(s)	BaSO4	4.20E-06	775.40
Be	(s)	Be2SiO4	2.10E-07	604.30
Bi	(s)	BiO+	9.92E-11	274.80
Br2	(l)	Br	8.73E-04	101.00
C	(s)	CO2	3.37E-04	410.27
Ca	(s)	CaCO3	1.40E-03	729.10
Cd	(s)	CdCO3	1.22E-08	298.40
Ce	(s)	CeO2	1.17E-06	1054.70
Cl2	(g)	Cl	5.66E-01	123.70
Co	(s)	CoFe2O4	2.85E-07	313.40
Cr	(s)	K2Cr2O7	1.35E-06	584.40
Cs	(s)	Cs+	2.34E-09	404.60
Cu	(s)	CuCO3	5.89E-06	132.60
D2	(g)	D2O	3.37E-06	263.90
Dy	(s)	Dy(OH)3	4.88E-08	976.00
Er	(s)	Er(OH)3	4.61E-08	972.80
Eu	(s)	Eu(OH)3	2.14E-08	1003.80
F2	(g)	CaF2, 3Ca3(PO4)2	2.24E-04	505.80
Fe	(s)	Fe2O3	6.78E-03	374.30
Ga	(s)	Ga2O3	2.98E-07	515.00
Gd	(s)	Gd(OH)3	9.21E-08	969.00
Ge	(s)	GeO2	9.49E-08	557.70
H2	(g)	H2O	2.17E-02	236.12
He	(g)	He	4.89E-06	30.31
Hf	(s)	HfO2	1.15E-07	1063.10
Hg	(l)	HgCl2	5.42E-10	107.90
Ho	(s)	Ho(OH)3	1.95E-08	978.70
I2	(s)	IO3	5.23E-07	175.70
In	(s)	In2O3	2.95E-09	436.90
Ir	(s)	IrO2	3.59E-12	247.00
K	(s)	K+	1.04E-02	366.70
Kr	(g)	Kr	9.78E-07	34.30
La	(s)	La(OH)3	5.96E-07	994.70
Li	(s)	Li+	2.54E-05	392.70
Lu	(s)	Lu(OH)3	7.86E-09	945.80
Mg	(s)	Mg3Si4O10(OH)2	8.67E-04	626.90
Mn	(s)	MnO2	2.30E-05	487.70
Mo	(s)	MoO4	1.08E-07	731.30
N2	(g)	N2	7.63E-01	0.67
Na	(s)	Na+	4.74E-01	336.70
Nb	(s)	Nb2O3	1.49E-07	899.70
Nd	(s)	Nd(OH)3	5.15E-07	970.10

Ne	(g)	Ne	1.76E-05	27.14
Ni	(s)	NiO	1.76E-06	242.60
O2	(g)	O2	2.05E-01	3.92
Os	(s)	OsO4	3.39E-13	368.40
P	(s)	HPO42	4.86E-07	861.30
Pb	(s)	PbCO3	1.04E-07	249.20
Pd	(s)	PdO	6.37E-11	138.70
Pr	(s)	Pr(OH)3	1.57E-07	963.90
Pt	(s)	PtO2	1.76E-11	141.20
Pu	(s)	PuO2	8.40E-20	1100.10
Ra	(s)	RaSO4	2.98E-14	824.20
Rb	(s)	Rb+	1.46E-06	388.70
Re	(s)	Re2O7	3.66E-12	559.60
Rh	(s)	Rh2O3	3.29E-12	179.70
Ru	(s)	RuO2	6.78E-13	318.60
S	(s)	SO4	1.24E-02	609.30
Sb	(s)	Sb2O5	1.08E-10	438.20
Sc	(s)	Sc2O3	3.73E-07	925.30
Se	(s)	SeO4	1.18E-09	347.50
Si	(s)	SiO2	4.07E-01	855.00
Sm	(s)	Sm(OH)3	1.08E-07	993.70
Sn	(s)	SnO2	4.61E-07	551.80
Sr	(s)	SrCO3	2.91E-05	749.80
Ta	(s)	Ta2O5	7.45E-09	974.10
Tb	(s)	Tb(OH)3	1.71E-08	998.50
Te	(s)	TeO2	9.48E-12	329.30
Th	(s)	ThO2	2.71E-07	1202.70
Ti	(s)	TiO2	1.63E-04	907.20
Tl	(s)	Tl2O4	1.49E-09	194.90
Tm	(s)	Tm(OH)3	7.59E-09	951.80
U	(s)	UO3	1.49E-08	1196.60
V	(s)	V2O5	1.83E-06	721.30
W	(s)	WO4	5.64E-10	828.50
Xe	(g)	Xe	8.81E-08	40.27
Y	(s)	Y(OH)3	1.00E-06	965.60
Yb	(s)	Yb(OH)3	4.61E-08	944.30
Zn	(s)	ZnCO3	7.45E-06	344.70
Zr	(s)	ZrSiO4	2.44E-05	1083.00

APPENDIX B

Isentropic Efficiency vs. Rational Efficiency

Comparison of the conventional isentropic efficiency with the rational exergy efficiency for rotary machines such as turbine is worth noting.

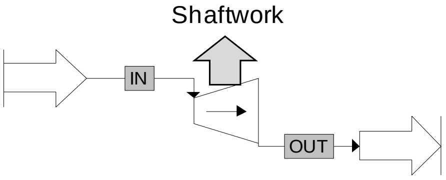


Figure B.1. A typical expander

Let us take an expander as an example. In power plants expansion generally occurs at temperature above the environmental temperature. Most common expander is turbine and is usually treated as adiabatic. Hence, the exergy balance for the control surface of the turbine is:

$$B_{IN} - B_{OUT} = B_{\mathrm{Shaftwork}} + I \tag{B.1}$$

Since the process involves some degree of irreversibility, a part of the input is dissipated. The relationship is shown on a Grassmann diagram in Figure B.2.

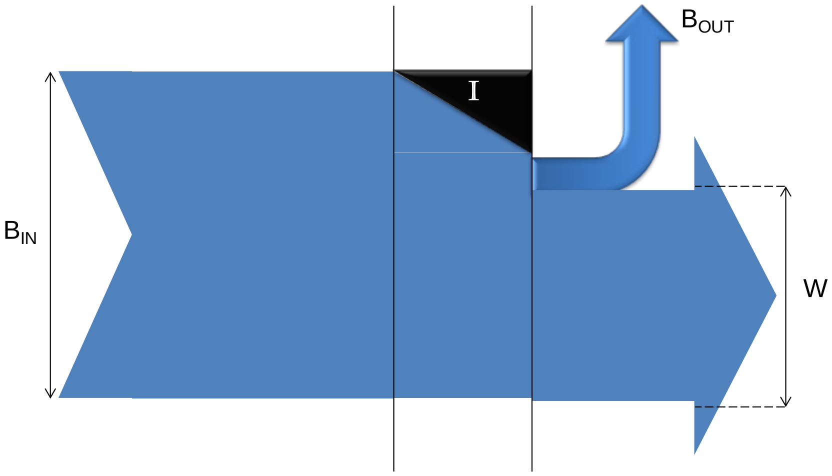


Figure B.2. Grassmann diagram of turbine

As the desired output from device is W, it follows that the necessary input is the reduction in the exergy of the stream ($B_{IN} - B_{OUT}$). Then the exergetic efficiency becomes:

$$\Psi = \frac{B_{\mathrm{Shaftwork}}}{B_{IN} - B_{\mathrm{OUT}}} = \frac{H_{IN} - H_{\mathrm{OUT}}}{B_{IN} - B_{\mathrm{OUT}}} \tag{B.2}$$

For comparison, the well-established criterion of performance, the isentropic efficiency η can be put in the well-known form:

$$\eta = \frac{H_{IN} - H_{\mathrm{OUT}}}{H_{IN} - H_{\mathrm{OUT}}^{ISENTROPIC}} \tag{B.3}$$

Now, exergetic efficiency (ψ) and isentropic efficiency (η) are two criteria of performance which assesses the perfection of the process on different bases. Exergetic efficiency (ψ) compares the actual process with a reversible process with the same inlet and exit. Isentropic efficiency (η) compares the actual process with an isentropic process starting from the same inlet state but ending in a different exit state, though at the same exit pressure at the actual process.

To analyze further these criteria, they are rearranged:

$$\Psi = \frac{H_{IN} - H_{\mathrm{OUT}}}{\left(H_{IN} - H_{\mathrm{OUT}}\right) + T^{00}\left(S_{\mathrm{OUT}} - S_{IN}\right)} \tag{B.4}$$

$$\eta = \frac{H_{IN} - H_{\mathrm{OUT}}}{\left(H_{IN} - H_{\mathrm{OUT}}\right) + \left(H_{OUT} - H_{\mathrm{OUT}}^{ISENTROPIC}\right)} \tag{B.5}$$

Note that the quantity which makes ψ smaller than 1 is $T^{00}\left(S_{\mathrm{OUT}} - S_{IN}\right)$ which is the irreversibility of this processes, shown as a black colored area on the T-s diagram in Figure B.3. The quantity which makes the value of η less than 1 is $\left(H_{OUT} - H_{\mathrm{OUT}}^{ISENTROPIC}\right)$, shown as a grey and black colored area in Figure B.3. This enthalpy difference can be regarded a frictional reheat. Because of frictional reheat, the enthalpy and exergy of the working fluid in the final state of the actual process are greater than they would have been under isentropic conditions.

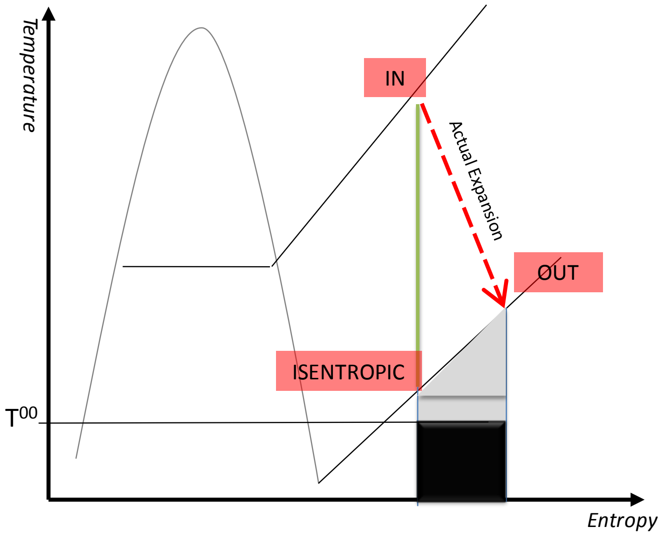


Figure B.3. Temperature-entropy diagram

APPENDIX C

Rational Efficiency Calculation

C.1 EXPANDER

The expander can have two possible functions:

1: Shaftwork generation in power plants (steam turbine)

Desired exergy output is the power generation:

$$B_{\text{desired exergy output}} = B_{\text{Shaftwork}} \tag{C.1}$$

The different between total exergy input and output through expansion become the exergy used to get the power

$$B_{\text{exergy used}} = B_{IN} - B_{\text{OUT}} \tag{C.2}$$

2. Reduce temperature in cryogenic systems (Cryo-expander)

In subambient process, the primary function of cryo-expander is to obtain higher thermal component of exergy. Certainly, there will be power generated by the expander:

$$B_{\text{desired exergy output}} = \left(B_{\text{IN}}^{\Delta T} - B_{\text{OUT}}^{\Delta T}\right) + B^{Q} + B_{\text{Shaftwork}} \tag{C.3}$$

These functions will be achieved at the expense of reduction of mechanical component of exergy of given stream:

$$B_{\text{exergy used}} = B_{\text{IN}}^{\Delta P} - B_{\text{OUT}}^{\Delta P} \tag{C.4}$$

C.2 THROTTLING VALVE

It can have two possible functions:

1. Above ambient: Reduce pressure of steam in power plants

It is a common practice in steam system to throttle the steam to meet the required conditions at the steam mains. As this is a dissipative process, it does not have any desired exergy output:

$$B_{\text{desired exergy output}} = 0 \tag{C.5}$$

Despite the zero exergy output, the difference between exergy input and output is used or in other words, is dissipated:

$$B_{\text{exergy used}} = B_{IN} - B_{\text{OUT}} \tag{C.6}$$

2. Sub-ambient: Reduce temperature in cryogenic systems

In subambient process, the function of this valve is to obtain higher thermal component of exergy.

$$B_{\text{desired exergy output}} = B_{\text{IN}}^{\Delta T} - B_{\text{OUT}}^{\Delta T} \tag{C.7}$$

This function is achieved at the expense of reduction of mechanical component of exergy of given stream:

$$B_{\text{exergy used}} = B_{\text{IN}}^{\Delta P} - B_{\text{OUT}}^{\Delta P} \tag{C.8}$$

C.3 COMPRESSOR

Depending on the heat exchange between the compressor and the cooling media surround by the compressor, there are two possible functions as shown hereunder:

1. Adiabatic

In this case through the 'adiabatic' process as well as the pressure of the given stream the temperature will be increased as well. This means the desired exergy output is difference between exergy input and output:

$$B_{\text{desired exergy output}} = B_{\text{OUT}} - B_{\text{IN}} \tag{C.9}$$

This function is achieved at the expense of reduction of shaft power input:

$$B_{\text{exergy used}} = B_{\text{Shaftwork}} \tag{C.10}$$

2. Non-adiabatic

As the process is non-adiabatic, the function is the compressor is to keep the temperature of the stream fixed as it was at the inlet and increase of pressure:

$$B_{\text{desired exergy output}} = B_{\text{OUT}}^{\Delta P} - B_{\text{IN}}^{\Delta P} \tag{C.11}$$

This function is achieved at the expense of reduction of shaft power input:

$$B_{\text{exergy used}} = B_{\text{Shaftwork}} \tag{C.12}$$

C.4 PUMP

Generally, it is used to increase the incompressible fluids:

$$B_{\text{desired exergy output}} = B_{\text{OUT}}^{\Delta P} - B_{\text{IN}}^{\Delta P} \tag{C.13}$$

This function is achieved at the expense of shaft power input:

$$B_{\text{exergy used}} = B_{\text{Shaftwork}} \tag{C.14}$$

C.5 A TYPICAL SEPARATOR

There are a number of processes for separation. For most of them, the function is to separate different products from feed.

$$B_{\text{desired exergy output}} = B_{\text{Prodcut }1} + B_{\text{Prodcut }2} - B_{Feed} + B_{Useful\ Heat} \tag{C.15}$$

This function is achieved at the expense of shaft power and heat input:

$$B_{\text{exergy used}} = B_{Used\ Heat} + B_{Shaftwork} \tag{C.16}$$

C.6 ENDOTHERMIC REACTOR

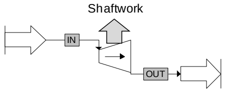
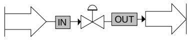
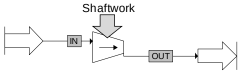
There are a number of types of reactor. For most of them, the function is to produce a special product from the given material at the feed:

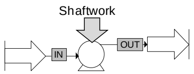
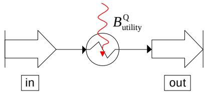
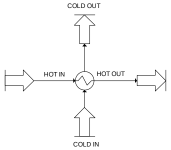
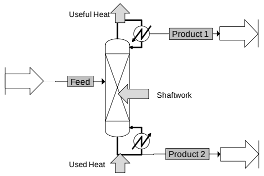
$$B_{\text{desired exergy output}} = B_{\text{prodcut}}^{ch} - B_{\text{feed}}^{ch} \tag{C.17}$$

This function is achieved at the expense of heat input:

$$B_{\text{exergy used}} = B_{endothermic}^{Q} \tag{C.18}$$

Table C.1. Rational efficiency for the most commonly used unit operations

Defined by the user			Calculated	
Unit operation	**Function**	**B** **Desired Output**	**B** **Used**	**Exergy efficiency**
Expander  	Steam turbine: Shaftwork generation in power plants	$B_{\text{Shaftwork}}$	$B_{IN}-B_{\text{OUT}}$	$\Psi=\frac{B_{\text{Shaftwork}}}{B_{IN}-B_{\text{OUT}}}$
	Cryo-expander: Reduce temperature in cryogenic systems	$\left(B_{\text{IN}}^{\Delta T}-B_{\text{OUT}}^{\Delta T}\right)+B^{Q}+B_{\text{Shaftwork}}$	$B_{\text{IN}}^{\Delta P}-B_{\text{OUT}}^{\Delta P}$	$\Psi=\frac{\left(B_{\text{IN}}^{\Delta T}-B_{\text{OUT}}^{\Delta T}\right)+B^{Q}+B_{\text{Shaftwork}}}{\left(B_{\text{IN}}^{\Delta P}-B_{\text{OUT}}^{\Delta P}\right)}$
Throttling valve  	Reduce pressure of steam in power plants	-	$B_{\text{IN}}-B_{\text{OUT}}$	$\Psi=\frac{0}{B_{\text{IN}}-B_{\text{OUT}}}=0$
	Reduce temperature in cryogenic systems	$B_{\text{IN}}^{\Delta T}-B_{\text{OUT}}^{\Delta T}$	$B_{\text{IN}}^{\Delta P}-B_{\text{OUT}}^{\Delta P}$	$\Psi=\frac{B_{\text{IN}}^{\Delta T}-B_{\text{OUT}}^{\Delta T}}{B_{\text{IN}}^{\Delta P}-B_{\text{OUT}}^{\Delta P}}$
Compressor  	Adiabatic: Increase of exergy	$B_{\text{OUT}}-B_{\text{IN}}$	$B_{\text{Shaftwork}}$	$\Psi=\frac{B_{\text{OUT}}-B_{\text{IN}}}{\mathrm{B}_{\text{Shaftwork}}}$
	Non-adiabatic: Increase of pressure	$B_{\text{OUT}}^{\Delta P}-B_{\text{IN}}^{\Delta P}$	$B_{\text{Shaftwork}}$	$\Psi=\frac{B_{\text{OUT}}^{\Delta P}-B_{\text{IN}}^{\Delta P}}{\mathrm{B}_{\text{Shaftwork}}}$

Pump 	Increase of pressure	$B_{\mathrm{OUT}}^{\Delta P} - B_{\mathrm{IN}}^{\Delta P}$	$B_{\mathrm{Shaftwork}}$	$\Psi = \dfrac{B_{\mathrm{OUT}}^{\Delta P} - B_{\mathrm{IN}}^{\Delta P}}{\mathrm{B}_{\mathrm{Shaftwork}}}$
Heater or cooler 	Heating or cooling by utilities	$B_{\mathrm{OUT}} - B_{\mathrm{IN}}$	$B_{\mathrm{utility}}^{\mathrm{Q}}$	$\Psi = \dfrac{B_{\mathrm{OUT}} - B_{\mathrm{IN}}}{B_{\mathrm{utility}}^{\mathrm{Q}}}$
Two-streams heat exchanger	Heating	$B_{\mathrm{cold\_out}}^{\Delta T} - B_{\mathrm{cold\_in}}^{\Delta T}$	$\left(B_{\mathrm{hot\_in}} - B_{\mathrm{hot\_out}}\right) + \left(B_{\mathrm{cold\_in}}^{\Delta P} - B_{\mathrm{cold\_out}}^{\Delta P}\right)$	$\Psi = \dfrac{B_{\mathrm{cold\_out}}^{\Delta T} - B_{\mathrm{cold\_in}}^{\Delta T}}{\left(B_{\mathrm{hot\_in}} - B_{\mathrm{hot\_out}}\right) + \left(B_{\mathrm{cold\_in}}^{\Delta P} - B_{\mathrm{cold\_out}}^{\Delta P}\right)}$
	Cooling	$B_{\mathrm{hot\_in}}^{\Delta T} - B_{\mathrm{hot\_out}}^{\Delta T}$	$\left(B_{\mathrm{cold\_out}} - B_{\mathrm{cold\_in}}\right) + \left(B_{\mathrm{hot\_in}}^{\Delta P} - B_{\mathrm{hot\_out}}^{\Delta P}\right)$	$\Psi = \dfrac{B_{\mathrm{hot\_in}}^{\Delta T} - B_{\mathrm{hot\_out}}^{\Delta T}}{\left(B_{\mathrm{cold\_out}} - B_{\mathrm{cold\_in}}\right) + \left(B_{\mathrm{hot\_in}}^{\Delta P} - B_{\mathrm{hot\_out}}^{\Delta P}\right)}$
***Separato*r** 	Separation of product 1 and 2 from feed	$B_{\mathrm{Prodcut\ 1}} + B_{\mathrm{Prodcut\ 2}} - B_{Feed} + B_{Useful\ Heat}$	$B_{Used\ Heat} + B_{Shaftwork}$	$\Psi = \dfrac{B_{\mathrm{Prodcut\ 1}} + B_{\mathrm{Prodcut\ 2}} - B_{Feed} + B_{Useful\ Heat}}{B_{Used\ Heat} + B_{Shaftwork}}$
Endothermic Reactor	Production of a special product	$B_{\mathrm{prodcut}}^{ch} - B_{\mathrm{feed}}^{ch}$	$B_{endothermic}^{Q}$	$\Psi = \dfrac{B_{\mathrm{prodcut}}^{ch} - B_{\mathrm{feed}}^{ch}}{B_{endothermic}^{Q}}$

APPENDIX D

Stream Properties of HDA Process

Table E.1. Stream properties (base case)

Streams	CW (in)	CW (out)	Feed	HP Steam (in)	HP Steam (out)	Product	Purge	Reactor (in)	Reactor (out)	Separator (in)	Separator (out-Liq)	Separator (out-vapor)
Temperature (°C)	25.00	30.00	10.00	250.00	180.49	116.89	116.89	200.02	267.46	120.00	116.89	116.89
Pressure (atm)	1.00	1.00	38.72	10.00	10.00	32.93	32.93	38.72	38.72	38.72	32.93	32.93
Total flow (kg/h)	632 524.53	632 524.53	32 267.00	8 377.12	8 377.12	4 974.94	27 292.05	32 267.00	32 267.00	32 267.00	4 974.94	27 292.05
Mole fractions												
TOLUENE	-	-	0.12	-	-	0.30	0.02	0.12	0.03	0.03	0.30	0.02
BENZENE	-	-	0.01	-	-	0.63	0.07	0.01	0.10	0.10	0.63	0.07
METHANE	-	-	0.74	-	-	0.06	0.87	0.74	0.84	0.84	0.06	0.87
BIPHENYL	-	-	0.00	-	-	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HYDROGEN	-	-	0.13	-	-	0.00	0.03	0.13	0.03	0.03	0.00	0.03
WATER	1.00	1.00	-	1.00	1.00	-	-	-	-	-	-	-

Table E.2. Stream properties (integrated case)

Streams	CW (in)	CW (out)	Feed	HP Steam (in)	HP Steam (out)	Product	Purge	Reactor (in)	Reactor (out)	Separator (in)	Separator (out-Liq)	Separator (out-vapor)
Temperature (°C)	25.00	30.00	10.00	250.00	180.49	257.44	36.99	200.00	267.44	120.00	116.89	116.89
Pressure (atm)	1.00	1.00	38.72	10.00	10.00	32.93	32.93	38.72	38.72	38.72	32.93	32.93
Total flow (kg/h)	516 504.76	516 504.76	32 267.00	4 963.27	4 963.27	4 974.96	27 292.04	32 267.00	32 267.00	32 267.00	4 974.96	27 292.04
Mole fractions												
TOLUENE	-	-	0.12	-	-	0.30	0.02	0.12	0.03	0.03	0.30	0.02
BENZENE	-	-	0.01	-	-	0.63	0.07	0.01	0.10	0.10	0.63	0.07
METHANE	-	-	0.74	-	-	0.06	0.87	0.74	0.84	0.84	0.06	0.87
BIPHENYL	-	-	0.00	-	-	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HYDROGEN	-	-	0.13	-	-	0.00	0.03	0.13	0.03	0.03	0.00	0.03
WATER	1.00	1.00	-	1.00	1.00	-	-	-	-	-	-	-

APPENDIX E

Calculation of Heat Transfer Area

Although many types of heat transfer equipment are used in the industries, the most commonly used type (the shell-and-tube heat exchanger) is taken for our case study. In the conceptual design of heat exchanger, the overall heat transfer coefficient can be taken from tables in literature (Ludwig, 2001) as a guide to the order of magnitude. The overall heat transfer coefficient is the sum of the individual coefficient of heat transfer for the (a) fluid film inside the tube, (b) scale or fouling film inside the tube, (c) tube wall, (d) scale or fouling film outside the tube, and (e) fluid film outside the tube. For our case, 283.91 $Wm^{-2}K^{-1}$ is taken for overall heat transfer coefficient (U). Then required effective outside heat transfer surface area based on net exposed tube area can be calculated:

$$A = \frac{Q}{U\left(LMTD_{cor}\right)} \tag{E.1}$$

where

$LMTD_{cor}$: Corrected logarithmic mean temperature difference

U: Overall heat transfer (fouled) coefficient

To determine the true overall temperature difference, the correction factors F shown in Figure E.1 are used to correct for the deviations involved in the construction of multi-passes on the shell and tube sides of the exchanger.

$$LMTD_{cor} = (F)(LMTD) \tag{E.2}$$

LMTD: defined by Eq. (E.5).

F: Correction factor as defined by the charts

Note that R of the charts represents the heat capacity rate ratio, and P is the temperature efficiency of the exchanger:

$$P = \frac{t_2 - t_1}{T_1 - t_1} \tag{E.3}$$

$$R = \frac{T_1 - T_2}{t_2 - t_1} \tag{E.4}$$

Based on the temperature profile shown in Figure E.2, the Log Mean Temperature Difference (LMTD) is represented by Eq. (E.5).

$$\Delta T = \frac{(T_2 - t_1) - (T_1 - t_2)}{\ln\left(\dfrac{T_2 - t_1}{T_1 - t_2}\right)} = \frac{GTD - LTD}{\ln \dfrac{GTD}{LTD}} = LMTD \tag{E.5}$$

where

GTD: Greater Terminal Temperature Difference,

LTD: Lesser Terminal Temperature Difference,

LMTD: Logarithmic Mean Temperature Difference,

T_1 : Inlet temperature of hot fluid

T_2 : Outlet temperature of hot fluid,

t_1 : Inlet temperature of cold fluid,

t_2 : Outlet temperature of cold fluid.

Note that the logarithmic mean temperature difference should be used when the following conditions generally apply for conditions of true counter-current or co-current flow:

- Constant overall heat transfer coefficient.
- Complete mixing within any shell cross pass or tube pass.
- The number of cross baffles is large (more than 4).
- Constant flow rate and specific.
- Enthalpy is a linear function of temperature.
- Equal surfaces in each shell pass or tube pass.
- Negligible heat loss to surroundings or internally between passes.

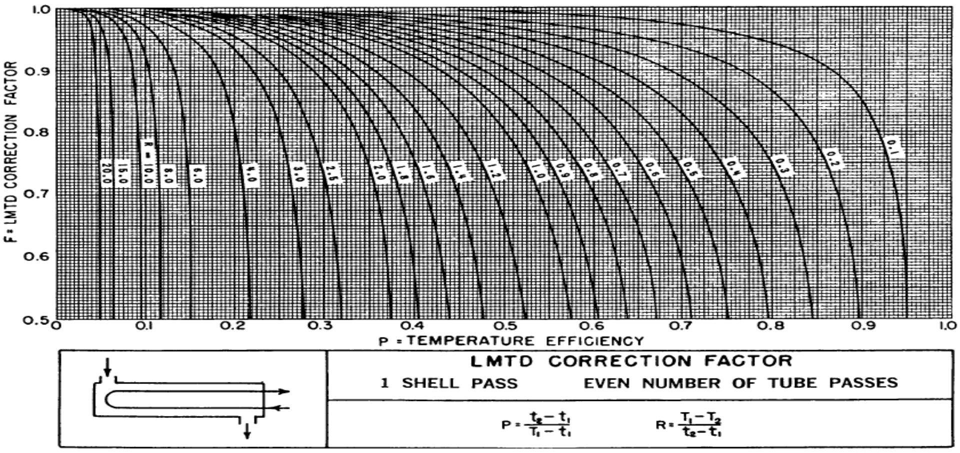


Figure E.1. Correction factor (Ludwig, 2001)

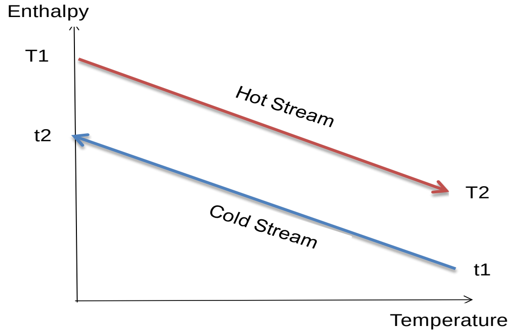


Figure E.2.Temperature path in heat exchanger

APPENDIX F

Calculation of Utilizable Exergy Coefficient for Case Study of NGL Recovery

F.1. IDENTIFICATION OF USEFUL STREAMS

The transiting exergy is defined by equations given in Chapter 3. It requires first the definition of useful stream in order to evaluate the term B^{tr}_{useful}. For this case study, the utilizable exergy coefficient is calculated for the utility system and the utility/process heat exchangers E-210, E-220 and E-230 are included inside the utility systems. As a consequence, the useful streams are the process cold streams of heat exchangers E-210, E-220 and E-230, i.e. streams 112, 122 and 132.

F.2. DEFINITION OF MATERIALLY CONNECTED STREAMS

The definition of the transiting exergy for a given process relies on the **definition of materially connected streams**. As shown in Figure F.1, we can observe the existence of five groups of material streams. The three first groups are related to process streams heating in the E-210, E-220 and E-230. On the utility side, the fourth group is related to water and fifth group is related to fuel. The different colors related to each group and their status (useful or not) are reported in Table F.1.

Table F.1. Description of groups

	Color	Description	Useful (Yes / No)
Group 1	Yellow	Process stream to E-210	Yes
Group 2	Green	Process stream to E-220	Yes
Group 3	Red	Process stream to E-230	Yes
Group 4	Blue	Utility stream (Water)	No
Group 5	Grey	Utility stream (Fuel and air)	No

F.3. CALCULATION OF TRANSITING EXERGY FOR USEFUL STREAMS

The next step is to calculate the transiting exergy for the useful streams identified in section F.1 (i.e. streams 112, 131 and 132 in order to calculate the exergy efficiency. For useful streams of group 1, we have:

$$B^{ch,tr}_{GROUP1} = \sum_{m,n} B^{ch,tr}_{(m,n)} = \sum_{m,n}\sum_{i} \min\left[n_m ; n_n\right].\min\left[b^{ch}_{i,m} ; b^{ch}_{i,n}\right]$$

$$B^{ch,tr}_{GROUP1} = B^{ch,tr}_{(111,112)} = \sum_{i} \min\left[n_{111} ; n_{112}\right].\min\left[b^{ch}_{i,111} ; b^{ch}_{i,112}\right] \tag{F.1}$$

As there is no change in molar flow rate of each chemical component in group 1, the minimum molar flow rate is equal to molar flow rate of input stream 111.

$$\min\left[n_{i,111} ; n_{i,112}\right] = n_{i,111} \tag{F.2}$$

Furthermore, the stream 111 is only passing through a heat exchanger. As a consequence, there is no change in chemical exergy of streams of Group 1. The minimum molar chemical exergy is equal to molar chemical exergy of input stream 111.

$$\min\left[b_{i,m}^{ch};b_{i,n}^{ch}\right]=\min\left[b_{i,111}^{ch};b_{i,112}^{ch}\right]=b_{i,111}^{ch} \tag{F.3}$$

After substituting, we have:

$$B_{GROUP1}^{ch,tr}=B_{(111,112)}^{ch,tr}=\sum_i n_i^{111}b_{i,111}^{ch}=B_{111}^{ch} \tag{F.4}$$

Likewise for groups 2 and 3, the transiting exergy is equal to chemical exergy of 121 and 131, respectively.

$$B_{GROUP\,2}^{ch,tr}=B_{121}^{ch} \tag{F.5}$$

$$B_{GROUP\,3}^{ch,tr}=B_{131}^{ch} \tag{F.6}$$

Concerning the physical transiting exergy, we have:

$$\begin{gathered}B_{GROUP\,1}^{ph,tr}=\sum_{m,n}B_{(m,n)}^{ph,tr}=B_{(111,112)}^{ph,tr}=\sum_{m,n}.\min\left[n_{111},n_{112}\right]\min\left[b_{111}^{ph};b_{112}^{ph}\right]\\ B_{GROUP\,1}^{ph,tr}=n_{111}\min\left[b_{111}^{ph};b_{112}^{ph}\right]=n_{111}b_{111}^{ph}=B_{111}^{ph}\end{gathered} \tag{F.7}$$

Likewise for groups 2 and 3, the transiting exergy is given by following expressions:

$$B_{GROUP2}^{ph,tr}=n_{121}\min\left[b_{121}^{ph};b_{122}^{ph}\right]=n_{121}b_{121}^{ph}=B_{121}^{ph} \tag{F.8}$$

$$B_{GROUP3}^{ph,tr}=n_{131}\min\left[b_{131}^{ph};b_{132}^{ph}\right]=n_{131}b_{131}^{ph}=B_{131}^{ph} \tag{F.9}$$

As a consequence, total transiting exergy is sum of all of transiting exergy of group 1-3:

$$B_{useful}^{tr}=B_{GROUP\,1}^{ch,tr}+B_{GROUP\,2}^{ch,tr}+B_{GROUP\,3}^{ch,tr}+B_{GROUP\,1}^{ph,tr}+B_{GROUP\,2}^{ph,tr}+B_{GROUP\,3}^{ph,tr} \tag{F.10}$$

Total exergy input is sum of exergy of streams 261, 262, 251, 111, 121 and 131:

$$B_{in}=\left(\underline{B_{261}+B_{262}+B_{251}}\right)+\left(\underline{\underline{B_{111}+B_{121}+B_{131}}}\right)+B_{in}^{W,P-201} \tag{F.11}$$

Total exergy output is sum of exergy of streams 264, 252, 253, 242, 112, 122 and 132:

$$B_{useful}^{out}=B_{112}+B_{122}+B_{132}+B_{W}^{T-201}+B_{W}^{T-202} \tag{F.12}$$

Replacing the values associated with each term in the following equation, the efficiency will be calculated:

$$\eta=\frac{B_{useful}^{out}-B_{useful}^{tr}}{B_{in}-B_{useful}^{tr}}=\frac{B_{W}^{T-201}+B_{W}^{T-202}+B_{112}+B_{122}+B_{132}-B_{111}^{ch}-B_{121}^{ch}-B_{131}^{ch}-B_{111}^{ph}-B_{121}^{ph}-B_{131}^{ph}}{\underline{\underline{\underline{B_{261}+B_{262}+B_{251}}+B_{111}+B_{121}+B_{131}-B_{111}-B_{121}-B_{131}+B_{in}^{W,P-201}}}} \tag{F.13}$$

$$\eta = \frac{B_W^{T-201} + B_W^{T-202} + (B_{111} - B_{112}) + (B_{121} - B_{122}) + (B_{131} - B_{132})}{B_{261} + B_{262} + B_{251} + B_{in}^{W,P-201}} \qquad (F.14)$$

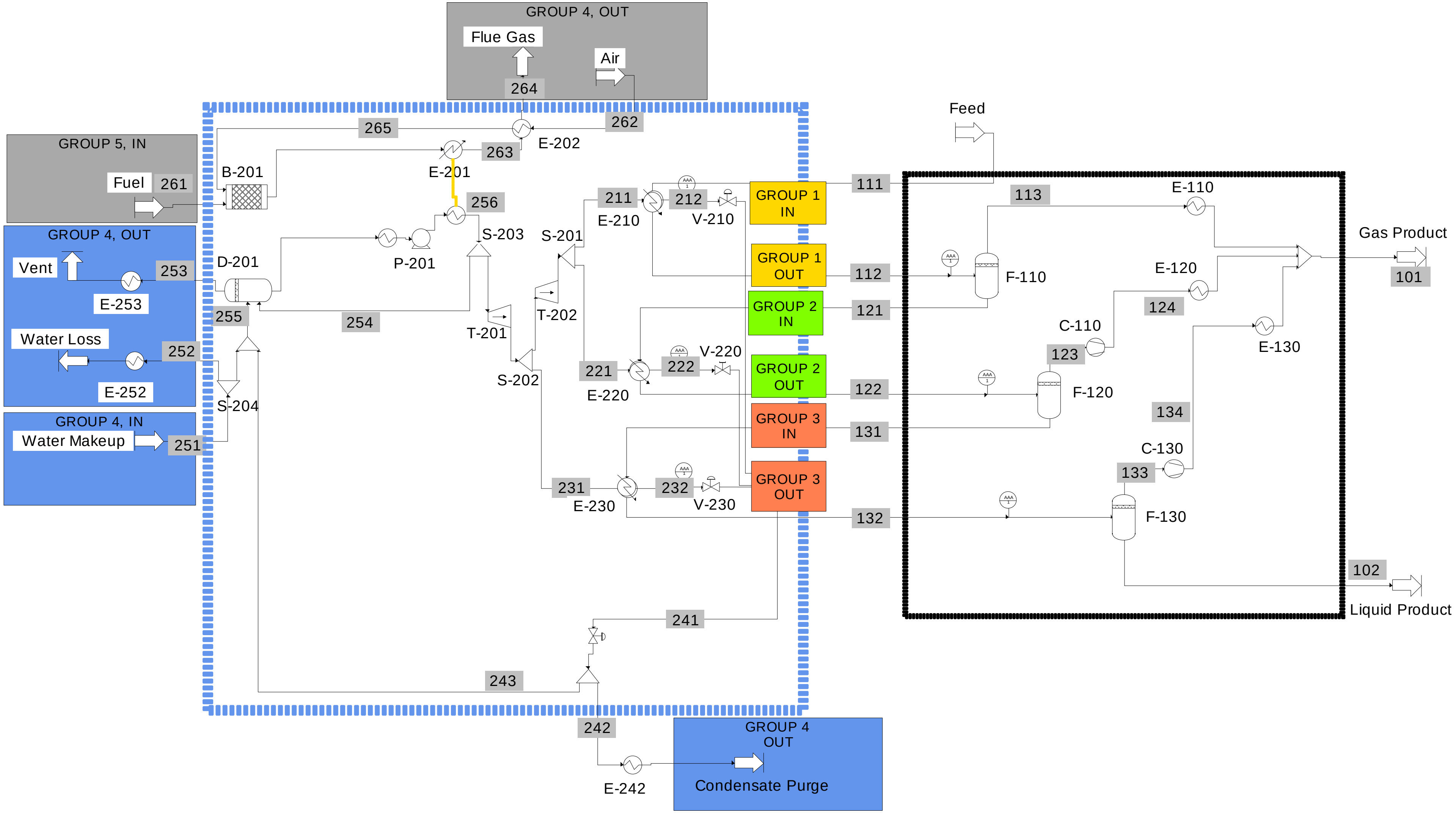


Figure F.1. Different groups of materially connected streams

APPENDIX G

Parameters of Successive Quadratic Programming (SQP)

The parameters of SQP method are as follows:

Tolerance on the Kuhn Tucker parameter: The default value (i.e. 10^{-4}) for the tolerance on the Kuhn Tucker parameter is chosen.

Tolerance for the non-evolution of the variables: The default value (i.e. 10^{-4}) is chosen for the value of the deviation on variables between two consecutive iterations below which the deviation is considered to be zero.

Tolerance for the non-evolution of the criterion: The default value (i.e. 10^{-4}) is chosen for the value of the deviation on the criterion between two consecutive iterations below which the deviation is considered to be zero.

Tolerance on the violation of the constraints: The default value (i.e. 10^{-4}) is chosen for the minimum value below which the constraints are considered satisfied.

Maximum number of iterations: The default value (i.e. 200) is taken for the maximum number of iterations allowed to the optimization process.

Maximum number of runs in the MCN: The default value (i.e. 1000) is taken for the maximum number of runs in the MCN allowed to the optimization process.

Inequality constraints: The number of inequality constraints of the optimization problem is chosen as described earlier.

Number of rest steps: The default value (i.e. 2) is chosen for number of sequential runs in the MCN for initializing the iterative process.

Intermediates outputs: Allows printing the value of the minimization criterion, the optimization variables and the values of the constraints at regular intervals in terms of iterations (by default prints are made every iteration).

Order for the calculation of the gradient: As defined by default, the first order is used to indicate the type of finite differences used for the evaluation of the gradient.

Actions variables–Bounds and increments: As recommended, we have provided the bounds of the actions variables (iterative variables for the optimization).

APPENDIX H

Toward an Approach Combining Exergy Analysis and Pinch Analysis: Application to a Pulp and Paper Process

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Vers une approche combinant analyse exergétique et analyse Pinch pour l'amélioration de l'efficacité énergétique des sites industriels: application à un procedé de pâtes et papiers

Toward an approach combining exergy analysis and pinch analysis for improving the energy efficiency of industrial sites: application to a pulp and paper process

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Résumé

Cette contribution présente les résultats de la première étape du projet qui vise à coupler l'analyse pincement et de l'analyse exergétique dans une même plateforme logicielle reposant sur l'outil de simulation de procédés ProSimPlus. Après une rapide présentation du site industriel retenu comme cas d'étude, une modélisation sous ProSimPlus du procédé proprement dit mais aussi des utilitaires associés est réalisée. Reposant sur ce modèle, les analyses de pincement et exergétique du site sont ensuite détaillées. Concernant l'analyse pincement, une nouvelle approche de définition des flux thermiques du procédé étudié est proposée, afin de définir une méthodologie systématique pour cette analyse, pouvant ensuite être généralisée à l'étude de tout site industriel. Enfin, une analyse comparative des résultats obtenus par les deux approches permet de dresser un bilan des avantages et inconvénients de ces méthodes et de dégager des voies d'amélioration permettant de proposer les bases d'une nouvelle méthodologie, plus complète exploitant les atouts de chaque approche.

Mots-clés : Efficacité énergétique, exergie, analyse Pinch, pâtes et papiers

Abstract

This work presents the results of the first stage of a project which aims at combining pinch and exergy analyses in the same simulation platform to propose guidelines for optimization of industrial sites. In this paper, an industrial case study (pulp and paper process) is studied using both approaches. One of the originalities of the proposed methodology relies on the use of ProSimPlus® software for the simulation of the process and related utilities. This enables an automatic calculation of data necessary for both exergy and pinch analysis (exergy of heat and material streams, data concerning hot and cold streams …). Based on this simulation, exergy and pinch analysis of the site is then carried out and complementaries of both approaches are highlighted in order to lay the foundations of the combined approach.

Key-words : Energy efficiency, Retrofit, Exergy, Pinch analysis, Pulp and paper

1. Introduction

Industrial sector accounts for one third of global energy consumption. A common feature of industrial processes is reliance on fossil fuels as the primary source of energy and a large part of the energy

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consumption is spent on production of utilities (electricity, steam at various pressure levels, hot/cold water, hot flue gas…). As this reliance on fossil fuels has huge negative impact on the environment, the scientific world makes an significant effort to find alternative sources of energy. However, even by the most optimistic assessments, all these alternatives are long-term solutions and many projections show that in near future fossil fuels will remain as primary sources of energy. Then, efforts must be made to seek best practice that will minimize the damage caused by the fossil fuels. A short term and sustainable solution consists in improving energy efficiency of industrial processes (IPCC, 1996). Currently, this can be achieved by two approaches:

1. The pinch analysis (Linnhoff 1994), as a well-known screening and scoping tool, enables to set the "targets" on minimum energy consumption and to identify the type of required utility prior to the detailed design of heat exchangers network.
2. The exergy analysis (Szargut et al. 1988) for a given detailed process flowsheet aims at identifying the inefficiencies of the process, translating all kinds of inefficiencies to the primary fuel consumption, and proposing how to reduce these inefficiencies.

In this context, as shown by literature (Staine and Favrat 1996, Feng and Zhu 1997, Mateos-Espejel et al. 2010), it seems appropriate to implement a methodology combining exergy analysis and pinch analysis. In this work, the proposed platform relies on the use of ProSimPlus® simulation tool and its purpose is to propose a set of technical solutions enabling to improve the energy performance of a site by optimizing the process but also the utility supply. In this paper the results of the first stage of the project are presented: both exergy and pinch approaches are compared based on an industrial pulp and paper case study. This is an emblematic example because of its large energy consumption, cumbersome data extraction and also including the production of utilities which finally leads to a global site analysis.

2. Data extraction and simulation of the industrial site

The energetic analysis of an industrial site (through exergetic analysis or pinch analysis) always requires performing a rigorous data extraction. This data extraction consists in:

- Collecting all the necessary data for mass and heat balances on the process and on the existing utility systems. In this step, discussions with the site manager are essential in order to be able to classify the process data according to process specifications, degrees of freedom, process parameters. Furthermore, concerning the existing utility systems, it is essential to answer the following question: *Can the process/utility system be completely replaced or the purpose of the analysis is just to improve the existing process/utility systems?*
- Capitalizing the collected information by performing heat and mass balances which can either be performed on a simple spreadsheet or more advances tools such as process simulation software. In the approach which we propose, ProSimPlus® simulator has been used.

2.1 Brief description of the industrial site

The studied industrial site is a pulp and paper production plant (see figure 1). In this process, the raw material is wood pulp (cellulose fibers) made of 90% of dry materials. Raw pulp is first mixed with water to form a paper sheet. This paper sheet is then dried (mechanically and thermally) to obtain pulp paper with 95.5% dry material. The electric power consumption essentially comes from the drying and mechanical packaging. The plant operates on average 8500 hours per year and the average flowrate of paper (dry only) is 5.9 t/h. Energy consumption is divided into three parts as follows: 49300 MWh of electricity, 52100 MWh of superheated steam generated by steam boiler house and 31875 MWh of natural gas only for the fired heater beside the one required by steam boiler house. Figure 1 highlights the utilization of different kinds of utilities: electricity for mechanical operation (ranging from 0.02 MW for the pump at the inlet of scrubber to 1.7 MW for mechanical drying) and hot flue gas through direct heat transfer in the thermal dryer. Hot flue gas is produced from fresh air and natural gas in fired heaters. Fresh air from ambient conditions is preheated up to 230°C in a waste heat exchanger by the flue gas exiting the thermal dryer. The preheated air is divided into two streams. One is used as combustion air in fired heaters, the other one is used as the make-up air in the drying gas loop. At the outlet of the waste heat exchanger, moist flue gas is at 240°C (hot humid air in figure 1). As it contains suspended fiber particles, it has to be treated in a scrubber where water coming from the storage tank is sprayed. The moist flue gas leaving the scrubber is discharged to the environment at 75°C. In addition, condensation of a portion of the water contained in the moist air occurs in the scrubber: this ensures both heat recovery and water recovery (thus reduction of fresh water make-up to the site). The studied process is now in operation; consequently some process units cannot be modified: the existing steam production system cannot be revamped. In addition, the technological choices, concerning the thermal dryer and the scrubber, have to be left out of the analysis.

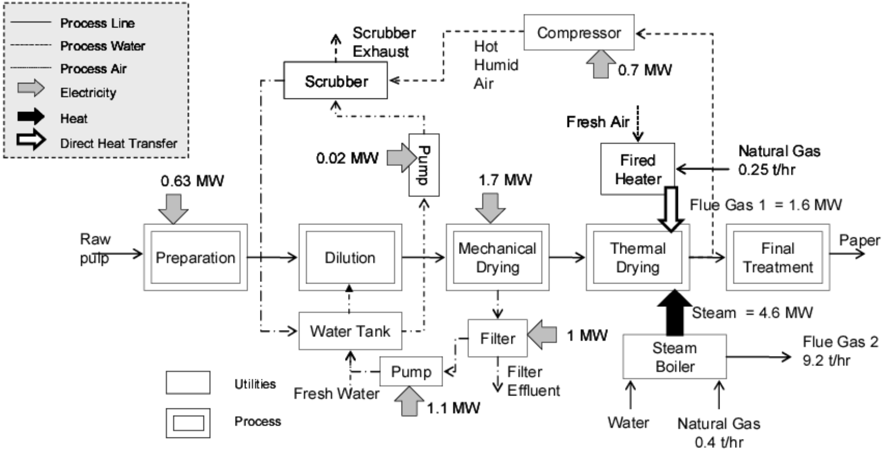

Figure 1. Simplified scheme of paper production process and its utilities

2.2 Simulation of the industrial site with ProSimPlus®

Using all the collected data, simulation of the industrial site has been performed with ProSimPlus® software. To account for the thermodynamic properties of the three sets of chemical components circulating in the paper, water and gas loops, three thermodynamic profiles have been defined. As the process simulation provides us with the process picture close to the real conditions, it can eliminate further measurements and data extraction along the energetic and exergetic analysis.

3. Exergy Analysis

By offering the possibility to make automatic calculation of exergy of material and heat streams and to present the result of exergy balance in different forms such as pie or bar diagram for the given process or utility zone in an automated way, ProSimPlus® simulator facilitates exergy analysis on the process (Ghannadzadeh et al. 2011). Figure 2 summarizes the results of exergy analysis by detailing the internal and external exergy losses.

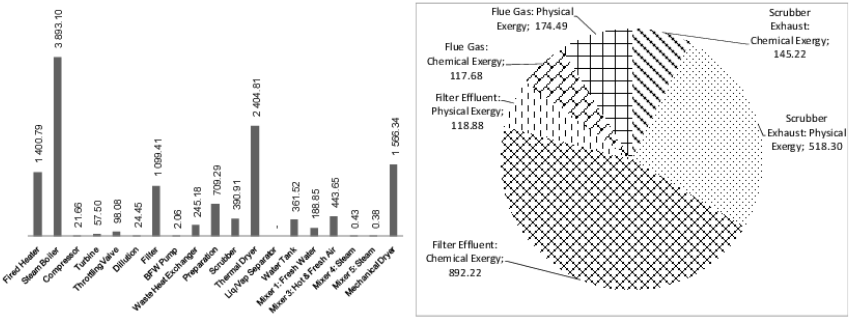

Figure 2. Exergy losses: a) internal exergy losses (kW) or irreversibilities (kW), b) external losses (kW)

As can be seen in figure 2, the largest irreversibilities occur in reaction-based units like steam boiler and furnace. The second-largest irreversibility occurs in the dryer; this is due to the finite temperature difference in the heat transfer. Table 1 takes a step further by presenting the source of irreversibility and way of improvements for each unit operation.

Table 1. Internal exergy losses, sources of irreversibility and improvement ways

Unit Operation	**Source of Irreversibility**	**Suggestion of improvement**
Steam Boiler	Mixing of feed streams, Combustion	Pre-heating of feeds
Thermal Dryer	Thermal gradients, Pressure drop, Mechanical friction, Concentration gradients	Pre-drying, Equi-partition of driving force
Heat Exchanger	Temperature difference	Uniform gradient, as low as possible driving force
Throttling valve	Throttling	Avoid depressurizing steam
Mixer, Water Tank, Dilution	Temperature and composition difference	Isothermal mixing
Scrubber	Temperature and composition gradient	Multistage heat and mass transfer

Besides the internal exergy losses, external exergy losses have a significant contribution in total exergy losses. These exergy losses can be avoided provided that effluents are reused efficiently. Thus, to give hints for the recycling of these effluents, external exergy losses are classified according to physical and chemical exergy losses. For instance, heat recovery of hot streams can reduce the physical external exergy losses whereas recycling of components which do not belong to the reference environment, can reduce the chemical exergy losses. For example, the filter effluent accounts for about 50% of total exergy loss. This is due to both chemical (cellulose effluent that should be recycled) and physical exergy loss (relative high exhaust temperature) associated with this stream. After filter, scrubber is in the second place by losing 663.52 kW exergy. Unlike filter, exergy lost by scrubber is more due to the physical exergy. To reduce its external exergy loss, a waste-heat exchanger at the outlet of scrubber is required to recover further its thermal energy.

Besides, external loss in the boiler is due to both thermal and chemical potential. Thermal energy from flue gas should be recovered but the risk of corrosion due to acid dew point makes it impossible to decrease its temperature down to 25°C. Therefore, to reduce its physical external exergy loss, the thermal energy of flue gas should be recovered down to its relatively low dew point of 56°C as the fuel is assumed to be sulfur-free. To reduce its chemical external exergy loss, recycling of flue gas should be considered. All the streams which cause the external exergy losses due to temperature difference are the heat sources which can be potentially used (see table 2). The pinch analysis can now be brought into action to screen the streams which can play role as a heat source to be integrated with the heat sink. Note that pinch analysis does not take into account external exergy losses associated with chemical exergy.

Table 2. Low-grade Hot streams to avoid physical External Exergy Losses (LHEEL)

Stream	T_{out} (°C)	T_{Ref} (°C)	Heat load (MW)	Process/Utility
Filter Effluent	60	25	1.98	Process
Scrubber Exhaust	75	25	4.71	Process
Flue Gas	230	Acid Dew Point (56°C)	0.44	Utility

4. Pinch Analysis

4.1. Analysis of the process without the utility system

In this study, all the unit operations of the process cannot be revamped. For instance, concerning the thermal dryer for technological reasons the utilities conditions (steam and hot flue gas) cannot be modified. Consequently, in this case study the optimization of the process will mainly concern the utility system supplying the heat requirement and also the reuse of the heat inside the process boundary. As a first step, the process model excludes the utility system and displays two utility cold streams: fresh air, which must be heated up to 460 °C, and fresh water that must be transformed into steam to be used in the thermal dryer. Modeling this process using ProSimPlus$^{®}$ and applying the automatically extracted data, the process composite curve (CC) is drawn (see figure 3).

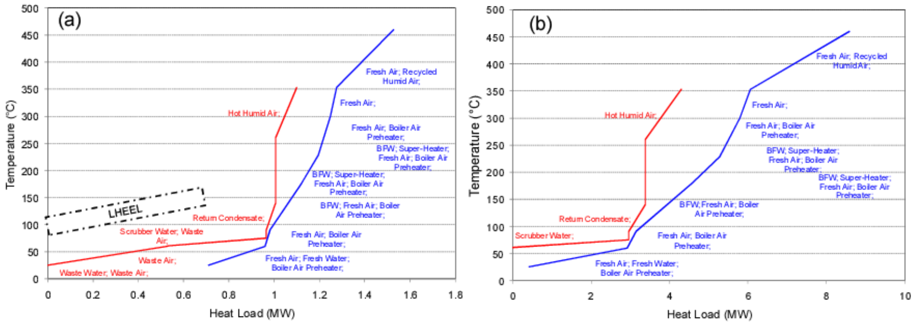

Figure 3. Composite curve: a) first version, b) second version excluding LHEEL

As can be seen in figure 3, LHEEL (see table 2) are all located below pinch temperature. This means that these streams are not good candidate to achieve the Minimum Energy Requirement (MER) of the process as they result in increase of the minimum cold utility requirement. As a consequence, a new set of data have to be built in which LHEEL are excluded. The new CC (see figure 3b) shows the minimum hot and cold utility requirement, respectively equal to 4.3 MW and 0.4 MW.

Furthermore, as shown in figure 4 which represents the process grand composite curve (GCC), it is obvious that the flue gas generated by the steam boiler (T_{stack}=1360 °C) is sufficient to meet the global hot utility requirement of the process.

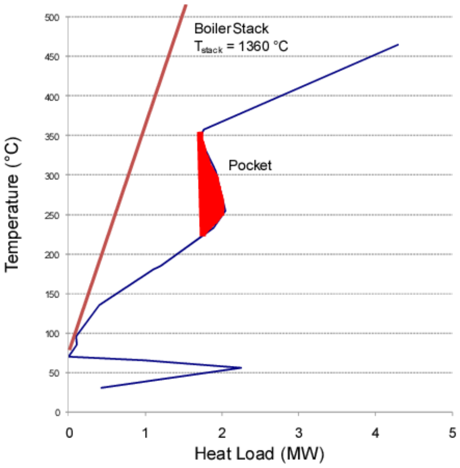

Figure 4: Grand Composite Curve (GCC) of the

4.2. Suggestion of improvement

As depicted in figure 4, a single utility can be used to satisfy the heating requirements for both hot gas production and steam generation. Assuming sulfur-free fuel with relatively low dew point of 56°C, the level of hot utility is imposed by process pinch neither utility pinch nor acid dew point. To use only one hot utility, we might exclude the fired heater and in turn revamp the steam boiler to increase its capacity. The use of the process simulator will help us to determine the required natural gas flowrate and to evaluate the performance of the retrofit process. Figure 5 shows the grid diagram of Heat Exchanger Network generated by the HINT software developed by Martín and Mato (2008) for the revamped process with only one

Table 3. Base case vs. retrofit process

Consumption/ Emission	Base case	Retrofit: Only Boiler	% Saving
Natural gas (t/h)	0.649	0.580	10.6
Fresh air (t/h)	27.7	21.0	24.2
Fresh water (t/h)	55.0	54.7	0.5
Cold utilities (kW)	1343	1087	19.1
CO_2 (t/h)	1.77	1.59	10.2
External exergy losses (kW)	1966	1843	6.3
Exergy efficiency	0.77	0.79	2.6

boiler as the hot utility. Table 3 compares the performances of the retrofit process with the base case process. The reduction of resource (e.g. natural gas, fresh air and water) and CO_2 emission is obvious. In addition, exergy efficiency is increased as external exergy loss is reduced by recycling of the flue gas.

5. Combining Exergy Analysis (EA) and Pinch Analysis (PA)

The study of an industrial case study has permitted to highlight the strengths of each approach and to propose a first way of combining EA and PA in a sequential strategy: first, the EA permits to obtain a diagnosis of the existing process. First, it evaluates the irreversibilities of each unit operation and suggests technical ways to reduce these internal exergy losses. Then, it locates and calculates external exergy losses. When exergy is decomposed into thermal, mechanical and chemical terms, it allows quantifying the contribution of each parameter which are temperature (T), pressure (P) and chemical (composition z), to a common unit: kW. The way of using EA or PA and of coupling these approaches depends of the contribution of each term (T, P, z) in the exergy balance. Here, we have illustrated the case of chemical and thermal exergy losses. In the case of chemical exergy loss (i.e. cellulose in the case study) some recycling solutions could be considered. In the case of thermal exergy, the concerned streams become hot or cold streams for the PA. Then, starting from the list of hot and cold streams, PA proposes different solutions to optimize both process and the utility system and also to reduce the energy consumption of the global system. Finally, calculation of the exergetic efficiency of the different configurations can help the process manager to make a choice between several solutions.

6. Conclusion

This paper presents how the integration of PA and EA in a process simulator can be useful for finding solutions to save energy and natural resources. In addition, EA which pinpoints the sources of inefficiency in the given system, can serve as a preliminary step for defining the set of hot and cold streams for PA which ultimately screens them for maximum heat recovery. In the presented industrial case study, the process constraints do not allow us to propose any process modification, especially on the thermal dryer which is the most energy intensive unit operation. Therefore, we have shown how retrofit of utilities can reduce the consumption of natural resources and CO_2 emission. This can be further developed by introducing a cogeneration system to reduce the net cost of energy required as shown by Kemp (2007). PA and EA can be coupled together to find the best configuration of cogeneration system using the conventional presentation of Carnot Factor in the GCC as shown by Brown et al. (2005).

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NOMENCLATURE

General symbols

Symbol	Description	*Unit*
B	exergy flow	*W*
A	flow of affinity of reaction	*W*
b	molar exergy	*J/mol*
G	Gibbs free energy flow	*W*
g	molar Gibbs free energy	*J/mol*
H	enthalpy flow	*W*
h	molar enthalpy	J/mol
n	molar flowrate	mol/s
N	number of species	-
NS	number of streams	-
P	pressure	*bar*
Q	heat flow	*W*
q	heat per mole	*J/mol*
R	universal gas constant	*8.3144621J/(mol K)*
S	entropy flow	*W/K*
s	molar entropy	*J/(mol K)*
T	absolute temperature	*K*
W	power	*W*
w	work per mole	*J/mol*
$\mathbf{x}$	liquid fraction	-
$\mathbf{y}$	vapor fraction	-
$\mathbf{z}$	global composition of material stream	-
v	stoichiometric coefficients	-
V	velocity	m/s
g	standard gravity	$9.80665\ m/s^2$
l	height	*m*
f	friction factor	-

Greek symbols

μ	chemical potential	
ω	vapor ratio	
$\Delta G^{\circ}_{v\mapsto L}$	standard Gibbs energy of condensation	J/mol
ΔG°_{f}	standard Gibbs energy of formation	J/mol
σ	Stefan–Boltzmann constant	$\mathrm{W\ m^{-2}\ K^{-4}}$
ξ	progress of reaction	

Subscripts

c	components in the given material stream
el	reference element
f	formation
gen	generated entropy
j	reference substance
j, i	reference substance j from process substance i
M	related to material stream
Q	related to heat stream
ref	references substance
rev	reversible
useful	useful stream
W	related to work stream
waste	waste stream
Intrinsic	Intrinsic exergy efficiency

utilizable	utilizable exergy coefficient
degraded	degraded work
recoverable	recoverable exergy

Superscripts

*	perfect gas
ch	chemical
E	excess enthalpy or entropy
L	liquid phase
Ph	physical
V	vapor phase
W	work
ΔP	mechanical component of physical exergy
ΔT	thermal component of physical exergy
In	input streams
Out	output streams
0	standard state (pure-component, perfect gas, $T^0=298.15$ K, $P^0=1$ atm)
00	standard dead state
Tr	transiting exergy
P	produced exergy
C	consumed exergy
pu	produced utilizable exergy

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