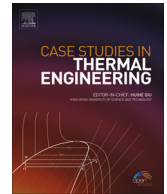




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## Energy and exergy analysis of an aromatics plant



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## ABSTRACT

Energy and exergy balances were evaluated for the units that constitute the Aromatics plant of a refinery in Portugal (FAR): pre-distillation (Un-0100), Arosolván (Un-0200), Parex (Un-0300), Isomar (Un-0400) and production of solvents (Un-0500).

The FAR had an overall energy yield of 0.81% and an exergetic efficiency of 65.9%. The equipment with higher energy losses, were the condensers, representing 25.9% of the energy losses, followed by air coolers, with 15.4% of the energy losses. The furnaces were in third place with 14.7% of the energy losses. Most of the energy lost in FAR was due to the cooling process. The irreversibilities observed in the condensers and air coolers were equivalent to 1.61% and 0.86% of the total plant irreversibility. Furnaces represent 14.7% of energy losses, but stand out above the irreversibilities analysis with 14.5% of the total. This equipment presents a high potential of energetic and exergetic performance improving, with natural positive impact on energetic and exergetic performance in the FAR.

The unaccounted thermal losses represented 32.9% which is mainly justified by the unknown mass flow rate of the gaseous effluent burned in the flare.

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## 1. Introduction – the energy in the petrochemical industry

One of the biggest challenges for mankind in the 21st century is to find out new ways to increase the availability of high energy and, at the same time, to minimize climate impacts. For oil refineries, this challenge is even more important, because it is also necessary to enhance the quality and the profitability of their products. Most of the times, the obligatory investments aim to a decrease of the emission of greenhouse gases, but, frequently, such is not accompanied by a production increase. One way to minimize the undesirable gaseous emissions and to increase the production is the process optimization, leading to a better energy efficiency of the involved technological processes [1].

According to the thermodynamic laws, the energy analysis of technological systems can be carried out through two distinct ways. The analysis through the first law of thermodynamics is an analysis based on energy conservation principles and is supported by the concept that energy can be only transformed but never created or destroyed [2]. However, in any energy process, there is always a certain amount of high quality energy that is converted into lower quality energy [3]. In spite of this, the energy balances always place the different energy forms at the same level and give no information as far as internal losses are concerned. The other kind of energy analysis is based upon a combination of the first and second law of thermodynamic, the exergy analysis. The exergy balances are similar to the energy ones, nevertheless they consider, not only the amounts of energy being processed, but also their qualities. Since the quality of the energy can be destroyed, this means that the balances under analysis have to take into account the degradation of the quality of energy that flows through

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the boundaries of the control volumes. This destruction of the quality of the energy is tied to the energy that is being wasted, or inadequately used because of the fact that all real processes are irreversible [4].

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, while the exergy destruction, or losses, is a quantitative measure of the process inefficiencies [4]. The exergy analysis has been lately considered a key tool for the definition of a more sustainable society. In fact, the exergy analysis has been used in the design and simulation of thermal, electrical and chemical systems. The obtained data can be used for the development of programs suitable for the definition of national energy policies [5].

Costa et al. [6] developed a program to calculate the exergy efficiency of distillation columns and found that exergy analysis was vital to find out energy deficiencies in the industrial processes and as such this technique should be used in process design and optimization. Fábrega et al. [7] through the exergy analysis of the refrigeration cycles in the production of ethylene and propylene reached the same conclusion, stressing that this technique is a useful guiding tool for the rational use of energy. Khoa et al. [8] proposed new exergetic methodologies for the optimal design of distillation columns, while Benali et al. [9] described a specific application of energy consumption improvement, through changes in the process flow of atmospheric distillation of petroleum and quantified the energy degradations in the distillation columns. More recently [10] different methods for thermal energy integration in a distillation column for the separation of benzene, toluene, xylenes and C9 isomers were carried out. The thermal energy integration path was also studied in [11] whereas the concern on the definition of energy efficiencies for the oil and gas industry was discussed by Nguyen et al. [12].

But there are not many studies on the plants as a whole and the present work concerns the aromatics plant from this refinery (FAR) which can handle 850,000 t/year of reformate that is supplied by the fuel plant of the same refinery or from other sources. The following scheme explains in a simplified way the operation of the aromatics plant as well as the interconnections among its subunits (Fig. 1).

## 2. Methodology of the analysis

The first step of the study was to perform an overall energy balance of the plant. A global energy efficiency of the plant was determined, corresponding to the ratio between the useful output energy in the process flow currents and the consumed energy. 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. The main objective was not to question the technological process being followed in the FAR, but to find out situations where the exploitation of energy wastes and losses could improve the energetic performance of the plant in its present operating layout.

In order to perform such energy assessment, a scrutiny of the different energy quantities involved in the subunits of the plant was carried out according to the energy balance sheets of the company 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. This corresponded to a total of 156,000 data values. Whenever necessary, mass and energy balances of the equipment were executed in order to complement missing values from the plant data sheets.

The energies supplied to this plant 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

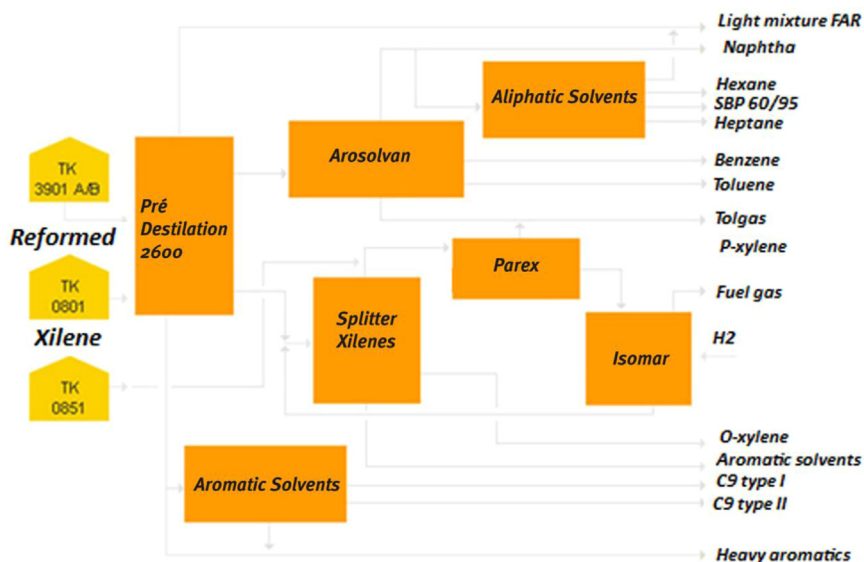


Fig. 1. The subunits that compose the aromatics plant from the refinery.

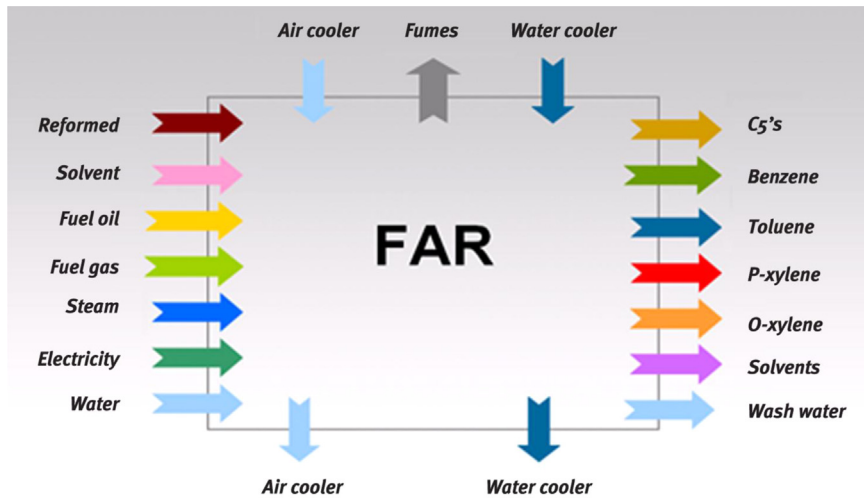


Fig. 2. Energy inlets and outlets of the aromatics plant.

by high and medium pressure steam, also from the refinery. The reformat flow rate that entered the subunit Un-0100 as well as the solvent flow entering the Un-0200 were also, due to their high inlet temperature, considered as inlet energy flows. As far as the flows leaving the aromatics plant were concerned, the processing flows leaving the different subunits like the C5's cuts (light gasolines), the benzene cuts, the toluene, the para-xylene, orto-xylene and the solvents that were produced in the Un-0500, were also assumed as exiting energy flows.

In Fig. 2 are represented all input and output energy flows of the FAR. For these flows, all the thermodynamic and thermochemical properties were calculated for 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 for the average temperature between the reference temperature and the vaporization temperature, whereas the gaseous phase properties were determined for 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 currents

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 perfect. 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 gases, were easily found.

For the calculation of the corresponding enthalpies, average liquid and gaseous phase specific heats were used. 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 vapor pressures. Knowing the vapor pressure, the vaporization temperature for each component was determined [13], through the extended Antoine equation,

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

where  $A_1$ ,  $B_1$ ,  $C_1$ ,  $D_1$  and  $E_1$  are the Antoine constants, the vapor pressure  $p_{vap}$  is in mmHg and the vaporization temperature  $T_{vap}$  in K. A shorter version of Antoine equation was also used [14],

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

where the vapor pressure  $p_{vap}$  is still in mmHg, but the vaporization temperature  $T_{vap}$  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 [13] was used,

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

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

Two correlations proposed by Perry and Green [14] were used for the calculation of the specific heat at constant pressure in molar base for gaseous fluids. The first was, specifically, for the propilbenzene,

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

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.

For the fluids that compose the solvent flow entering the subunit Un-0200 (Monoetilenoglicol (MEG), Dietilenoglicol (DEG) and N-metil-2-pirrolidona (NMP)), as well as for methane, ethane, propane and butane, the specific heats were calculated from fitting correlations developed from tabled values using the least-squares method.

When necessary, the latent heat of vaporization, in molar basis, was calculated from the correlation [14],

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

Constants  $A_6$ ,  $B_6$ ,  $C_6$  and  $D_6$  were chosen according to the components and  $T_r$  is the respective reduced temperature,

The reference state of  $p_{amb}=1$  atm and  $T_{amb}=0$  °C, used for the calculation of the energy flows, was chosen to coincide with the ambient reference state also used in the exergy calculations. However, as further explained, the reference state for the thermochemical data is,  $p_0=1$  atm and  $T_0=25$  °C.

If all the mixture components were in the liquid state, the enthalpy of a given current mixture of components was the weighted value according to,

$$\dot{H} = \dot{m}_f \sum h_{li} y_i \quad (7)$$

In this equation,  $\dot{m}_f$  was 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  $i$  which had a mass fraction  $y_i$ . When the current was a mixture of liquid and gaseous components,

$$\dot{H} = \dot{m}_f \left[ \sum h_{li} y_{li} + \sum h_{gi} y_{gi} \right] \quad (8)$$

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,

$$\dot{Q}_L = \dot{H}_{in} - \dot{H}_{out} \quad (9)$$

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

$$\dot{Q}_L = \Delta \dot{H}_a - \Delta \dot{H}_b \quad (10)$$

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.

Whenever there were chemical reactions, the enthalpies of formation of the different components were used. But these enthalpies are usually available for 25 °C and 1 atm. However, to be compatible with the chosen reference environment state for the calculations of the exergies, the adopted reference state was 0 °C and 1 atm. The following equation quantifies the error occurring with the use of the reference state of  $p_{amb}=1$  atm and  $T_{amb}=0$  °C for enthalpies and exergies calculations, and the use of the reference state  $p_0=1$  atm and  $T_0=25$  °C for the calculation of the enthalpies of formation,

$$\text{Error} = \left( \sum \dot{m}_{p_i} c_{p_i} - \sum \dot{m}_{R_i} c_{R_i} \right) (T_0 - T_{amb}) \quad (11)$$

Because the calorific capacities of reactants,  $\sum \dot{m}_{R_i} c_{R_i}$ , and products,  $\sum \dot{m}_{p_i} c_{p_i}$ , are very similar, the error is, always, negligible.

The enthalpy of formation (at  $T_0$ ) of the current was the corresponding weighted average,

$$\dot{H}_f = \dot{m}_f \sum h_{fi}^0 y_i \quad (12)$$

where  $\dot{H}_f$  is the enthalpy power of formation of a given current,  $\dot{m}_f$  the mass flow rate of such current and  $h_{fi}^0$  the enthalpy of formation of component  $i$  with a mass fraction  $y_i$ . Accordingly, the enthalpy power of reaction in a given control volume was defined as,

$$\Delta \dot{H}_f = \dot{H}_{f-out} - \dot{H}_{f-in} \quad (13)$$

### 3.2. Fuel gas and fuel oil

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

$$\dot{F}_F = \dot{m}_F LHV_F + \dot{m}_F c_F (T - T_{amb}) \quad (14)$$

$$\dot{F} = \dot{F}_{FO} + \dot{F}_{FG} \quad (15)$$

where  $\dot{F}$  is the total fuel input power,  $\dot{F}_{FO}$  the fuel oil input power,  $\dot{m}_{FO}$  the mass flow rate of fuel oil and  $LHV_{FO}$  the low heating value of the fuel oil, while  $\dot{F}_{FG}$  is the fuel gas input power,  $\dot{m}_{FG}$  its mass flow rate and  $LHV_{FG}$  the low heating value of the fuel gas.

### 3.3. High and 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 all the condensate return was saturated liquid. There was also medium pressure steam being used as fuel atomizing fluid in the furnaces. For high pressure steam, the enthalpy power input was defined as the difference between the input enthalpy and the output medium pressure steam.

### 3.4. Electricity

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

### 3.5. Combustion gases

The exhaust combustion gases expelled at high temperatures from the furnaces towards the environment still had elevated energy values. This energy quantity 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 the 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 enthalpy power of this flow of combustion gases was then expressed as,

$$\dot{H}_{g-out} = \left( \dot{m}_{g-out} cp_{g-out} + \dot{m}_{H_2O-in} cp_{H_2O} + \dot{m}_{mv-in-F} cp_{mv-in-F} \right) (T_{g-out} - T_{amb}) \quad (16)$$

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 being 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 considered, taken on account the typical atmospheric conditions found in the region for the time period under analysis. A mass flow rate of the atomization steam of 0.5 kg of steam per kg of fuel oil was used as a standard ratio. The specific heat of the combustion products was an average value 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 fumes exhaust temperature was daily monitored, while the mass flow rate of fumes was unknown. However, knowing the fuel composition and some data of the fumes composition, the remaining information was determined through combustion calculations and furnace energy balance. In this energy balance, the input energy was 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, Fig. 3.

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. The corresponding mass fractions of the fuel gas components were calculated accordingly and from the balance of chemical species, plus the knowledge of the molar fraction of oxygen in the combustion products, the quantities of 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 [15,16]. Here, the radiation and convection thermal losses were determined according to average local atmospheric and wind conditions and also by taking into account data and reactor column dimensions. For the calculation of the columns heat losses, an average velocity was determined based on monthly

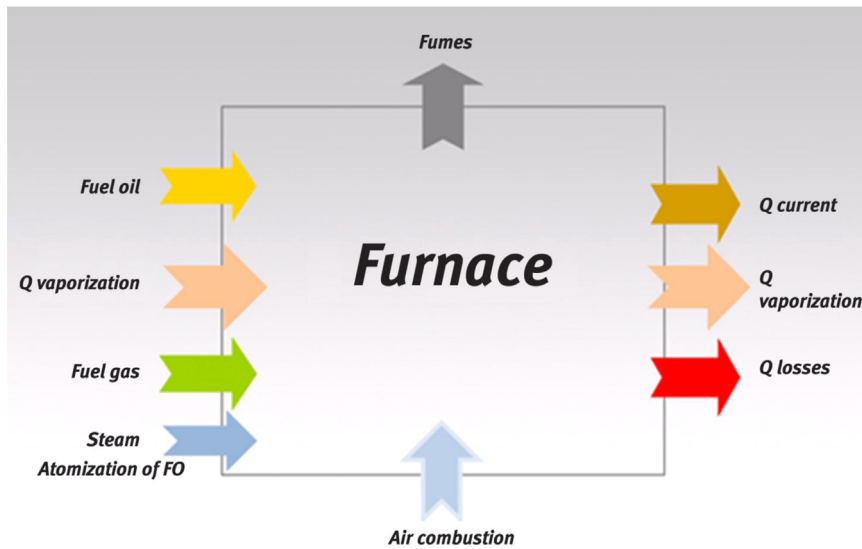


Fig. 3. Furnace energy inlet and outlet.

average wind velocities in the plant region and also an average wall external temperature, determined according to the average temperature of the current that flowed in the columns.

### 3.7. Energy efficiency

The energy efficiency was defined as the ratio between the energy supplied and the energy available in the output currents of the processed fluids, i.e., the useful energy.

$$\eta_{En} = \frac{\dot{P}_{out}}{\dot{P}_{in}} \quad (17)$$

where  $\dot{P}_{out}$  is the total power output in the exiting flows of the unit under analysis, while  $\dot{P}_{in}$  is the total power input in the inflow currents and utilities serving the unit.

## 4. Exergy balance

### 4.1. Exergy concept

The exergy is a combined property of the system and the environment, as it takes into account both the system thermodynamic state and the reference environment state [3]. 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 coenthalpy [17] and chemical, in the present work only the physical and the chemical exergies were considered. For a steady state flow condition, the exergy balance is given by,

$$\sum \dot{E}x_{in} = \sum \dot{E}x_{out} + \dot{I}_p \quad (18)$$

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. In some situations, the irreversibility power was determined through the Guoy-Stodola [4] equation,

$$\dot{I}_p = T_{amb} \dot{I} \quad (19)$$

where  $\dot{I}$  is the increase of the universe entropy per unit of time.

### 4.2. Chemical exergy

For the units where there were only distillation processes, Un-0100, Un-0200 and Un-0500, only the physical exergy of the several involved components were accounted for. In units Un-0300 and Un-0400, chemical reactions took place and

accordingly, the physical exergy and the chemical exergy were considered. 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.

The chemical exergy for a perfect gas [4] can be written in mass base as

$$\epsilon_{amb,i} = R_i T_{amb} \ln \frac{p_{amb}}{p_{amb,i}} \quad (20)$$

where  $\epsilon_{amb,i}$  is the chemical exergy of component  $i$  per unit of mass flow at  $T_{amb}$  and at its partial pressure in the environment  $p_{amb,i}$  and  $R_i = \bar{R}/M_i$  is the gas  $i$  particular constant.

For perfect gases mixtures, the molar chemical exergies  $\bar{\epsilon}_{amb}$  is given by [4],

$$\bar{\epsilon}_{amb} = \sum x_i \bar{\epsilon}_{amb,i} + \bar{R} T_{amb} \sum x_i \ln x_i \quad (21)$$

Eq. (28) can also be equally applied to liquid mixtures [4] where for real solutions, the mixture exergy depends also on the activity coefficient  $\gamma_i$  of each mixture component  $i$ :

$$\bar{\epsilon}_{amb} = \sum x_i \bar{\epsilon}_{amb,i} + \bar{R} T_{amb} \sum x_i \ln(\gamma_i x_i) \quad (22)$$

The second term of the second member of this equation represents the compositional exergy of the flow under consideration. For the balance, it was then necessary to know the activity coefficients for each component. However, if they are supposed as unity [18,19], this means an error of about 0.0052% in the total exergy. This approximation was assumed in the present work.

So, the total chemical exergy was given by,

$$\dot{E}x_{chem} = \dot{m} \epsilon_{amb} \quad (23)$$

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

The above explained determination of the chemical exergy in mass base at the reference temperature,  $T_{amb} = 0^\circ\text{C}$ , for a given fuel, is a bulky process as defended in Kotas [4], who recommends a more pragmatic approach,

$$\epsilon_{amb} = \beta LHV \quad (24)$$

which was followed in this work, where  $\beta$  is the correction factor for the chemical exergy. However, the  $LHV$  is defined at  $25^\circ\text{C}$ , while the reference temperature in this work is  $0^\circ\text{C}$ . According to Kotas [4], the effect of this difference is so small that it can be neglected. Assuming this approximation, in a mass basis it can be said that

$$\epsilon_{amb} = \epsilon_0 = \beta LHV \quad (25)$$

This approach was also applied to the components of the process flow mixtures under evaluation. This means that, like in the energy balance, where the enthalpies of formation were defined at the standard thermochemical reference state of  $T_0 = 25^\circ\text{C}$ , the chemical exergies were also based on this same reference state. The error of this assumption is meaningless [4].

The factor  $\beta$  is a function of the mass fractions of carbon  $y_c$ , hydrogen  $y_{H_2}$ , oxygen  $y_{O_2}$ , sulfur  $y_s$  and nitrogen  $y_{N_2}$  and is easily available [18,19],

$$\beta = 1.0401 + 0.1728 \frac{y_{H_2}}{y_c} + 0.0432 \frac{y_{O_2}}{y_c} + 0.2169 \frac{y_s}{y_c} \left( 1 - 2.0628 \frac{y_{H_2}}{y_c} \right) + 0.0428 \frac{y_{N_2}}{y_c} \quad (26)$$

There was a single exception to this calculation procedure, the  $H_2$ . The adopted chemical exergy value is tabled in Kotas [4].

The standard chemical exergy values calculated through Rivero et al. [18,19] methodologies were compared with the values available in Kotas [4] for some of the components of this study and the associated errors of the followed approach were in the 0–5.36% range. In can then be said that the methodology applied is coherent with the data proposed by Kotas [4], and no significant bias was imposed in the results.

#### 4.3. Physical exergy

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

$$\dot{E}x_{in} = \dot{E}x_{phys.} = \dot{m} \sum y_i \epsilon_{phys i-in} \quad (27)$$

where  $\epsilon_{phys i-in}$  is the specific physical exergy of the component  $i$ , having a mass fraction of  $y_i$ , entering the control volume.

The specific physical exergy, or coenthalpy, is defined as [4,17],

$$\epsilon_{\text{phys},i} = (h_i - h_{\text{amb}}) - T_{\text{amb}}(s_i - s_{\text{amb}}) \quad (28)$$

so, for a given mass flow rate of components entering a given control volume  $\dot{m}$ ,

$$\dot{E}x_{\text{in}} = \dot{m} \left( \sum y_{li} \epsilon_{\text{phys } il-\text{in}} + \sum y_{gi} \epsilon_{\text{phy } gi-\text{in}} \right) \quad (29)$$

where the first term of the second member concerns the components entering the control volume in the liquid phase, while the second concerns the components entering the control volume in the gaseous phase. For any current leaving the control volume a similar procedure was adopted.

#### 4.4. 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,

$$\dot{E}x_{\text{phys-Fuel}} = \dot{m}_{\text{Fuel}} \sum \left[ y_i c_{p_i} (T_{\text{Fuel}} - T_{\text{amb}}) - y_i T_{\text{amb}} \left( c_{p_i} \ln \frac{T_{\text{Fuel}}}{T_{\text{amb}}} - R_i \ln \frac{p_{\text{Fuel}}}{p_{\text{atm}}} \right) \right] \quad (30)$$

with  $c_{p_i}$  the specific heat at constant pressure for the fuel (either gas or oil) component  $i$ , and  $p_{\text{Fuel}}$  and  $T_{\text{Fuel}}$  the fuel supply pressure and temperature.

The fuel chemical exergy was determined through,

$$\dot{E}x_{\text{chem-Fuel}} = \dot{m}_{\text{Fuel}} \epsilon_{\text{chem-Fuel}} \quad (31)$$

where  $\dot{E}x_{\text{chem-Fuel}}$  is the fuel chemical exergetic power,  $\epsilon_{\text{chem-Fuel}}$  its standard specific chemical exergy and  $\dot{m}_{\text{Fuel}}$  its mass flow rate.

The total exergy power for the fuels flow was then given by,

$$\dot{E}x_{\text{combl}} = \dot{E}x_{\text{phys-fuel}} + \dot{E}x_{\text{chem-FO}} + \dot{E}x_{\text{chem-FG}} \quad (32)$$

#### 4.5. Medium and high pressure steam exergy

The calculation of the exergy of steam flows was similar to what was done for the energy accountancy. The difference in the inlet steam and outlet condensate exergies was quantified, with the exception of the direct steam used for fuel atomization in the furnace, whose exergy flow was added to the fuel inlet. The total exergy power for the medium pressure steam was,

$$\dot{E}x_{\text{mv-in-T}} = \sum \dot{E}x_{\text{mv-in-HE}} + \dot{E}x_{\text{mv-in-F}} \quad (33)$$

where  $\dot{E}x_{\text{mv-HE}}$  is the exergy power for the steam used in the heat exchangers and  $\dot{E}x_{\text{mv-in-F}}$  the exergy power for the direct steam used for fuel oil atomization. Because the atomizing steam did not suffer any chemical reaction, only its physical exergy was taken into consideration.

#### 4.6. Combustion gases exergy

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

$$\dot{E}x_{g-\text{out}} = \dot{E}x_{g-\text{phys-out}} + \dot{E}x_{g-\text{chem-out}} + \dot{E}x_{\text{H}_2\text{O/air-phys}} + \dot{E}x_{\text{mv-F}} \quad (34)$$

being  $\dot{E}x_{g-\text{phys-out}}$  the physical exergy power,  $\dot{E}x_{g-\text{chem-out}}$  the chemical exergy power,  $\dot{E}x_{\text{H}_2\text{O/air-phys}}$  the physics exergy power of the combustion air moisture and  $\dot{E}x_{\text{mv-in-F}}$  the exergy power for the direct steam used for fuel oil atomization.

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

$$\dot{E}x_{g-\text{out}} = \dot{m}_{g-\text{out}} \sum \left[ y_i c_{p_i} (T_{g-\text{out}} - T_{\text{amb}}) - y_i T_{\text{amb}} \left( c_{p_i} \ln \frac{T_{g-\text{out}}}{T_{\text{amb}}} - R_i \ln \frac{p_{g-\text{out}}}{p_{\text{atm}}} \right) \right] \quad (35)$$

where  $T_{g-\text{out}}$  and  $p_{g-\text{out}}$  are the exhaust temperature and pressure of the combustion gases.

The chemical exergy power of the combustion gases was determined through the following equation,

$$\dot{E}x_{g-\text{chem-out}} = \dot{m}_{g-\text{out}} \epsilon_{g-\text{chem-out}} \quad (36)$$



where  $\varepsilon_{g\text{-chem-out}}$  is the specific chemical exergy of the combustion gases.

#### 4.7. Irreversibility power

The irreversibility power,  $\dot{I}_p$ , was easily determined through Eqs. (18) or (19). However, there were some particular situations where the calculation of the exergy destruction was 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, by the exergy difference between the inlet and the outlet flows,

$$\dot{I}_p = \dot{E}X_{\text{in}} - \Delta\dot{E}X_{\text{out}} \quad (37)$$

where  $\dot{I}_p$  is the irreversibility power 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,

$$\dot{I}_p = \Delta\dot{E}X_a - \Delta\dot{E}X_b \quad (38)$$

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

$$\Delta\dot{E}X_a = \dot{E}X_{a\text{-in}} - \dot{E}X_{a\text{-out}} \quad (39)$$

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

$$\Delta\dot{E}X_b = \dot{E}X_{b\text{-out}} - \dot{E}X_{b\text{-in}} \quad (40)$$

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

#### 4.8. Exergy efficiency

The exergy efficiency for any equipment was defined as,

$$\eta_{Ex} = \frac{\sum \dot{E}X_{\text{out}}}{\sum \dot{E}X_{\text{in}}} = 1 - \frac{\dot{I}_p}{\sum \dot{E}X_{\text{in}}} \quad (41)$$

This classical formulation of the exergy efficiency was thoroughly followed in the present study. There were however some situations where the resulting values were meaningless, and if such happened, Kotas [4] proposed for separation processes the rational exergy efficiency concept. The information obtained from this rational exergy efficiency becomes relevant when the exergies of the processing currents are quite high compared with the exergies from the heat and work supplied to the process. In this situation, the standard exergy efficiencies, calculated according to equation 52, can lead to inconsistent results. If the weight of these chemical exergies cannot be subtracted in the quantification of processing currents exergies, the importance of the irreversibilities in the overall exergetic efficiency can be masked. The rational exergy efficiency was thus defined as [4],

$$\eta_{Ex-r} = \frac{\sum \dot{E}X_{\text{out}} - \sum \dot{E}X_{\text{in}}}{\dot{E}X_{\text{Heat-in}} + \dot{E}X_{\text{Work-in}}} \quad (42)$$

where  $\sum \dot{E}X_{\text{out}}$  are the process flow exergies leaving the control volume while  $\sum \dot{E}X_{\text{in}}$  are the process flow exergies entering the control volume.  $\dot{E}X_{\text{Heat-in}}$  and  $\dot{E}X_{\text{Work-in}}$  referred to the heat and work exergies supplied to the control volume.

## 5. Results from the aromatics plant of the refinery

### 5.1. Energy and exergy results for Un-0100

Through the energy and exergy analysis of Un-0100, the energy and exergy efficiencies of 13.4% and 2.3%, were obtained, whereas the exergetic rational efficiency was 2.1%. These values were rather low, especially the energy efficiency, indicating that there was a large basis for improvement as far as the energy consumption was concerned.

In Fig. 4, the Sankey and Grassmann diagrams for Un-0100 are shown. It can be seen that the set of equipment with greater energy losses are the air coolers with a fraction of 69.2% of the unit losses which corresponds to 11.5% of the unit irreversibilities. On the other end, the furnace of this unit is the component with higher irreversibilities corresponding to 57.6% of the total. There is a fraction of 4.6% of energy losses that were not clearly identified, corresponding to 29.3% of the irreversibilities. These unaccounted losses are due to limitations, irregularities and uncertainties of the experimental measurements carried out during the normal operation of the plant. They will also appear in the analysis of the other units of the plant and are the inevitable consequence of working with data gathered in the actual industrial process.

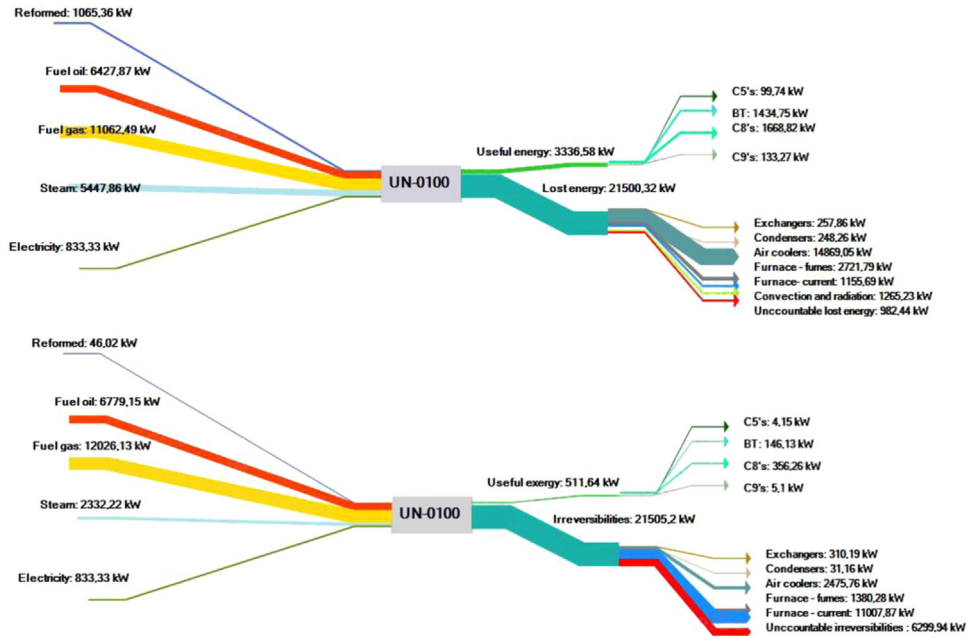


Fig. 4. Sankey and Grassmann diagrams for Un-0100.

Convection and radiation heat losses represent 5.9% of the energy entering the unit and a deeper evaluation of its weight will depend upon future mapping of the superficial temperatures of the unit components.

5.2. Energy and exergy results for Un-0200

For the Un-0200 the obtained energy and exergy efficiencies were respectively 3.6% and 0.4%. The obtained values are again quite low, indicating that there must be a large field for improvement. Analyzing Fig. 5, representing the Sankey and Grassmann diagrams for this unit, it is clear that condensers are the pieces of equipment with greater energy losses, 42.7% of

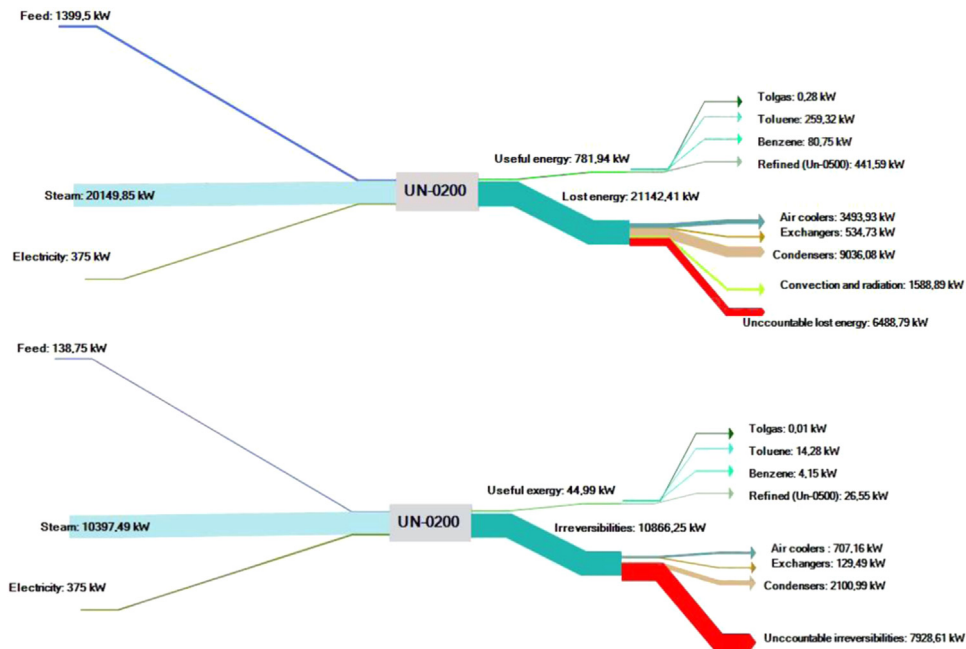


Fig. 5. Sankey and Grassmann for Un-0200.

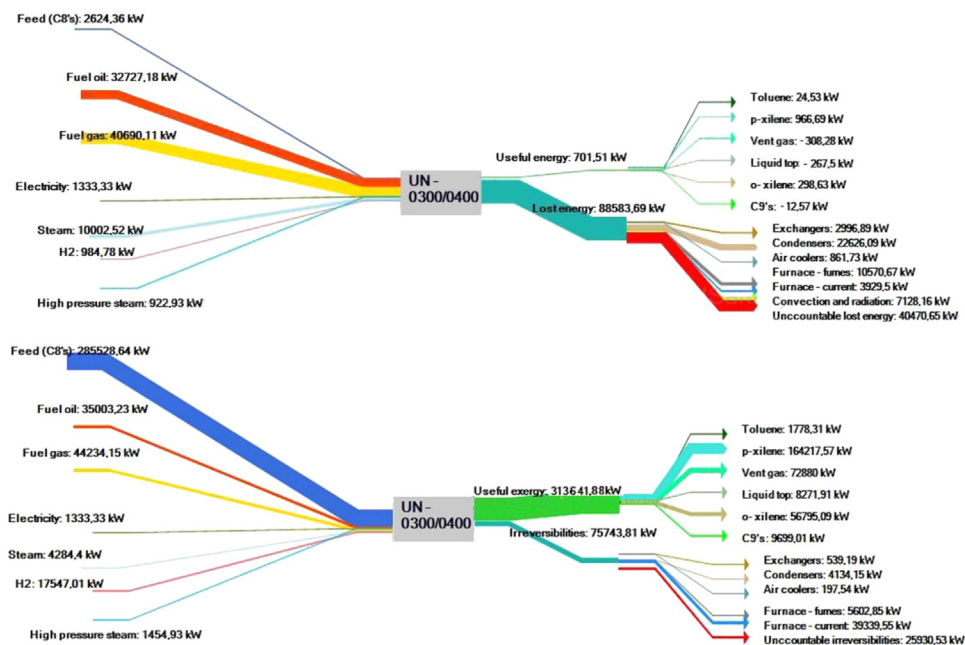


Fig. 6. Sankey and Grassmann for Un-0300/0400.

the unit global energy losses which correspond to 19.3% of Un-0200 irreversibilities. The unaccounted energy losses are 29.3% of the unit energy losses, equivalent to 73% of the unit irreversibilities. The convective and radiation losses for the distillation columns are 7.5% of the energy losses.

### 5.3. Energy and exergy results for Un-0300/0400

For Un-0300/0400 the calculated energy and exergy efficiencies were respectively 0.8% and 80.5%. The rational exergy efficiency was of 27.1%, meaning that the input exergy was transferred to the exergy of the processing currents. These exiting currents exergies are mainly chemical exergies, 53.5%, of the total exergy in such flows.

This extremely low energy efficiency is explained because the chemical potential of the leaving process fluid flows is quite similar to the input processing fluid flows. Also the input and output physical exergies are quite similar. There are then huge thermal energy losses in the process due to unavoidable evidence considering the chemical process undergone by the processing fluid currents. However, it is unacceptable that there is no further exploitation of these enormous thermal energy losses. On the other end, the exergy accountancy clearly shows that the energy was used to separate an input fluid flow into six process fluid flows having a high degree of purity, or in other words, a lower exergy input fluid flow was separated into six separated high exergy purer fluid flows.

Fig. 6 presents the *Sankey* and the *Grassmann* diagrams for Un-0300/0400. The equipment with greater energy losses are the condensers with 25.5% corresponding to 5.5% of the unit exergy losses. The furnaces of this combined unit have 16.4% energy losses and their irreversibilities represent 59.3% of the combined unit irreversibility. The furnace combustion products have temperatures in the 550 K (furnace H-0402) to 980 K (furnace H-0303) range, which explains how significant is the thermal energy that is presently rejected.

The unaccounted energy losses correspond to 45.7% of the input energy while the unaccounted irreversibilities correspond to 6.7% of the input exergy and 34.2% of the irreversibilities. These results are quite expressive, meaning that a deeper accountancy of the energy expenses must be carried out by the refinery, mainly about the furnaces where the standard deviation of the fuel flow rates, are of the order of magnitude of such flow rates. This abnormality has a strong impact upon the furnaces efficiencies leading to deviations on these results of the order of 20–30%.

The convection and radiation losses of the distillation columns represent 8% of the unit input energy.

### 5.4. Energy and exergy results for Un-0500

From the energy and exergy analysis, the calculated energy and exergy efficiencies are respectively 35.4% and 11.2%. These values are better than those obtained for the other units, because the exit temperature of the process flows are superior to the inlet temperature and according to the applied efficiencies definitions, this appears as an advantage.

From the *Sankey* and *Grassmann*, Fig. 7 diagrams, it is clear that bigger energy losses come from the condensers, 38.7% of the unit global losses corresponding to 11.4% of the unit irreversibilities. In this unit there is a condenser (reference E-0513)

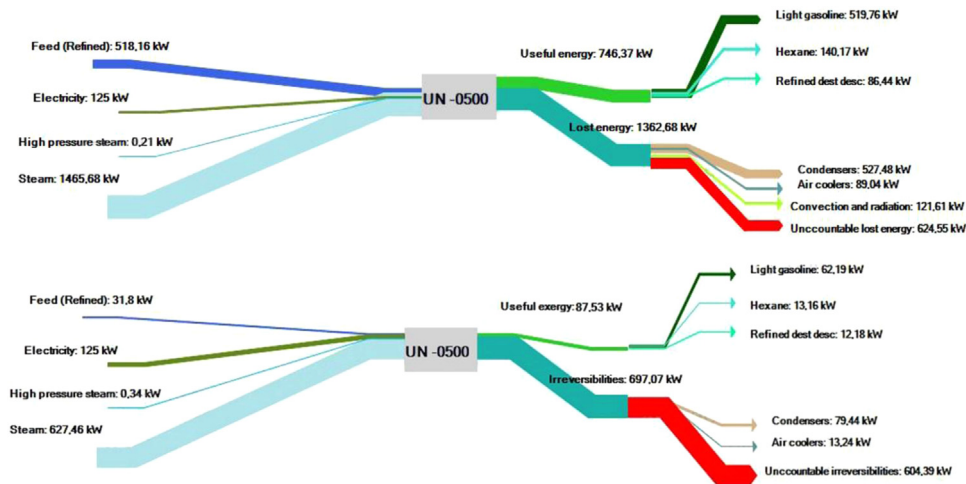


Fig. 7. Sankey and Grassmann diagrams for Un-0500.

that represents 86% of the condensers energy losses and 87.4% of the condensers irreversibilities and consequently it is the condenser with larger improving potential.

The unaccounted energy losses are 29.6% of the unit inlet energy or 86.7% of the irreversibilities. The convection and conduction energy losses of the distillation columns represent 5.8% of the unit energy input.

### 5.5. Overall energy and exergy results

Although in the analysis of the units 0100, 0200 and 0500, because there were no chemical reactions, the enthalpies of formation and the respective chemical exergies were not taken into account, in the overall balance such chemical energies and exergies were considered to obtain the correct energy repartition, as it was individually done for the evaluation of the 0300/0400 unit.

From the global analysis of the aromatics plant (FAR) it was found that it had an energy efficiency of 0.81% and an exergy efficiency of 65.9%. Concerning the total energy losses in the plant components, 25.9% refer to condensers losses, while the air coolers, the furnaces and the other heat exchangers had respectively 15.4%, 14.7% and 3.0%, of the total thermal energy losses. The unaccounted thermal losses represented 32.9%. This result is justified by the lack of data concerning mass flow rates and temperatures, in particular, the unknown mass flow rate of the gaseous effluent burned in the flare that constitutes a non-negligible share of the total thermal energy losses of the aromatics plant.

The rational exergetic efficiency of the FAR was 1.4%, a value which represents the influence of the effect of the chemical exergy in the total exergy flows.

## 6. Conclusions

The presented energy and exergy balances for the aromatics plant of refinery in the north of Portugal show that, even not considering the potential changes on the chemistry of the process, by only analyzing the energy losses and the corresponding exergy destructions, there is a huge potential for the energy utilization through the adequate conversion of the rejected thermal energy. They also demonstrate that the spent energy was essentially used to separate an input low exergy process current into six high exergy different output flows having a relatively high degree of purity.

As a main consequence of this analysis some suggestions, although not fully detailed in the present text, were presented to the FAR management. Several of the suggestions concerned good housekeeping procedures like storage tanks isolation, evaluation of the quality and structural integrity of the reactors isolations, analysis of the condensate lines and steam traps. However, the most important suggestions were:

- Implementation of an organic Rankine cycle (ORC) to exploit the thermal energy wasted in air coolers;
- Implementation of an ORC to exploit the thermal energy wasted from the combustion products of the furnaces;
- Implementation of a cogeneration unit producing 11 MW of electrical and 14 MW of thermal energy to supply the FAR.

The implementation of the ORC solutions would be non-intrusive because they would simply take profit from the actual situation, by exploiting the large thermal energy wastes available for the production of electricity. By its turn, the implementation of the cogeneration unit would be intrusive as the main furnace of the FAR would be replaced. Through the application of the cogeneration, the energy efficiency of the FAR would increase from the present 0.8–7%, whereas the

**Table 1.**  
Comparison of the energy and exergy efficiencies found for the FAR and its units.

	Un-0100	Un-0200	Un-0300/0400	Un-0500	FAR	FAR+ cogeneration	FAR+ cogeneration + ORC
$\eta_{En}$	13.4	3.6	0.8	35.4	0.81	7.0	8.1
$\eta_{Ex}$	2.3	0.4	80.5	11.2	65.9	66.1	67.0

exergy efficiency would increase from 65.9% to 66.1%. The payback period for this cogeneration unit would be in the range of 2–6 years, depending on the cost of selling electricity to the net and the type of fuel being consumed.

The combination of this cogeneration plant with the ORC exploiting the thermal energy wasted from the air coolers would result in the best solution, leading to a further increase of the FAR energy efficiency towards 8.1% and the corresponding exergy efficiency towards 67%.

Table 1 represents a summary of the main results for the FAR and its units, and presents also the influence of some of the suggestions to be implemented on the energetic and the exergetic efficiencies of the plant.

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