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Exergetic Analysis of Combustion Processes of Variable Mixtures of Refinery Residual Gas: Effect of Propane

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Due to the depletion of non-renewable natural resources, the increase in the emission of pollutants and the growing global energy demand, it is increasingly important to implement strategies that lead to a sustainable use of available resources and to improve the efficiency of the processes currently employed; A tool widely used for this purpose is the exergy analysis. Currently, refining processes use refinery gases as the main source of energy, which consist of mixtures of natural gas and residual gases; these are obtained as by-products in different processing units, so their composition varies according to the process they come from, highlighting their content of gases such as ethylene, hydrogen, propane and propylene. In this order of ideas, in this work we evaluated the effect of the variation of the proportion of residual gas (propane) with respect to natural gas, on the thermodynamic behaviour of combustion in a refinery furnace; through the methodology of exergy analysis. The process was simulated using the software Aspen-Plus®-v.8.8, obtaining thermodynamic properties of the flows involved in the combustion for each of the propane-natural gas mixtures analysed. Then, the exergy analysis was performed, obtaining profiles of irreversibility and exergetic efficiency, finding that the variation of the residual gas at the entrance of the furnace does not greatly affect the exergetic efficiency (variations less than 1 %); however, the irreversibilities of the process increase up to 70 % as the proportion of residual gas increases.

1. Introduction

One of the processes necessary for the use of current energy resources is the refining of oil; in this, between 4 % and 8 % of the extracted oil is used for the generation of energy consumed in the process (Elías et al., 2015). Energy consumption represents around 40 % of the total operating cost (Zargarzadeh et al., 2007), with thermal processes being the largest energy consumers with around 70 % (Campos Avella et al., 2007). The processes of separation and transformation are those that require more energy consumption (Wauquier, 2004). In order to obtain the necessary energy for these processes, furnaces are generally used, in which combustion of refinery gases takes place. In addition, the increase in demand and the cost of energy have led this industry to develop more efficient energy consumption strategies (Mehdizadeh Fard et al., 2017). Some of these initiatives include energy conservation, processes intensification, quality and quantity of products and an adequate disposal of energy waste for its later use (Hey, 2017). Environmental regulations are also a factor that encourages industries to consider energy efficiency in their processes as a key aspect to reduce greenhouse gas emissions (Mehdizadeh Fard et al., 2017).

At present, refining processes use refinery gases as a main source of energy, consisting of a mixture of natural gas and residual gases; which are obtained as by-products in the different units of processes and are used as partial or total substitutes for natural gas. The composition of these gases varies according to the process from which they come, highlighting in their content compounds such as ethylene, hydrogen, propane and propylene (Cala et al., 2013).

To evaluate the use of these gases as fuel, the concept of "interchangeability" is used, referring to the ability to substitute a gaseous fuel for another without affecting the performance of the equipment used for combustion (Natural Gas Council Plus, 2005). From its study, different indexes have emerged that allow the evaluation of the quality of the resulting fuel based on its physicochemical and thermodynamic properties, highlighting the

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Wobbe index (Cala et al., 2013) for its effectiveness and simplicity; Weaver's indexes and those of the American Gas Association (American Gas Association Laboratories, 1946) were developed in the United States as complementary factors to Wobbe's, while in Europe prevailing graphic methods such as Delbourg and Dutton (Cala et al., 2013). These indexes have allowed to better understand the interchangeability of gases and has served as a basis for the design of strategies to improve the combustion processes.

The interchangeability of gases is an alternative of great economic interest in the oil refining industry because of its direct impact on the reduction of fuel costs, as well as the direct effect it has on the useful life of the furnaces used.

Recently, studies about the effect of gas exchangeability on combustion processes have been conducted from an energy point of view (Cala et al., 2013). Additionally, methodologies have been developed that allow the study of chemical processes, including combustion, performing separate analyses on the availability of resources (Meriño, 2015), environmental and safety aspects (Gómez, 2015), thermodynamic behaviour and economic competitiveness. However, a study has not been carried out that jointly evaluates these three aspects in the combustion carried out in refinery furnaces with residual gases, which could contribute to a better understanding of the process, as well as to lead the strategies of utilization of the available energy resources towards a sustainability approach.

Taking into account the limitations of the studies carried out previously, the Research Centre for Sustainable Development in Industry and Energy CIDES of Universidad Industrial de Santander is evaluating the thermoeconomic performance of combustion in a furnace using variable mixtures of refinery gas (Meriño, 2015). In this work the exergetic behaviour of the combustion was evaluated, evaluating the influence of the propane on the total performance of the process, allowing comparing the thermodynamic performance of different operating configurations through the exergetic efficiency and the irreversibilities of the process.

2. Methodology

The exergy of a system is defined as the maximum work that the system can perform in conjunction with a specific reference state (usually the environment), until the system reaches equilibrium with the reference state (Moran et al., 2011). While energy is conserved for all processes, according to the first law of thermodynamics, exergy is only conserved in reversible processes, according to the second law of thermodynamics. The exergy is a measure of quantity and quality, while energy is only a measure of quantity (Dincer and Rosen, 2007).

The exergy analysis allows to quantify the thermodynamic imperfections as destructions of the exergy, which represent losses in the quality of the energy. Like energy, exergy can be transported across the boundaries of the system. Each type of energy transfer has a type of exergy transfer associated with it.

The exergy of matter flow $\mathrm{Ex}_{\mathrm{flow}}$ can be expressed in terms of physical $\mathrm{Ex}_{\mathrm{ph}}$, chemical $\mathrm{Ex}_{\mathrm{ch}}$, kinetic $\mathrm{Ex}_{\mathrm{kin}}$ and potential $\mathrm{Ex}_{\mathrm{pot}}$ components as follows:

$$\mathrm{Ex}_{flow} = \mathrm{Ex}_{ph} + \mathrm{Ex}_{ch} + \mathrm{Ex}_{kin} + \mathrm{Ex}_{pot} \tag{1}$$

The kinetic and potential components tend to have such a tiny effect that they are neglected, leaving then the physical and chemical components, calculated with the following equations:

$$Ex_{ph} = m\sum_{i}(fm_i[(h-h_0)-T_0(s-s_0)]) \tag{2}$$

$$Ex_{ch} = n\sum_{i}\left[x_i E_{ch,}{}^{*} + RT_0 x_i \ln(x_i)\right] \tag{3}$$

n: mole flow; m: mass flow; x_i: mole fraction of component i in the stream; fm_i: mass fraction of component i in the stream; $\mathrm{Ex}_{\mathrm{ch}}$*: Specific chemical exergy of each component; T_0: reference state temperature; h: enthalpy of component i; s: entropy of component i. h_0, s_0: enthalpy and entropy of component i at the reference state.

The transfer of exergy associated with work, as well as that associated with electricity, takes the value of energy (Dincer and Rosen, 2007).

$$Ex_w = W \tag{4}$$

The transfer of exergy associated with heat transfer depends on the temperature T at which it occurs in relation to the temperature of the reference state T0 according to the Carnot efficiency (Dincer and Rosen, 2007); it is calculated by the following equation:

$$Ex_Q = \left(1 - \frac{T_0}{T}\right) Q \tag{5}$$

The irreversibility of a piece of equipment, a stage and the overall process is obtained through an exergy balance as shown in the following equation:

$$I_{1,2} = Ex_{Corriente.Entran} - Ex_{Corriente.Salen} + (Ex_Q)_{1,2} - (Ex_W)_{1,2} \tag{6}$$

The efficiency is calculated with the Eq(7)

$$Ef = \frac{Ex_{Products} + (Ex_W)_{1,2}}{Ex_{Input\ streams} + \left(Ex_Q\right)_{1,2}} \tag{7}$$

The methodology followed to carry out this work is shown in Figure 1.

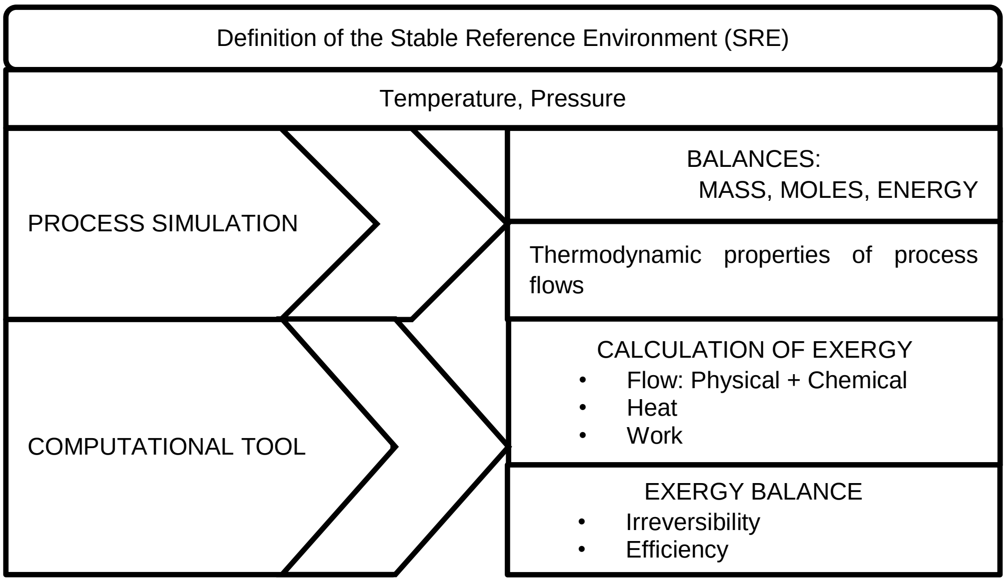

Figure 1: Methodology of Exergetic Analysis

In this work, the stable reference environment (SRE) is defined according to the temperature and pressure conditions of the standard natural environment, that is, 25ºC and 1 atm. In order to obtain the thermodynamic properties necessary to perform the exergy analysis, mainly enthalpy and entropy flows, the process was simulated by Aspen-Plus®-v.8.8 simulation software. Due to the large number of calculations necessary to perform the exergy analysis, it is essential to develop a calculation tool that contributes to the repeatability of the analysis and thus allows reliable results to be obtained. For this purpose, Microsoft Excel (with macros) was used. The reports generated in Aspen-Plus were taken to a spreadsheet, where each stream was analysed by programming determining its composition, enthalpy and entropy flow, as well as its origin and destination. The physical exergy of each stream was calculated according to Eq. (2). To calculate the chemical exergy of each stream according to Eq. (3) its components were searched in a list of specific chemical exergy previously created based on data reported in scientific papers. Then, the pieces of equipment were analysed and the associated heat exchange and work values were stored. Finally, an exergy balance was made for each piece of equipment and its irreversibility and exergy efficiency as well as the corresponding values of the overall process were determined.

3. Results

The simulation of the combustion process was carried out in stable state, using the Peng-Robinson thermodynamic properties model, whose suitability to represent hydrocarbon processes is widely recognized. The furnace was represented by a stoichiometric reactor with fuel premix and air with a relative humidity of 50 %. In order to analyse the effect of the use of propane as a partial substitute for natural gas on the irreversibilities and exergy efficiency of the process, the flow of natural gas was kept constant while that of propane increased from 0% in the base case to 100 % with respect to the initial gas flow. In each case, air was used in stoichiometric proportion, guaranteeing complete combustion as the composition of the fuel changes and reducing the influence that the excess air may have on the thermodynamic behavior of the evaluated process.

Table 1 shows the composition of natural gas used in the Barrancabermeja refinery, taken as the basis for the simulation. The components are named according to their molecular formula.

Table 1: Composition of natural gas. Report data from Moreno Tapias (2015).

Component	C1	C2	C3	iC4	nC4	iC5	N_2	O_2	CO_2	H_2O
Molar percentage – Report	88.36	7.90	0.80	0.15	0.15	0.07	0.30	0.02	1.90	0.31
Molar percentage - Simulation	91.04	8.14	0.82							

* C1: methane, C2: ethane, C3: propane, iC4: isobutane, nC4: butane, iC5: isopentane

Figure 2, taken from the simulation in Aspen Plus, represents the refinery furnace. The amount of air to be fed is determined in stoichiometric proportion with respect to the fuel gas obtained by mixing propane with natural gas.

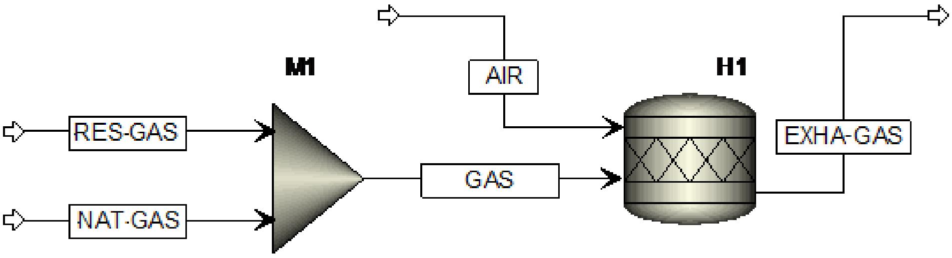

Figure 2: Furnace operation Flowsheet

The furnace was configured with an adiabatic thermodynamic behaviour, so that the combustion gases are obtained at adiabatic flame temperature.

The simulator was configured to report mass and molar flows, enthalpy and entropy of each stream to the operating conditions and reference conditions; the streams were considered as ideal solutions to calculate their enthalpies and entropies from their components. Likewise, the heat exchange and work values that occur in each piece of equipment were reported. The reference state was characterized by a temperature of 25 °C and a pressure of 1 atm. The exergy balance proposed in Eq(1) was made for the mixer and the furnace.

Table 2 shows a resumed report of the simulation in Aspen Plus, taken of the simulation without residual gas entrance.

Table 2: Enthalpy and entropy flows of each stream. Reported data from simulation in Aspen Plus

	Units	AIR	GAS	EXH-GAS	NAT-GAS
Mass Flow	kg/hr	291.66	17.36	309.02	17.36
Enthalpy	kJ/hr	-39083.72	-74187.42	-113270.00	-74187.42
Enthalpy (SRE)	kJ/hr	-39083.72	-74187.42	-960730.00	-74187.42
Entropy	kJ/kg-K	0.14	-4.86	2.57	-4.86
Entropy (SRE)	kJ/kg-K	0.14	-4.86	-0.07	-4.86

The components of physical, chemical, thermal and work exergy were calculated according to Eq(2) to (5). Finally, the irreversibilities and exergetic efficiencies of the combustion process were determined according to Eq(6) and (7). This procedure was performed for each analysed mixture.

Once each case study was evaluated, it was found that the increase of propane in the fuel has a direct effect on the irreversibilities of the combustion process carried out in the furnace. Figure 3 shows this trend.

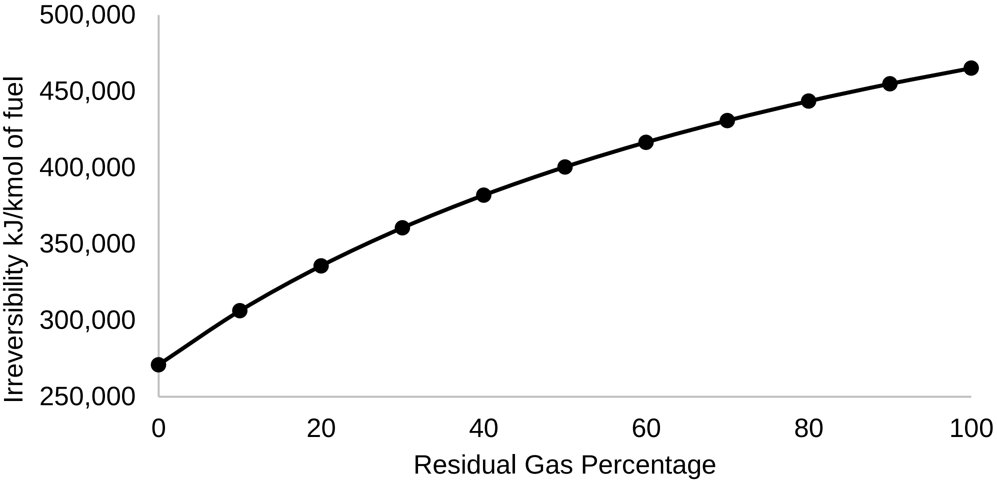

Figure 3: Specific Irreversibility

As can be seen in Figure 3, as the percentage of propane increases, the irreversibility of the combustion increases. This indicates that although propane fulfils the purposes of reducing natural gas costs of the process and supplying energy requirements, it negatively impacts on the exergy behaviour of the process by increasing the irreversibility by fuel flow used up to 70 % in the case of 1-1 mixing between the two gases.

4. Conclusions

In this work the exergetic analysis of combustion processes of variable mixtures of refinery residual gas was developed and the effect of content of propane on process efficiency was established.

The presence of propane in residual gases used as fuel in refinery furnaces negatively impacts the exergetic performance of the combustion process, given that at high proportions with respect to natural gas the value of irreversibilities is increased by up to 70 %.

The use of waste gases with a high content of propane mixed with natural gas as a fuel for refinery furnaces is recommended in low proportions, in order not to substantially increase the irreversibility of the process and thus promote a better energy use of the available resource.

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