

Energy and Exergy Analysis of a Pre-distillation Unit. A Case Study.

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Abstract

Energy and exergy balances were evaluated for the pre-distillation unit (Un-0100) of an aromatics plant from a Portuguese refinery. The main objective of the study was to find out the relevant thermal energy losses in order to implement energy recovery procedures, without questioning the operating processes of the plant. In its overall analysis, the Un-100 obtained an energy efficiency of 13.4% and an exergy efficiency of 2.3%. The equipment that has higher energy losses in this unit is the air coolers, representing 59.9% of the energy losses, i.e., most of the energy lost in this unit is due to the cooling process. The irreversibility observed in these equipment groups was 11.2%. Moreover, the furnace represents 15.6% of energy losses, but this component stands out in the irreversibility analysis, with 56.3% of the total. Based on these values, it can be said that this equipment presents a high potential of improvement of its energy and exergy performance. These results, concern a small part of a more general case study about the performance of the aromatics plant, and clearly show the need to establish complementary energy and exergy balances in order to increase the energetic performance of the unit.

Keywords: *Energy efficiency; exergy efficiency; irreversibility; pre-distillation.*

1. Introduction - The Energy in the Petrochemical Industry

In oil refineries, a reasonable amount of energy is used for processing. Refineries ensure all the services required for their operation through more or less complex transformations of energy, using some of the products obtained by oil processing. Therefore, the oil to refineries is not only a raw material but also the main source of energy, needed for crude oil processing.

The level of energy consumption can be represented by a special indicator, which is no more than the amount of oil required for the refinery to meet its energetic needs. This proportionally, the fraction of total quantity of processed oil used for energy production is often observed as an indicator of bad or good energy performance of the refinery. Currently, for oil refineries, the share of crude oil used for energy production is between 4% and 8%, depending on the level of complexity of refineries [1].

Inefficient refineries can reduce their energy consumption by about 20-30% through the use of more efficient technologies and better energy solutions. This percentage is not small, considering the share of energy costs in total costs of crude oil processing; a refinery whose oil quota is 5% energy for own consumption, has to operate 16 days per year to meet its energy needs [1].

In recent decades there has been a marked development of the petrochemical industry, driven by increased demand for high value-added products. This factor, coupled with the need to respond to an increasingly competitive global market and the obligation to respond to environmental compliance, increased the concern of the petrochemical industry towards increasing energy efficiency [2]. This recent concern lead to some studies concentrating on the recovery of flare gas energy [3, 4], on the adequate use of

waste heat through organic Rankine cycles [5] and through the retrofitting of some refinery processes to improve the energy efficiency in oil refineries [6].

The thermodynamic analysis of the separation systems, either through conventional basic approaches [7], or through the use of adequate commercial software [8,9], has not only been oriented towards the petrochemical systems, but also for the biodiesel production [10]. The work that has been carried out in the thorough analysis of the distillation processes is justified by the heavy energy burden the distillation processes impose upon the petrochemical and chemical industries [11]. There is consequently the need to improve the environmental and energy sustainability of these industries [12,13]. Of course the main target is to minimize energy usage and waste formation through adequate process integration procedures [14].

An exergy balance of any equipment or process can say quite a lot about its potential in terms of the useful work that is being processed. The exergy destruction, or losses, is a quantitative measure of the process inefficiencies [15]. Therefore the exergy analysis represents a new light with respect to an energy-efficient target [16]. Accordingly, exergy analysis, when used in conjunction with the mass energy balances, becomes an effective tool both to achieve an efficient use of energy with low environmental impact and high sustainability, and to provide optimal points of operation in the process and in systems design [17-19].

The pre-distillation unit studied in this text, Figure 1, is usually feed by reformed produced in the combustibles unit to which it is attached. This unit is constituted by three distillation columns (AS(T)-0101, AS(T)-0102, AS(T)-0103), one furnace (H-0101), three heat exchangers (E-0101, E-0109, E-0110), two reboilers (E-0104, E-01074) and two steam exchangers (E-0102, E-0108).

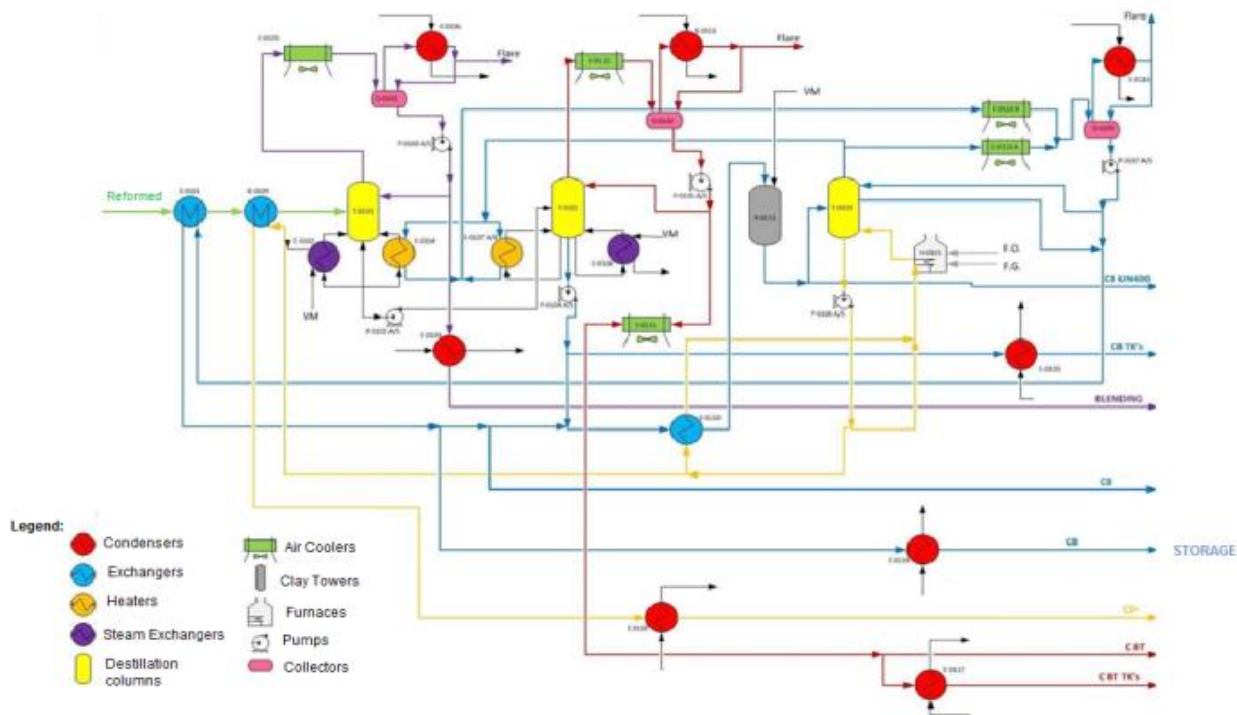


Figure 1. Diagram process of Un-0100 [20].

The cooling of the unit is made through eight air cooled condensers (E-0103, E-0106, E-0113, E-0116, E-0117, E-0118, E-0119, E-0120), and five air coolers (E-0105, E-0111, E-0112, E-0115A, E-0115B). Besides, the unit has six fluid circulation pumps (P-0102, P-0103, P-0104, P-0105, P-0106, P-0107) and three collectors (D-0101, D-0102, D-0103), as shown in Figure 1.

The main objective of the present study was not to question the technological process being followed in the unit, or to present any new methodology of analysis, but to find out situations where the exploitation of energy wastes and losses could improve the energy performance of the plant in its present operating layout. This study refers to a small part of a more general case study concerning the energy and exergy performances of an aromatics plant where this pre-distillation unit is used [21].

In the present study the relative importance of the main components of Un-100 is discussed, while in the general case [21] the discussion is centralized on the relative weights of all the units composing the aromatics plant without going into the detail analysis of the respective equipment. Although there are advanced software tools that can be applied to the analysis of chemical units, in the present work a basic conventional approach by means of the development of a worksheet, was the adopted procedure.

2. Methodology of the Analysis

The first step of the study was to perform the overall mass and energy balances of Un-0100. The global energy efficiency of the unit was determined, corresponding to the ratio between the useful output energy in the process flow currents and the consumed energies. In the second step, the energy analysis was complemented by an exergy analysis, looking at the qualities of the several energy forms that were handled in the process.

In order to perform such energy assessment, a scrutiny of the different energy quantities involved in the equipment of the unit was carried out according to the energy balance sheets of the unit from January to July 2011. Based on the daily energy consumption, processing currents mass flow rates, as well as temperature and pressure readings, monthly and annual average values were determined. Whenever necessary, mass and energy balances of the equipment were executed in order to complement missing values from the unit data sheets. The energies supplied to this unit were electrical, chemical and thermal. The electricity was consumed by pumps, fans and lighting. The chemical energy was supplied as fuel oil and fuel gas from the refinery. The thermal energy was composed by medium pressure steam at 260 °C and 1700 kPa absolute pressure, also from the refinery. The reformate flow rate entering unit Un-0100 at a high inlet temperature was also considered as an inlet energy flow. The output flows of the unit were C5's cuts (light gasolines), the benzene and toluene cut, and a mixture (p-xylene, o-xylene, m-xylene and ethyl benzene) of C8's cut and C9's cut. For these flows, all the thermodynamic and thermochemical properties were calculated at the average temperature between the reference state temperature and the temperature of the fluid under consideration. When phase changes took place, the liquid phase properties were determined at the average temperature between the reference temperature and the vaporization temperature, whereas the gaseous phase properties were determined at the average temperature between the vaporization temperature and the temperature of the gaseous phase under consideration. The adopted reference state was 1 atm and 0 °C.

3. Energy Balance

3.1 Enthalpies of the Operating Mass Flows

For the energy balance, steady state operating conditions were assumed. In the calculation of the

thermodynamic properties of the several fluids, the liquids were considered incompressible and the gases as perfect gases. This simplified approach was imposed by the difficulty of finding thermodynamic tables for all the fluids considered in the analysis. On the other end, correlations or tables, for the calculations of specific heats, either for liquids or for vapors, were easily found.

For the calculation of the corresponding enthalpies, average liquid and gaseous phase specific heats were used, as well as the latent heats of boiling or condensation, according to the phase change taking place. To find out whether the fluids under analysis were either in the liquid or in the gaseous phase, their temperatures were compared with the boiling temperatures, function of the corresponding pressures. Knowing the pressure through the extended Antoine equation,

$$\log_{10} p_{\text{vap}} = A_1 + \frac{B_1}{T_{\text{vap}}} + C_1 \log_{10} T_{\text{vap}} + D_1 T_{\text{vap}} + E_1 T_{\text{vap}}^2 \quad (1)$$

the vaporization temperature for each component was determined [22]. Here, A_1 , B_1 , C_1 , D_1 and E_1 are the Antoine constants; the vaporization pressure p_{vap} is in mmHg and the vaporization temperature T_{vap} in K. A shorter version of Antoine equation was also used [23],

$$\log_{10} p_{\text{vap}} = A_2 - \frac{B_2}{C_2 - T_{\text{vap}}} \quad (2)$$

where p_{vap} is still in mmHg, but T_{vap} is now, in °C. A_2 , B_2 and C_2 are the constants for this shorter version of the Antoine equation.

For the calculation of the molar base specific heats for the liquid phase region, the correlation proposed by Yaws [22] was used,

$$\bar{c}_l = A_3 + B_3 T + C_3 T^2 + D_3 T^3 + E_3 T^4 \quad (3)$$

with A_3 , B_3 , C_3 and D_3 as the characteristics constants for each fluid under consideration and T taking values in K.

Two correlations proposed by Perry and Green [23] were used for the calculation of the specific heat at constant pressure in molar base for gaseous fluids. The first equation was for the propyl benzene,

$$\bar{c}_p = A_4 + B_4 \ln T + \frac{C_4}{T} + D_4 T \quad (4)$$

being A_4 , B_4 , C_4 and D_4 the constants for this component, while,

$$\bar{c}_p = A_5 + B_5 \left[\frac{\frac{C_5}{T}}{\sinh\left(\frac{C_5}{T}\right)} \right]^2 + D_5 \left[\frac{\frac{E_5}{T}}{\cosh\left(\frac{E_5}{T}\right)} \right]^2 \quad (5)$$

was used for the other components, with A_5 , B_5 , C_5 , D_5 and E_5 as the corresponding correlation constants.

When necessary, the latent heat of vaporization, in molar basis, was calculated from [23],

$$\bar{h}_v = A_6 (1 - T_r)^{B_6 + C_6 T_r + D_6 T_r^2} \quad (6)$$

where the constants A_6 , B_6 , C_6 and D_6 were chosen according to the components; T_r is the respective reduced temperature, while T_c is the fluid critical temperature.

So, for a component in the liquid phase, its specific enthalpy was calculated by,

$$h_l = c_{ll} (T_f - T_{\text{amb}}) \quad (7)$$

while, for a component in the gaseous phase,

$$h_g = c_{lg} (T_{\text{vap}} - T_{\text{amb}}) + h_{lv} + c_{vg} (T_f - T_{\text{vap}}) \quad (8)$$

The reference state of $p_{\text{amb}} = 1$ atm and $T_{\text{amb}} = 0$ °C was chosen to coincide with the ambient reference state also used in the exergy calculations.

The enthalpy of a given current mixture of components was the weighted value according to,

$$\dot{H} = \dot{m}_f \sum h_{li} y_i \quad (9)$$

if all the mixture components were in the liquid state. In this equation, \dot{m}_f is the total mass flow rate of the current entering or leaving a given component of the plant, h_{li} the specific enthalpy of the component i that has a mass fraction y_i .

When the current was a mixture of liquid and gaseous components,

$$\dot{H} = \dot{m}_f \left[\sum h_{li} y_{li} + \sum h_{gi} y_{gi} \right] \quad (10)$$

where y_{li} and y_{gi} are, respectively, the liquid and gas mass fractions of component i .

In the case of condensers and air coolers, a thermal heat loss power in absolute terms \dot{Q}_L , was defined as,

$$\dot{Q}_L = \dot{H}_{\text{in}} - \dot{H}_{\text{out}} \quad (11)$$

For other types of heat exchangers transferring heat between two processing flows, the thermal heat loss power in absolute terms was defined as,

$$\dot{Q}_L = \Delta \dot{H}_a - \Delta \dot{H}_b \quad (12)$$

with $\Delta \dot{H}_a$ as the enthalpy power reduction of the hotter flow and $\Delta \dot{H}_b$ as the enthalpy power increase of the cooler flow.

3.2 Fuel Gas and Fuel Oil

Fuel gas and fuel oil were the fuels used in the furnaces. Their input power was known through the annual average mass flow rate data and thus, for a generic fuel,

$$\dot{F}_F = \dot{m}_F LHV_F + \dot{m}_F c_F (T - T_{\text{amb}}) \quad (13)$$

being \dot{m}_f the mass flow rate of the generic fuel, LHV_f the corresponding low heating value, while $\dot{m}_f c_F (T - T_{amb})$ refers to its sensible energy. So the total fuel input power \dot{F} was given by

$$\dot{F} = \dot{F}_{FO} + \dot{F}_{FG} \quad (14)$$

3.3 Medium Pressure Steam

The power input associated to a given mass flow rate of medium pressure steam was determined through the difference between its enthalpy and the enthalpy of the corresponding saturated liquid state, assuming that the condensate return was saturated liquid,

$$\dot{H}_{mv-in} = \dot{m}_{mv-in} (h_{v-in} - h_{l-in}) \quad (15)$$

h_{v-in} is the steam enthalpy, h_{l-in} the corresponding saturated liquid enthalpy and \dot{m}_{mv-in} the mass flow rate of medium pressure steam entering the equipment.

There is also medium pressure steam being used as fuel atomizing fluid in the furnace. The input power of the atomizing medium pressure steam sent to the furnace was calculated through,

$$\dot{H}_{mv-in-F} = \dot{m}_{mv-in-F} h_{mv-in-F} \quad (16)$$

where $\dot{m}_{mv-in-F}$ is the mass flow rate of atomizing steam and $h_{mv-in-F}$ its specific enthalpy.

The total medium pressure steam input power for the unit was then,

$$\dot{H}_{mv-in-T} = \sum \dot{H}_{mv-in-HE} + \sum \dot{H}_{mv-in-F} \quad (17)$$

the index HE refers to the heat exchangers, while F to the furnace.

3.4 Electricity

The input electric power supplied to pumps and fans was daily controlled and registered by the utilities department of the plant. As electrical energy is pure exergy [15, 24 – 26], its calculation was immediate.

3.5 Combustion Gases

The exhaust combustion gases, expelled at high temperatures from the furnace towards the environment, still had elevated energy values. This energy was quantified, not only for auditing reasons, but also because it would be necessary to evaluate the possibility of its further use as an energy source. The mass flow rate of combustion gases had three main components: the wet base combustion gaseous products that include the water formed in the process \dot{m}_{g-out} ; the water vapor that entered in the air to the combustion \dot{m}_{H_2O-in} ; and the fuel atomizing steam sent to the furnaces, in the case of fuel oil combustion $\dot{m}_{mv-in-F}$. The thermal power of this flow of combustion gases was then expressed as,

$$\dot{H}_{g-out} = (\dot{m}_{g-out} cp_{g-out} + \dot{m}_{H_2O-in} cp_{H_2O} + \dot{m}_{mv-in-F} cp_{mv-in-F}) (T_{g-out} - T_{amb}) \quad (18)$$

where cp_{g-out} is the average specific heat at constant pressure of the combustion products and T_{g-out} the fumes exit temperature. For the quantification of the water introduced with the combustion air \dot{m}_{H_2O-in} , an average absolute humidity of 0.006 kg of water per kg of dry air was determined, taken into account the typical atmospheric conditions found in the region for the time period under analysis. The mass flow rate of the atomization steam, 0.5 kg of steam per kg of fuel oil, was obtained from a previous study on the evaluation of the performance of the furnace [27]. The specific heat of the combustion products was calculated by assuming that the combustion was complete with excess of air. The excess of air and the mass fraction of the fumes components were determined from the combustion mass balances based upon the measured composition data.

The exhaust temperature of the fumes was daily monitored and, knowing the fuel composition and the fumes composition, the remaining information was determined through combustion calculations and furnace energy balances. In these energy balances, the input energies were the fuel energy, the energy of the fuel atomizing steam and the latent heat of the water vapor in the combustion air. The energies leaving the control volume were the energy losses of the furnace, the useful heat transferred to the processing current and finally, the energy available in the exhaust combustion gases.

The fuel oil had 15% (w/w) of hydrogen and 85% (w/w) of carbon, while the fuel gas was composed by 80% (v/v) of methane, 10% (v/v) of propane and 10% (v/v) of butane. As the mass flows of fuel gas and fuel oil introduced in the furnaces were also known, their mass fractions were easily obtained,

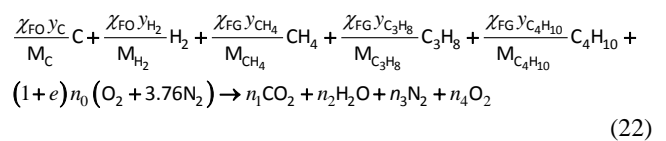
$$\chi_{FO} = \frac{\dot{m}_{FO}}{\dot{m}_{FO} + \dot{m}_{FG}} \quad (19)$$

$$\chi_{FG} = \frac{\dot{m}_{FG}}{\dot{m}_{FO} + \dot{m}_{FG}} \quad (20)$$

The global composition of the mixture of fuel gas and fuel oil supplied to a given furnace was then determined by the following equation where the y_i 's are the mass fractions of the components

$$\chi_{FO} y_C + \chi_{FO} y_{H_2} + \chi_{FG} y_{CH_4} + \chi_{FG} y_{C_3H_8} + \chi_{FG} y_{C_4H_{10}} \quad (21)$$

The chemical equation for the combustion with air in excess was then written as



where e is the excess air fraction.

From the balance of chemical species, plus the knowledge of the molar fraction of oxygen in the combustion

products all the n_i 's for the reactants and products were determined.

3.6 Convection and Radiation Losses

In the literature, radiation and convection losses are of the order of magnitude of 2% at maximum output regime of the plant, but can reach up to 10% for lower operating regimes [28, 29]. Here, the radiation and convection thermal losses were determined according to average local atmospheric and wind conditions and also by taking into account reactor and columns dimensions. For the calculation of the columns heat losses, an average velocity was determined based on monthly average wind velocities in the plant region and also on average wall external temperature, determined according with the average temperature of the current that flows in the columns minus 20 °C, corresponding to the thermal resistance in the wall.

3.7 Energy Efficiency

The energy efficiency was defined as the ratio between the energy available in the output currents of the processed fluids \dot{P}_{out} and the energy supplied \dot{P}_{in} in the inflow currents and utilities serving the unit,

$$\eta_E = \frac{\dot{P}_{out}}{\dot{P}_{in}} \quad (23)$$

4. Exergy Balance

4.1 Exergy Concept and Definitions

The exergy is a combined property of the system and of the environment as it takes into account both, the system thermodynamic state and the reference environment thermodynamic state [26]. In the present work, the environment reference state was considered as 1 atm and 0 °C. Although the exergy of a given current has several components, kinetic, potential, physical or co-enthalpy [15, 24] and chemical, in the present work only the physical and the chemical components were considered. As the process flows did not suffer any chemical reaction, only physical exergies were taken into account, whereas the chemical exergy was only considered in the analysis of the furnace. For a steady state flow condition the exergy balance is given by,

$$\sum \dot{E}x_{in} = \sum \dot{E}x_{out} + \dot{I}_p \quad (24)$$

where $\sum \dot{E}x_{in}$ is the total exergy power entering the control volume, $\sum \dot{E}x_{out}$ the total exergy power leaving the control volume and \dot{I}_p the irreversibility power or exergy losses.

The physical exergy for a given flow neglecting the kinetic and the potential components [15, 24] is,

$$\dot{E}x_{phy} = (\dot{H} - \dot{H}_{amb}) - T_{amb}(\dot{S} - \dot{S}_{amb}) \quad (25)$$

where \dot{H} is the current enthalpy power, \dot{H}_{amb} the current enthalpy power at the reference state conditions, \dot{S} the current entropy power and \dot{S}_{amb} the current entropy power at the reference state conditions.

The determination of the chemical exergy, in a mass base at the reference temperature $T_{amb} = 0$ °C for a given fuel, is a bulky process, as explained in Kotas [15]. However, as many fuels are mixtures of several components, frequently of unknown physical properties, the same author recommends a more pragmatic approach,

$$\varepsilon_{amb} = LHV \beta \quad (26)$$

which will be followed in this work. β is the correction factor for the chemical exergy [30]. There is however a point to take into account, as the LHV is defined at $T_0 = 25$ °C, and being $T_{amb} = 0$ °C in the present work, a correction should be required,

$$\varepsilon_{amb} = \beta LHV \frac{T_0}{T_{amb}} + LHV \frac{T_0 - T_{amb}}{T_0} \quad (27)$$

However, the difference between the values given by Eqs. (26) and (27) is so small that it can be neglected.

For the determination of the chemical exergy of the furnace exhaust gases, the chemical exergy for any of its component, considered as a perfect gas, is [15],

$$\bar{\varepsilon}_{amb,i} = \bar{R} T_{amb} \ln \frac{p_{amb}}{p_{amb,i}} \quad (28)$$

where $\bar{\varepsilon}_{amb,i}$ is the molar chemical exergy at T_{amb} and at its partial pressure in the environment $p_{amb,i}$.

For a perfect gases mixture, the relation between $\bar{\varepsilon}_{amb,i}$ and $\bar{\varepsilon}_{amb}$ is [15]:

$$\bar{\varepsilon}_{amb} = \sum x_i \bar{\varepsilon}_{amb,i} + \bar{R} T_{amb} \sum x_i \ln x_i \quad (29)$$

and then,

$$\varepsilon_{amb} = \frac{\bar{\varepsilon}_{amb}}{M_{mix}} \quad (30)$$

where $M_{mix} = \sum x_i M_i$ is the molecular mass of the gaseous mixture, and x_i the molar fraction of the component i which has a molecular mass M_i . So, the total chemical exergy is given by,

$$\dot{E}x_{chem} = \dot{m} \varepsilon_{amb} \quad (31)$$

where $\dot{m} = \sum \dot{m}_i$, being \dot{m}_i the mass flow rate of component i of the mixture.

4.2 Exergy of the Components

As the unit Un-0100 has only distillation processes, the physical exergy of the several involved components were accounted for in the evaluation of the process flows. For each equipment, a control volume was defined and the corresponding inlet and outlet exergy flows were determined and, based on these exergy flows, the irreversibility of each equipment was evaluated. For a given

mass flow rate entering a control volume, the physical exergy when all the components are in the same phase, either liquid or gaseous, is,

$$\dot{E}x_{in} = \dot{E}x_{phys.} = \dot{m} \sum y_i \varepsilon_{phys i-in} \quad (32)$$

where $\varepsilon_{phys i-in}$ is the specific physical exergy of the component i entering the control volume, y_i its mass fraction, while \dot{m} is the total inlet mass flow rate.

The entropy of the several reactant flows involved in the system under analysis was calculated according to one of the two following equations. For a component in the liquid phase,

$$s_l = c_{ll} \ln \frac{T}{T_{amb}} \quad (33)$$

where s_l is the specific entropy of the liquid phase component, and for a component in the gaseous phase, assumed a perfect gas,

$$s_g = c_{lg} \ln \frac{T_{vap}}{T_{amb}} + s_{lv} + cp_{vg} \ln \frac{T}{T_{vap}} \quad (34)$$

where s_g is the specific entropy of the component in the gaseous phase and s_{lv} the corresponding vaporization entropy.

Considering that the enthalpies and entropies are calculated based on the reference state p_{amb} and T_{amb} , the specific physical exergy for a liquid component i entering the control volume is given by,

$$\varepsilon_{phys l i-in} = h_{l i-in} - T_{amb} s_{l i-in} \quad (35)$$

where $h_{l i-in}$ is the specific enthalpy for component i entering the control volume in the liquid phase, and $s_{l i-in}$ the respective specific entropy.

The specific physical exergy for component i entering the control volume in the gaseous phase $\varepsilon_{phys g i-in}$, is

$$\varepsilon_{phys g i-in} = h_{g i-in} - T_{amb} s_{g i-in} \quad (36)$$

where $h_{g i-in}$ is the specific enthalpy for the component i entering the control volume when it is in the gaseous phase, while $s_{g i-in}$ is the respective specific entropy.

When there are components in the liquid and in the gaseous phase then,

$$\dot{E}x_{in} = \dot{m} \left(\sum y_{li} \varepsilon_{phys l i-in} + \sum y_{gi} \varepsilon_{phys g i-in} \right) \quad (37)$$

The first term of the second member concerns the components entering the control volume in the liquid phase while the second term in the gaseous phase. For a current leaving the control volume the procedure is similar, only the temperature range under observation is different.

4.3 Exergy of the Fuel Gas and Fuel Oil

Fuel gas and the fuel oil were the furnace fuels and the corresponding physical exergies were determined by the following equation,

$$\dot{E}x_{phys-Fuel} = \dot{m}_{Fuel} \sum \left[y_i cp_i (T_{Fuel} - T_{amb}) - y_i T_{amb} \left(cp_i \ln \frac{T_{Fuel}}{T_{amb}} - R_i \ln \frac{p_{Fuel}}{p_{atm}} \right) \right] \quad (38)$$

with cp_i the specific heat at constant pressure for the fuel component i , and p_{Fuel} and T_{Fuel} the fuel supply pressure and temperature.

The fuel chemical exergy was determined through,

$$\dot{E}x_{chem-Fuel} = \dot{m}_{Fuel} \varepsilon_{chem-Fuel} \quad (39)$$

where $\dot{E}x_{chem-Fuel}$ is the fuel chemical exergy, $\varepsilon_{chem-Fuel}$ its standard specific chemical exergy and \dot{m}_{Fuel} its mass flow rate. The standard specific chemical exergy was determined by Eq. (26) and the total exergy for the fuels flow was then given by,

$$\dot{E}x_{combl} = \dot{E}x_{phys-fuel} + \dot{E}x_{chem-FO} + \dot{E}x_{chem-FG} \quad (40)$$

4.4 Medium Pressure Steam

The calculation process of the exergy of the steam flows was similar to that presented for the energy accountancy. The differences in the inlet steam and outlet condensate exergies were quantified, with the exception of the direct steam used for fuel atomization in the furnace, whose exergy flow was added to the fuel inlet.

For the steam used in the heat exchangers, its exergy power $\dot{E}x_{mv-HE}$ was determined by means of,

$$\dot{E}x_{mv-HE} = \dot{m}_{mv-HE} (h_{in-HE} - T_{amb} s_{in-HE}) \quad (41)$$

where \dot{m}_{mv-HE} is the steam flow rate consumed in the heat exchangers.

For the direct steam used for fuel oil atomization, its exergy power $\dot{E}x_{mv-in-F}$ was calculated by,

$$\dot{E}x_{mv-in-F} = \dot{m}_{mv-in-F} \varepsilon_{mv-in-F} \quad (42)$$

where $\varepsilon_{mv-in-F}$ is the inlet specific exergy of the atomizing medium pressure steam sent to the furnace, $\varepsilon_{mv-in-F} = h_{mv-in-F} - T_{amb} s_{mv-in-F}$, and $\dot{m}_{mv-in-F}$ the corresponding mass flow rate.

So, the total exergy for the medium pressure steam $\dot{E}x_{mv-in-T}$ is given by,

$$\dot{E}x_{mv-in-T} = \sum \dot{E}x_{mv-in-HE} + \dot{E}x_{mv-in-F} \quad (43)$$

The first term considers the heat exchangers while the second term refers to the atomizing steam sent to the furnace. Because the atomizing steam did not suffer any chemical reaction, only its physical exergy was taken into consideration

4.5 Combustion Gases

The combustion gases exiting the furnace still possess an exergy value to be used downstream, before their rejection to the environment. Their exergy power is determined through the following equation,

$$\begin{aligned} \dot{E}x_{g-out-T} &= \dot{E}x_{g-phys-out} + \dot{E}x_{g-chem-out} \\ &+ \dot{E}x_{H_2O/air-phys} + \dot{E}x_{mv-f} \end{aligned} \quad (44)$$

being $\dot{E}x_{g-phys-out}$ the physical exergy power, $\dot{E}x_{g-chem-out}$ the chemical exergy power, $\dot{E}x_{H_2O/air-phys}$ the physics exergy power of the combustion air moisture and $\dot{E}x_{mv-f}$ the physical exergy power of the atomizing steam.

The physical exergy power of the combustion gases was determined by assuming that they were a mixture of perfect gases,

$$\begin{aligned} \dot{E}x_{g-phys-out} &= \dot{m}_{g-out} \sum \left[y_i c p_i (T_{g-out} - T_{amb}) - \right. \\ &\left. y_i T_{amb} \left(c p_i \ln \frac{T_{g-out}}{T_{amb}} - R_i \ln \frac{p_{g-out}}{p_{atm}} \right) \right] \end{aligned} \quad (45)$$

where T_{g-out} and p_{g-out} are the exhaust temperature and pressure of the combustion gases, while the chemical exergy power of the combustion gases was determined through the following equation,

$$\dot{E}x_{g-chem-out} = \dot{m}_{g-out} \mathcal{E}_{g-chem-out} \quad (46)$$

4.5 Irreversibility

There are some particular situations where the calculation of the exergy destruction can be carried out with some more detail, such as in heat exchangers in general and in particular cases of condensers and air cooled exchangers. For the condensers and air cooled exchangers, the exergy difference between the inlet and the outlet flows,

$$\dot{I}_p = \dot{E}x_{in} - \Delta \dot{E}x_{out} \quad (47)$$

where \dot{I}_p is the irreversibility of the current being condensed or cooled, while for a more conventional heat exchanger transferring heat between two flows, the exergy destroyed is the difference between the exergy changed,

$$\dot{I}_p = \Delta \dot{E}x_a - \Delta \dot{E}x_b \quad (48)$$

$\Delta \dot{E}x_a$ is the exergy power reduction of the heat supply flow,

$$\Delta \dot{E}x_a = \dot{E}x_{a-in} - \dot{E}x_{a-out} \quad (49)$$

and $\Delta \dot{E}x_b$ is the exergy power of the heat reception flow,

$$\Delta \dot{E}x_b = \dot{E}x_{b-out} - \dot{E}x_{b-in} \quad (50)$$

$\dot{E}x_{a-in}$ is the input exergy power of the hot fluid, $\dot{E}x_{a-out}$ the output exergy power of the hot fluid, $\dot{E}x_{b-out}$ the output exergy power of the cold fluid and $\dot{E}x_{b-in}$ the input exergy power of the cold fluid.

4.6 Exergy Efficiency

According to Eq. (24), the exergy efficiency η_{Ex} for any equipment is,

$$\eta_{Ex} = \frac{\sum \dot{E}x_{out}}{\sum \dot{E}x_{in}} = 1 - \frac{\dot{I}_p}{\sum \dot{E}x_{in}} \quad (51)$$

This classical formulation of the exergy efficiency was thoroughly followed in the present study.

5. Results from the Analysis of Un-0100

5.1 Overall Energy and Exergy Results

Through the energy and exergy analysis of Un-0100, the obtained energy and exergy efficiencies were, 13.4% and 2.3%, respectively. These values are extremely low indicating that there is a large basis for improvement, as far as the energy consumption is concerned. In Figures 2 and 3, representing the Sankey and Grassmann diagrams for Un-0100, it can be seen that the set of equipment with greater energy losses are the air coolers with a fraction of 59.9% of the unit losses corresponding to 11.2% of the unit irreversibility. The furnace H-0101 is the single component with higher irreversibility, corresponding to 56.3% of Un-0100 irreversibility. There is a fraction of 4% of energy losses that are not clearly identified. These unaccounted losses are due to limitations and uncertainties of experimental measurements carried out during the normal operation of the plant. They are the inevitable consequence of working with data gathered in actual industrial processes. They correspond to 29.3% of the irreversibility of the unit.

Convection and radiation heat losses represent about 5% of the energy entering the unit. In terms of the exergy losses, the convection and radiation heat losses are included in the unaccountable irreversibility. The unaccountable irreversibility corresponds to 29.3% of all irreversibility or 3.96% of the input exergy of Un-100, Figure 3.

5.2 Analysis of the Main Components of the Unit

The energy input in the Un- 0100 refers to electricity, medium pressure steam, fuel oil, fuel gas and inlet reformed flow. The contributions of these sources of energy are represented in Table 1. The net power which leaves the unit is formed by C5's cut, benzene/toluene cut, C8's cut and C9's cut, Table 2.

The energy losses in the unit occur in the air coolers, heat exchangers, condensers and in the furnace H-0101. In this last equipment, losses were due to conduction, convection and radiation, and to the enthalpy of the released fumes. The equipment whose operational data are unknown (pressure, temperature, composition and mass flows) could not be analyzed. These losses were grouped together and called unidentified losses.

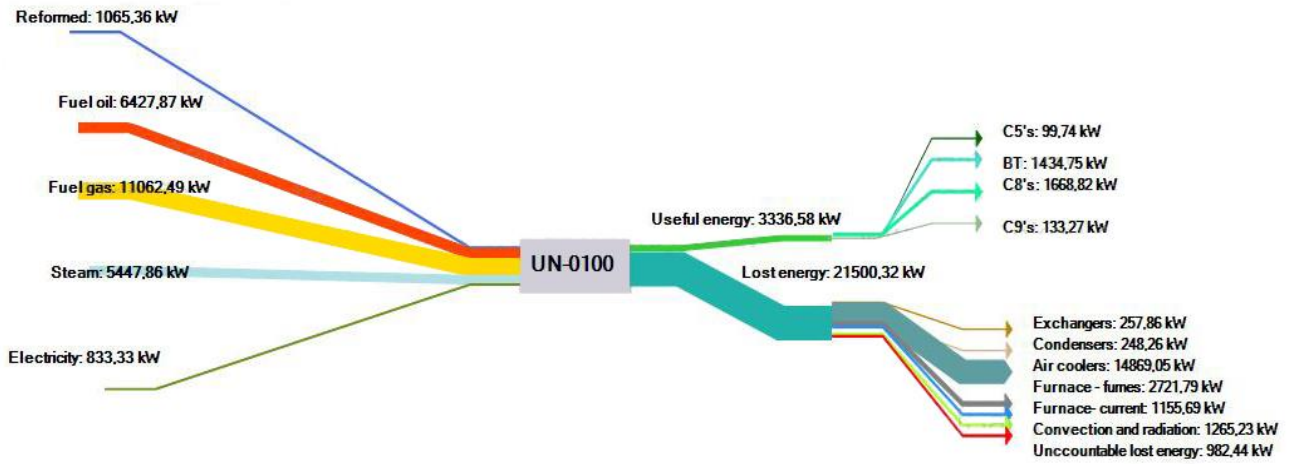


Figure 2. Sankey diagram for Un-0100.

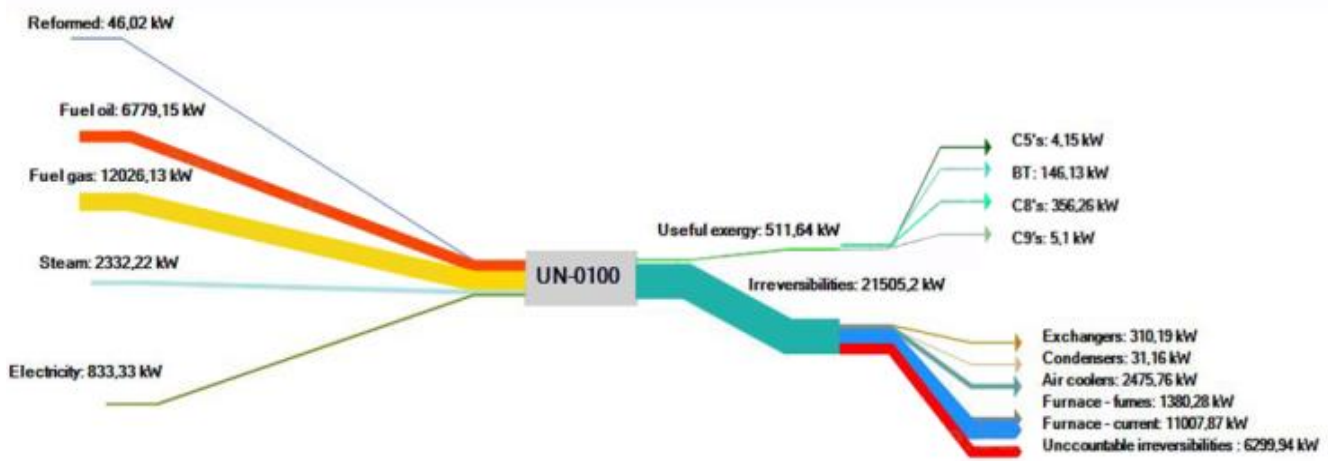


Figure 3. Grassmann diagram for Un-0100.

Table 1. Hierarchy of inlet energy.

Source	Relative weight (%)
Reformed	4
Fuel oil	26
Fuel gas	45
Steam	22
Electricity	3

Table 2. Hierarchy of outlet energy.

Source	Relative weight (%)
C5's cut	0
Benzene/toluene cut	6
C8's cut	7
C9's cut	1
Air coolers	60
Condensers	1
Exchangers	1
Furnace - fumes	11

In order to percept where the major energy losses are located, an energy losses hierarchy is presented in Table 3. The major percentage of energy losses are localized in the

air coolers. In this type of equipment all attention should be addressed to the E-0115 A, which is responsible for 48.1% of total losses. Figure 4 presents the hierarchy of losses in the air coolers.

Table 3. Hierarchy of energy losses.

Type of equipment	Equipment	Energy lost/ Equipment	Energy lost/ Type of equipment
Air coolers	E-0105	1.4 %	73 %
	E-0111	2.0 %	
	E-0112	10.3 %	
	E-0115 A	48.1 %	
	E-0115 B	10.6 %	
Condensers	E-0103	0.3 %	
	E-0118	0.5 %	1 %
	E-0119	0.4 %	
Exchangers	E-0120	0.0 %	
	E-0101	0.5 %	1 %
	E-0109	0.8 %	
Furnace- Fumes		13.3 %	13 %
Furnace - C9's cut		5.6 %	6 %
Convection and radiation		6.2 %	6 %

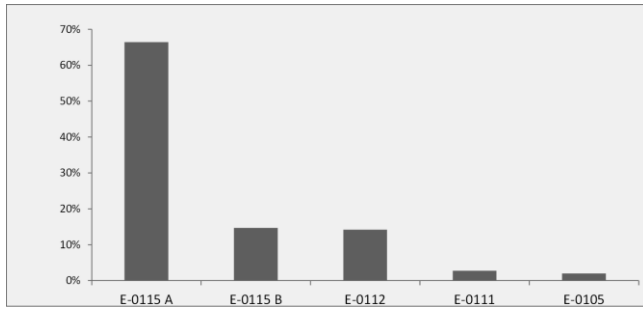


Figure 4. Hierarchy of energy losses of the air coolers.

From Table 4, it is observed that 86% of the exergy inserted in the unit comes from the fuels used in the furnace. These values, in conjunction with the results obtained in the energy analysis, clearly demonstrate the attention that should be paid to the furnace in order to obtain better energy and exergy efficiency of the unit.

Table 4. Distribution of inlet exergy.

Source	Exergy (%)
Reformed	0
Fuel oil	31
Fuel gas	55
Steam	11
Electricity	3

The useful exergy that leaves the unit refer to the C5's cut, benzene/toluene cut, C8's cut and C9's cut are in Table 5, while Table 6, presents the irreversibility hierarchy from the Un-0100.

Table 5. Distribution of useful exergy discharged from the unit.

Source	Exergy (%)
C5's cut	1
Benzene/toluene cut	29
C8's cut	69
C9's cut	1

Table 6. Irreversibility hierarchy.

Source	Irreversibility (%)
Output current exergy	2
Air coolers	11
Condensers	0
Exchangers	1
Furnace - fumes	6
Furnace- Combustion	50
Unidentified irreversibilities	29

Table 7. Hierarchy of outlet energy.

Source	Equipment	Irreversibility by equipment	Irreversibility by source
Air coolers	E-0105	0.31 %	16 %
	E-0111	0.55 %	
	E-0112	1.09 %	
	E-0115 A	11.96 %	
	E-0115 B	2.36 %	
Condensers	E-0103	0.05 %	0 %
	E-0118	0.06 %	
	E-0119	0.10 %	
	E-0120	0.00 %	
Exchangers	E-0101	0.68 %	2 %
	E-0109	1.36 %	
Furnace	Combustion	72.40 %	72 %
	Fumes	9.08 %	9 %

In Table 7, the hierarchy of irreversibility of the equipment susceptible of improvements is presented.

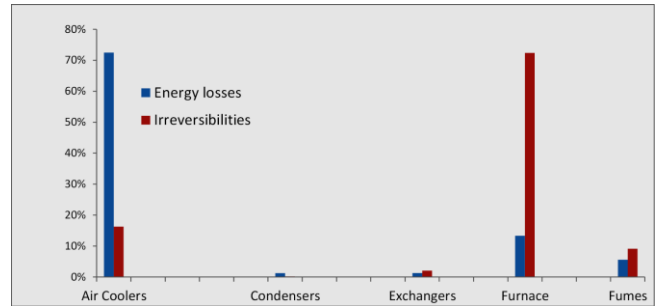


Figure 5. Hierarchy of energy losses and irreversibility by equipment.

Looking at Figure 6, that compares the energy and exergy losses in the air coolers, there is certain proportionality among the energy and exergy values, because the temperature of the wasted energy is very close in all the situations. Thus, in the air coolers, the exergy hierarchy corresponds to the energy hierarchy. The irreversibility of both air coolers E-0115 A and E-0115 B show that this equipment should be object of further attention in order to profit from the quality of the heat being wasted in both of them. From Figures 5 and 6, it is quite clear how important is the exergy analysis to correctly qualify thermal energy losses and consequently for prioritizing investments or equipment interventions, to improve the energy performance of the unit.

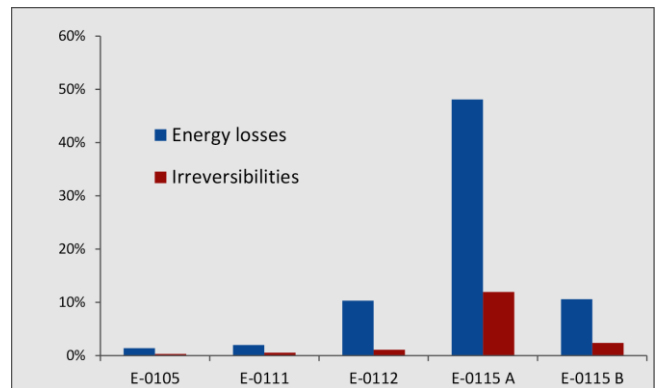


Figure 6. Hierarchy of energy losses and irreversibility in the air coolers.

The Sankey and Grassman diagrams (Figures 2 and 3) describe well this situation. It is evident that despite higher energy losses are encountered in the air coolers, the larger irreversibility was detected in the furnace H-0101.

These results clearly show that it would be advisable to evaluate the possibility of implementing thermal energy recovery systems and such was the authors' recommendation to the owner of the plant.

6. Conclusions

Energy and exergy analyses of a pre-distillation unit of an aromatics plant were carried out to characterize its relevant thermal energy losses. The objective was not to question the operational procedures of the equipment composing the unit, but to serve as a guideline for future waste energy recovery procedures.

The equipment group that stood out with higher energy losses was the air coolers with 59.9% of global losses

occurring in this unit and representing 11.2% of irreversibility recorded in the unit. In this equipment group, the equipment with greater performance improvement potential is the E-0115A/B, representing 81% of the energy loss and 88% of irreversibility observed in this type of equipment. These excessive energy and exergy losses are explained by the moderately high thermal energy rejected, about 144 °C. The furnace H-0101 stands out above all representing 56.3% of the irreversibility recorded in the unit. The authors advised the owner of the plant to evaluate the possibility of installing a thermal energy recovery system.

References:

- [1] O. Ocic, *Oil Refineries in the 21st Century – Energy efficient. Cost effective. Environmentally Benign.* Weinheim: Wiley-VCH, 2005.
- [2] J. G. Speight, *The refinery of the future.* Oxford: Gulf Professional Publishing, 2011
- [3] G. Comodi, M. Renzi, M. Rossi, “Energy efficiency improvement in oil refineries through flare gas recovery technique to meet the emission trading targets,” *Energy*, 109, 1-12, 2016.
- [4] N. Tahoumi, M. Gholami, M. H. “Panjeshahi, “Integration of flare gas with fuel gas network in refineries,” *Energy*, 111, 82-91, 2016.
- [5] H. Yu, X. Feng, Y. Wang, L. T. Biegler, J. Eason, “A systematic method to customize an efficient organic Rankine cycle (ORC) to recover waste heat in refineries,” *Applied Energy*, 179, 302–315, 2016.
- [6] X. G. Liu, C. He, C. C. He, J. J. Chen, B. J. Zhang, Q. L. Chen, “A new retrofit approach to the absorption-stabilization process for improving energy efficiency in refineries,” *Energy*, <http://dx.doi.org/10.1016/j.energy.2016.10.128>
- [7] Y. Demirel, “Thermodynamic analysis of separation systems,” *Separation Science and Technology*, 39, 3897-3942, 2004.
- [8] Y. Demirel, “Retrofit of distillation columns by thermodynamic analysis,” *Separation Science and Technology*, 41, 791-817, 2006.
- [9] Y. Demirel, “Assessment of thermodynamic performances for distillation columns,” *International Journal of Exergy*, 3, 345-361, 2006.
- [10] N. Nguyen, Y. Demirel, “Retrofit of distillation columns in biodiesel production plants,” *Energy*, 35, 1625-1632, 2010.
- [11] Y. Demirel, “Sustainable Operations for Distillation Columns,” *Chemical Engineering Process Techniques*, 1:1005, 2013.
- [12] M. Alhajji, Y. Demirel, “Energy and environmental sustainability assessment of crude oil refinery by thermodynamic analysis,” *Int J. Energy Research*, 39, 1925-1941, 2015.
- [13] M., Alhajji, Y. Demirel “Energy intensity and environmental impact metrics of the back-end separation of ethylene plant by thermodynamic analysis,” *Int. J. Energy Environmental Engineering*, 7, 45-59, 2016.
- [14] J. J. Klemeš, *Handbook of Process Integration (PI). Minimisation of Energy and Water Use, Waste and Emissions.* Oxford: Woodhead Publishing Limited, 2013.
- [15] T. L. Kotas, *The Exergy Method of Thermal Plant Analysis.* London: Butterworths, 1985.
- [16] G. Wall, “Conditions and tools in the design of energy conversion and management systems of a sustainable society,” *Energy Conversion Management*, 42, 1235-1248, 2002.
- [17] R. Rivero, G. Kojjer, “Entropy Production and Exergy Loss in Experimental Distillation Columns,” *Chemical Engineering Science*, 58, 1587-1597, 2003.
- [18] R. Rivero, C. Rendón, S. Gallegos, “Exergy and exergoeconomic analysis of a crude oil combined distillation unit,” *Energy*, 29, 1909-1927, 2004.
- [19] Y., Wang, Y. Hou, H. Gao, J. Sun, S. Xu, “Selecting the optimum Predistillation scheme for heavy crude oils,” *Industrial & Engineering Chemistry Research*, 10549-10556, 2011.
- [20] N. M. C. Costa, (2012). *Preliminary Energy and Exergy Analysis of Un-100 from the Aromatics Plant of Matosinhos Refinery.* (In Portuguese, M. Sc. Dissertation on Mechanical Engineering), FEUP, Porto, Portugal.
- [21] A. N. Vilarinho, J. B. L. M. Campos, C. Pinho, “Energy and exergy analysis of an aromatics plant,” *Case Studies in Thermal Engineering*, 8, 115-127, 2016.
- [22] C. L. Yaws, *Chemical Properties Handbook: Physical. Thermodynamic. Environmental. Transport. Safety. and Health Related Properties for Organic and Inorganic Chemicals.* New York: McGraw-Hill Companies, USA, 1999.
- [23] R. H. Perry, D. W. Green, *Perry’s Chemical Engineers Handbook, 7th Ed.* New York: McGraw-Hill Companies, USA, 1997.
- [24] L. Borel, *Thermodynamique et Énergétique. 1st Ed.* Lausanne: Presses Polytechniques Romandes. Switzerland, 1986.
- [25] I. Dincer, “Thermodynamics. Exergy and Environmental Impact,” *Energy Sources*. 22, 723-732, 2000.
- [26] I. Dincer, M. A. Rosen, *Exergy: Energy. Environment and Sustainable Development, 2nd Ed.* Oxford: Elsevier Science, UK, 2013.
- [27] L. E. P. Baptista, (2013). *Evaluation and Energetic Optimization of the Furnaces from the Aromatics Plant.* (In Portuguese, M. Sc. Dissertation on Chemical Engineering), ISEP, Porto, Portugal.
- [28] D. H. H. Kyi, “Progress Report on Oil Refineries Earlier Audited in Myanmar,” *Seminar on The Promotion on Energy Efficiency and Conservation (PROMECC) for Major Industries in Southeast Asia.* Myanmar, 2006.
- [29] P. Kumar, *Training Manual on Energy Efficiency for Small and Medium Enterprises.* Asian Productivity Organization, 2010.
- [30] R. Rivero, C. Rendón, L. Monroy, “The Exergy of Crude Oil Mixtures and Petroleum Fractions: Calculation and Application.,” *Int. J. Applied Thermodynamics*. 2, 115-123, 1999.