ANALYSIS OF THE ENVIRONMENTAL IMPACT OF FUEL HYDROTREATING THROUGH LIFE CYCLE ASSESSMENT AND PROCESS DATA

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ABSTRACT

This document presents an evaluation of the life cycle in the operating scenarios of a diesel hydrotreating (HDT) industrial unit, considering the Eco-Indicator 99 and the process data. First, the process data of the HDT unit were debugged and grouped into operating modes using the kmean algorithm and the silhouette coefficient. The operating modes were then analyzed for their performance differences. Life Cycle Assessment (LCA) was performed for each of the identified modes. According to the results, the statistical analysis of the process data led to the identification of two operating modes (Mode 1 and 2), characterized by their different levels of hydrotreatment severity. Mode 1 represented the higher severity conditions and, therefore, produced a diesel stream with lower sulfur content than that resulting from Mode 2. The LCA showed that the Mode 1 resulted in a greater environmental impact than that derived from Operating Mode 2, due to a higher consumption of industrial utilities and a higher CO_2 emission. The H_2 consumption and CO_2 emission influenced the impacts related to the Natural Resources category, while the electricity consumption influenced the Human Health category. Likewise, the environmental impact levels of the operation of the HDT industrial unit were found to increase by *ca* 84% in going from the less severe operation to the most severe condition.

1 INTRODUCTION

In a diesel hydrotreating (HDT) unit, high-sulfur diesel fuel is processed to produce a liquid effluent that meets regulatory specifications. The aim of these regulations is to improve the air quality. However, the improvement in air quality should be measured not only by the sulfur content of the fuel, but also by the environmental impact of producing low-sulfur fuel. In fact, air pollution and the impact on natural resources are increased by the flue gases generated by the HDT furnaces as well as by the consumption of industrial utilities. Several reports have focused on reducing hydrogen consumption and on the energy integration of the HDT process, without directly evaluating the environmental impact of the resulting operation. Wu et al. (2017) developed an optimization of hydrogen consumption in an HDT unit, with the goal of establishing a hydrogen network integration strategy at the refinery level. Bandyopadhyay et al. (2019) applied the Pinch method and an exergy analysis in the design of highly energy efficient HDT units. On the other hand, few reports have addressed the environmental impact of the HDT process, which is surprising given the environmental regulations. Jarullah (2011) simulated a three-phase reactor (trickle bed) for crude oil hydrotreating based on a pilot plant kinetic model. Jarullah found that a value of 2.66 for the length-to-diameter ratio of the reactor resulted in a 55.76% reduction in operating costs, with 64.2% of the savings in utility costs. Wu & Liu (2016) quantified the environmental impacts of the diesel HDT process, based on the life cycle analysis, the Eco-indicator 99 and an Aspen Plus simulation results. According to the authors, the hydrotreatment of diesel with sulfur content between 167.3-191.7 ppm results in the lowest environmental impacts with low production cost. Likewise, Wu & Liu reported that the environmental impact of the process showed a linear trend with

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the sulfur content of the feed. Consequently, the authors stated that the largest environmental impact is found in the hydrotreatment of diesel, rather than in the consumption of the produced low-sulfur fuel. Wu et al. (2018) applied nonlinear optimization (NLP) to the HDT process, with the simultaneous reduction of operating cost and utility consumption, considering the reaction temperature and pressure as independent variables, while product impurity levels were restricted according to the regulations. According to Wu et al., a reduction in temperature and pressure leads to a reduction in operating costs and environmental impact due to a reduction in hydrogen consumption. In the previous references the analysis of the environmental impact of the HDT process was based on models and simulations of industrial plants, without considering the different operating modes. In fact, industrial units, such as the HDT, have operating modes that result in different levels of efficiency, production and consumption of utilities, as well as different levels of emissions and environmental impact. These operating modes can be considered through analysis and statistical work on industrial process data (Bhaskar et al., 2004; Ivanna et al., 2008). The statistics obtained from the data can lead to the definition of environmental impact ranges, derived from the details of an industrial operation with the possible modes in a defined period. Abonyi et al. (2013) reported a model for monitoring energy consumption based on process data. The authors developed the model with the aim of evaluating key process energy indicators. The model was proposed based on the time series segmentation technique for data selection, according to the mode of operation. The model was applied to the monitoring of a heavy naphtha HDT unit. Sbaaei & Ahmed (2018) developed a simulation of the hydrotreatment-coking process in Aspen Hysys, using a three-month operational data for the calibration and validation of the corresponding Petroleum Refining Module. The authors used the simulation to analyze the sensitivity of operational variables on the process performance. Sbaaei & Ahmed performed a simulation-based optimization and reported that the industrial process can operate simultaneously with both high productivity and low energy consumption. The previous references, while illustrating the application of data from industrial HDT units, omitted the explicit determination of the environmental impact. In HDT units, the uncertainty of the H_2 requirement in the operation leads to the uncertainties in the environmental impact (Abella & Bergerson, 2012). Usually, the references average the data over a period losing the details of the operation and the performances of the processing modes (Mederos et al., 2009). These details can lead to larger environmental impacts that are not represented by gross averages. Due to the lack of research on the evaluation of impact intervals, this work was devoted to the application of life cycle analysis to each operating mode of an industrial HDT unit, based on information obtained from process data of a national refinery.

2 THEORETICAL FRAMEWORK

2.1 Diesel Hydrotreating

The purpose of hydrotreating is to remove substances that degrade diesel quality and pollute the environment. The sulfur compounds present in middle distillates are mainly thiophenes, benzothiophenes and dibenzothiophenes (Boesen et al., 2011; Mijatović et al., 2014). These substances are eliminated by reactions with hydrogen in the presence of a catalyst, which can be metals such as Ni and Mo supported on alumina (Pacheco et al., 2009). At the industrial level, a diesel hydrotreating unit is divided into three main sections, namely the heating, hydrodesulfurization, and stabilization sections. Figure 1 shows a simplified layout of a typical HDT unit. In the heating section, which consists of preheaters (HEN) and a furnace (H-1), the feed diesel stream is heated to the reaction temperature. In the second section, diesel desulfurization (HDS) is performed in a trickle-bed reactor (R-1) (Liu et al., 2008; Mederos et al., 2009; Jarullah, 2011; Li et al., 2013). HDS reactions are exothermic and irreversible at reactor operating conditions of 300 °C and 70 bar (Mijatović et al., 2014). In the stabilization section, the reactor effluent is cooled to separate the gaseous sour stream from the low-sulfur diesel stream in a series of stripping towers (S-1, S-2 and S-3). The gaseous sour stream is sent to an absorption tower (A-1) to recover and recycle H_2 (Ancheyta, 2013). The low-sulfur stream is further purified from a light stream in a distillation tower (T-1).

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2.2 Operating Modes

Statistical work with process data allows the description of operational fluctuations around the different steady states or operational modes that an industrial process may present (de Souza Jr. et al., 2006). The operating modes can be identified by applying clustering methods, such as the kmean method (Lee et al., 2004; Liukkonen et al., 2011). The kmean method divides the data into k groups, defined by the user, and applies a metric to measure the internal and external distances in the groups. One of the most used metrics corresponds to the Euclidean distance (Thakare & Bagal, 2015; Rousseeuw, 1987; Rao & Govardhan, 2015). The number of groups representing a data set can be obtained using the so-called silhouette coefficient. This coefficient is based on the averaged distances between points in the same group and the distances between nearby groups. According to Kauffman & Rousseeuw (1990), the larger the value of the silhouette coefficient, the better the distribution of observations in the cluster. For comparison, a value greater than 0.7 indicates a very clear clustering structure, while a value between 0.5 and 0.7 indicates a moderate degree of clustering, a value between 0.5 and 0.25 corresponds to a weak distribution, and a value below 0.25 indicates that no substantial clustering was found.

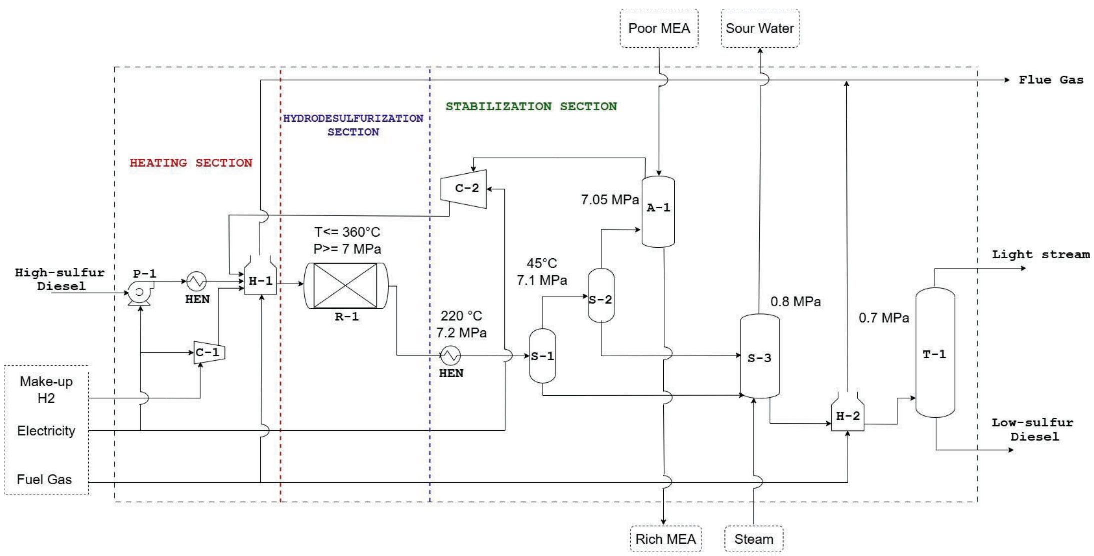

Figure 1. PFD for a simplified diesel HDT unit. Source: Modified from Wu & Liu (2016).

2.3 Life Cycle Assessment

Life Cycle Assessment (LCA) aims to determine the environmental impact of a product over its entire life cycle, from the raw materials used in its manufacture to the disposal of its waste (Finnveden et al., 2009). An LCA consists of four phases (ISO 2006a, ISO 14044): Goal and Scope Definition, Inventory Analysis, Impact Assessment, and Interpretation. Goal and scope definition includes the reason for developing the study, the use of the study, and the target audience. This phase also defines the boundaries of the system and the functional unit (quantitative measure of the product's function). The Life Cycle Inventory corresponds to a compilation of the inputs (resources) and outputs (emissions) of the product throughout its life cycle, in terms of the functional unit. Impact assessment aims to understand and quantitatively characterize the environmental impact. Finally, the interpretation evaluates the results of the previous phases with respect to the defined goal and scope, leading to conclusions and recommendations. The impact assessment can be calculated using the Eco-indicator 99 (Goedkoop, 2000; Frischknecht et al., 2007). This indicator is defined in terms of damage to the categories of human health (sources: climate change, ozone depletion, carcinogenic effects, respiratory effects and ionizing radiation), ecosystem quality (sources: ecotoxicity, acidification and eutrophication, and soil use), and natural resources (sources: additional energy demand for fossil fuel extraction and mining extraction), according to the following equation (Wu & Liu, 2016) (Shi et al., 2021).

$$EI = \left(\sum_u DAM_u\right) t \tag{1}$$

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In equation (1), *EI* corresponds to the total environmental impact of the process, expressed in ecopoints per year (Pt/year). A Pt is interpreted as one thousandth of the annual environmental load emitted by an average inhabitant in Europe (Dreyer et al., 2003; Frischknecht et al., 2007). Similarly, t corresponds to the annual operating hours (h/year) and the *DAM* corresponds to each of the damages caused by the u streams of the consumed industrial utilities or the pollution generated by the process. The *DAM* is defined by equations (2) and (3).

$$DAM_u = \sum_j IMP_{j,u} \qquad IMP_{j,u} = \sum_i m_u LCI_{i,u} \tag{2, 3}$$

In the equation (2), *IMP* corresponds to the impact on each of the j categories (ecosystem, human health, and natural resources). The *IMPs* are expressed in Pt/h. In the equation (3), the *LCI* denotes the impact factor of each i sources or items of the j categories according to the Eco-Indicator 99 database (Frischknecht et al., 2007). The *LCI* values refer to the normalization of the emission data (air emissions from Europe and soil and water emissions from the Netherlands). The m_u parameters refer to the flows of the u streams of the consumed utilities or the produced pollution (in kg/h or kW-h/h).

3 METHODOLOGY

Operating data for a diesel HDT unit was collected from the data management system of a Colombian refinery. The data included hourly samples of volumetric flows, sulfur content, temperatures, and pressures over a two-year period. The total number of measurements was 17,986, while the sulfur content values were 723 (daily values). The data were debugged to eliminate samples with blank or alphanumeric values or with feed flows less than 20 kBPD (per design). Outlier data were discarded according to the application of the interquartile range (Abebe at al., 2001). The kmeans cluster analysis was applied to the debugged data, according to the codes of the open-source program R. The internal distances between the clustering samples were determined using the kmeans function, while the average silhouette coefficient was determined using the silhouette function (both functions are available in R). The number of operating modes was elucidated using the silhouette coefficient values. The four phases of the LCA (ISO 2006a, ISO 14044) were applied for each mode of operation identified. The goal and scope of this evaluation were defined with the quantification of the environmental impact in each operating mode of the HDT unit, accounting for the consumption of industrial utilities and the generation of CO_2 and SO_x pollution. According to Figure 1, the main inputs to the system correspond to the feed, the industrial utilities (H_2 Make-up, electricity, and fuel gas), while the outputs are the product flows (diesel and gasoline) and the pollution (CO_2 and SO_2). The set of utility consumption and pollution generated to produce 8100 tons (72.2 kB) of 26 low-sulfur hydrotreated diesel (HDT diesel) was established as the functional unit on the basis on the average daily operation of the HDT unit. The Eco-indicator 99 was used through equations 2 and 3, considering the impact in each category of this indicator. Likewise, the consumption of industrial utilities and the pollution generated were calculated using the average values in each operating mode. The system boundaries defined for the LCA are presented in Figure 1. The inventory analysis and impact assessment were performed in an Excel® spreadsheet, as recommended by the Environmental Protection Agency (2006).

4 RESULTS AND ANALYSIS OF RESULTS

4.1 Operating Data

The operating variables analyzed in this work were inlet and outlet temperatures and pressures of the flows to reactors I and II, hydrogen to fuel ratio (H_2/oil), hydrogen makeup flow, fractionation tower temperatures (feed, top and bottom), H_2 cycle compressor power, power consumption (pumping and air coolers), power consumption for compression, and caloric requirements in the reactors and the fractionator. The trends of some of the operating variables are shown in Figures 2–4. For comparison, Figures 2–4 also show the values reported by the simulation developed by Wu & Liu (2016). From these figures, it is possible to mention that the operation of the HDT unit was maintained in quasi-stationary states most of the time; the unit was shut down 12 times (vertical sections of sudden changes in variables) due to corrective maintenance during the operating window. These maintenances lasted for less than a day, which is why the trends of the variables do not exhibit horizontal values at 0.

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According to the data, the variable with the greatest fluctuation corresponded to the feed flow (Figure 2), while the inlet pressure to the reactors was the variable with the greatest stability during the operating window, due to its lower impact on desulfurization, compared to the reaction temperature (Terán-Alemán, 2016; Ovalle-Orozco, 2020). Likewise, Figure 3 (left) shows that the reactor temperatures have a wide range of values, implying industrial operations with different levels of severity and therefore, different levels of desulfurization.

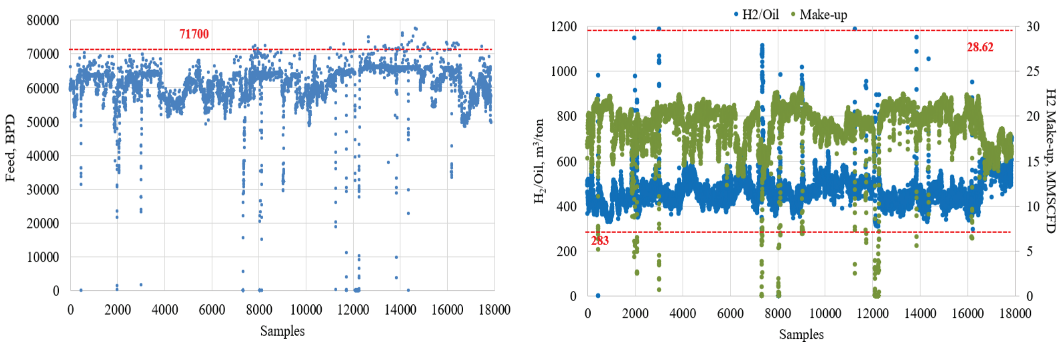

Figure 2. Variations in feed (left), H_2 make-up (right), and H_2/Oil (right) in the operating window, with values by Wu & Liu in red.

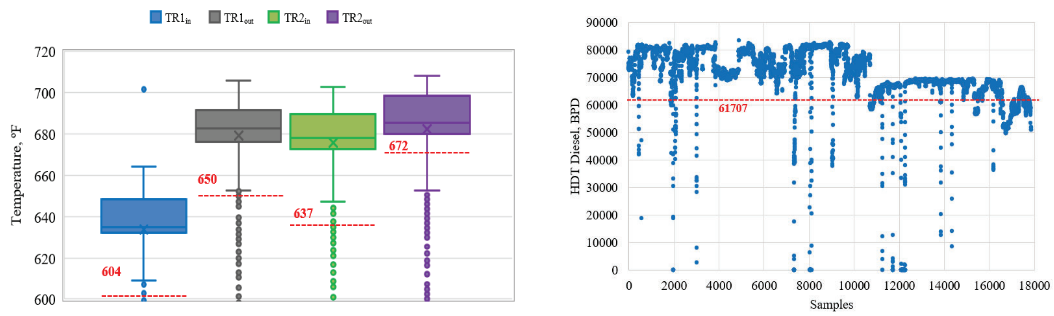

Figure 3: Reactor temperature boxplot (left) and HDT diesel (right), with values by Wu & Liu in red.

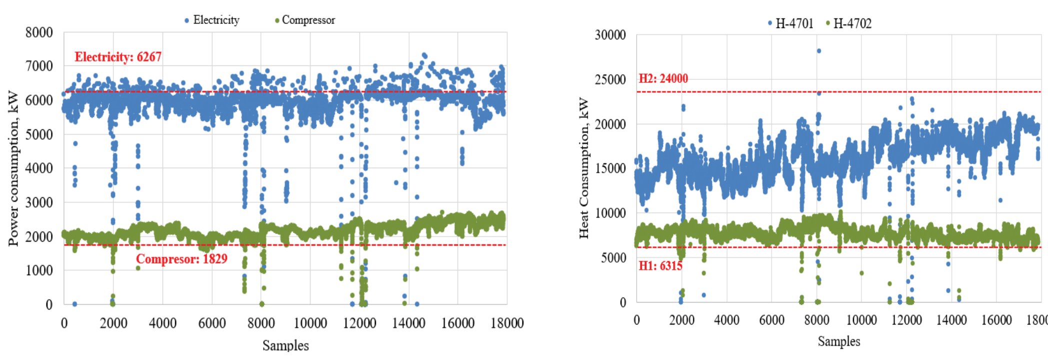

Figure 4: Pumping and compression (left) and furnace heat (right), with values by Wu & Liu in red.

Figure 5 shows the sulfur content in the feed stream and in the resulting HDT diesel. By comparing the data between Figure 3 and Figure 5, it can be concluded that the lower the reactor temperature values the higher the sulfur content of the hydrotreated diesel. Therefore, the high values of reactor temperatures resulted in sulfur contents of less than 20 ppm for the resulting HDT diesel product. On the other hand, the operation considered in the Wu & Liu simulation had a slightly higher feed rate, higher H_2 make-up requirement, lower H_2/oil ratio, higher reactor pressure, lower reactor temperature, similar power consumption (pumping and compression) and higher energy consumption in the furnaces than those corresponding to the industrial HDT unit. The higher operating pressure found in the Wu &

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Liu simulation is due to the higher sulfur content considered for the feed stream (Figure 2). Likewise, the energy consumption of the H-1 furnace (Figure 4, right) in Wu & Liu work (6315 kW) is higher compared to the HDT unit. This may be due to a more effective energy integration in the HDT unit than that obtained in the Wu & Liu process diagram. Despite the differences, there is an agreement between the values of the HDT unit data and those of the Wu & Liu simulation.

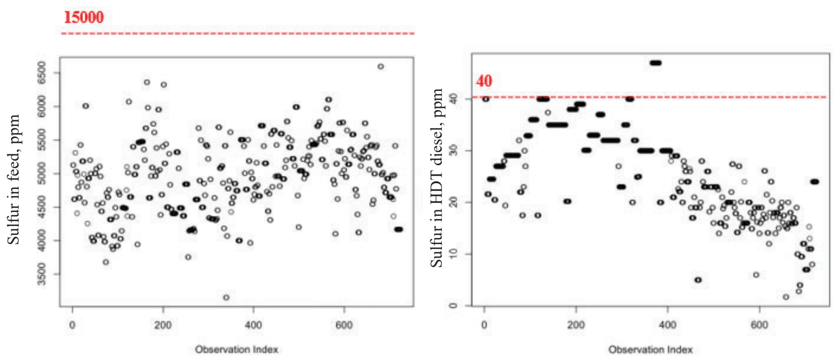

Figure 5: Sulfur content (ppm) in feed (left) and HDT diesel (right), with values by Wu & Liu in red.

4.2 Identification of Operational Modes

The silhouette coefficient results considering between 2–15 groups for the kmean method are shown in Figure 6. According to this figure, the highest average silhouette coefficient occurs with the formation of two groups or modes. The silhouette coefficient obtained for two groups or modes (0.35) shows a somewhat sparse conglomeration (Kauffman & Rousseeuw, 1990), which can be attributed to samples in a dynamic state. Due to the dynamic state, some samples lie between the boundaries of the two modes. This can be analyzed in the right graph of the Figure 6, which shows the distribution of the samples between the modes in the space of the first two principal components. According to this graph, there are samples of operation Modes 1 and 2 with values around 0 for the first principal component, Dim1 (58% variance), which defines the separation of the samples between the modes. In the same way, it can be seen from this figure that there are some circles in the section of the opposite mode (ca 8% of the samples). Nevertheless, many of the samples have a defined position in the operating modes of the HDT unit in the analyzed window. In line whit this, in this work it was assumed that the samples in a dynamic state fluctuated between the corresponding mode, and therefore these dynamic samples do not significantly alter the subsequent analysis.

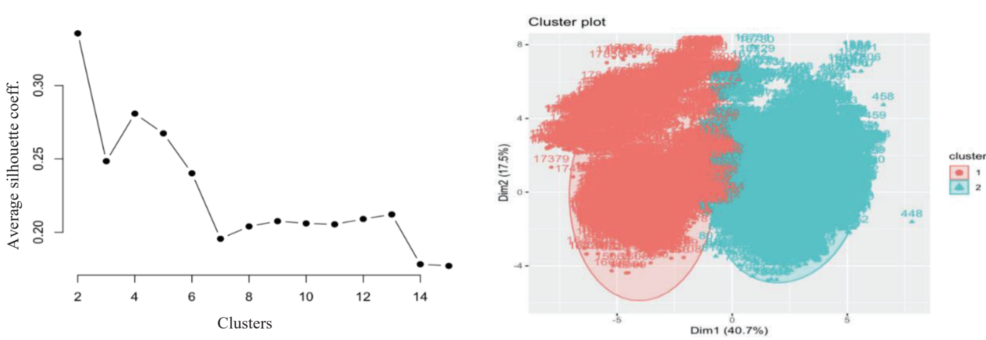

Figure 6: Average silhouette coefficient vs clusters (left) and plot of the principal components for two clusters or modes (right).

Mode 1 and Mode 2 consist of 6605 and 10764 samples, respectively. Figures 7 shows the location of the operating modes with respect to the variables feed, HDT diesel, feed sulfur content, and sulfur content in the HDT diesel. According to these figures, Mode 2, with a greater number of samples, is characteristic of the operation in the first part of the operating window (red circles). Likewise, Mode 1 shows a lower generation of HDT diesel compared to Mode 2 (Figure 6, right), although, it achieves a

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greater desulfurization of this product. The graphs in Figure 8 compare the produced streams of hydrotreated diesel produced in each mode. According to these graphs, operational Mode 1 (blue dots) shows the lower HDT produced diesel flows. The operating modes show different temperatures and pressures for the inlet flows to the reactors ($TR1_{in}$ and $TR2_{in}$ are the inlet temperatures of reactors 1 and 2, respectively). Operation Mode 1 (blue dots) exhibits higher values of reactor temperature and pressure (higher severity) than those in operation Mode 2 (fuchsia dots). Figure 9 depicts the sulfur content of the diesel produced for both modes. From Figures 8 and 9, higher severity in Mode 1 results in greater sulfur removal and therefore to lower sulfur content in the HDT diesel. Because of the severity, Mode 1 also has a greater consumption of compression power and heat for the furnaces. The operational differences between the samples of the two modes define the bounds of the variables. The differences between the modes are due to the type of feed. In Mode 1 (maximum condition), the feed corresponded mainly to diesel with a high-sulfur content, while in Mode 2 (severe condition), a mixture of diesel with a high-sulfur content and light cycle oil (LCO) from an FCC unit, is loaded into the unit. Table 1 shows the limits for the variables according to the mode of operation.

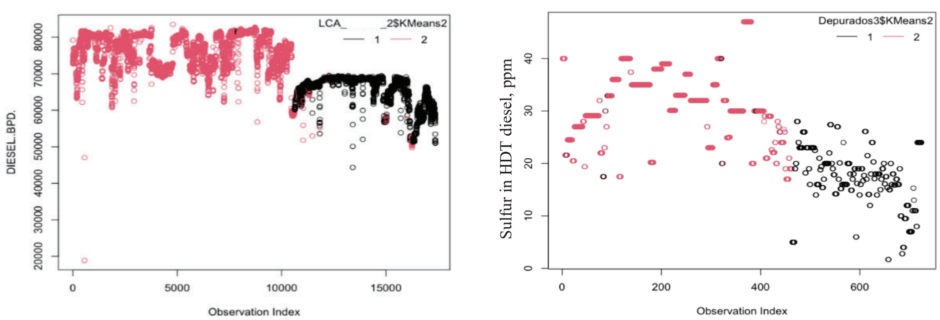

Figure 7: Samples of each mode for diesel product (left) and sulfur in diesel product (ppm) (right).

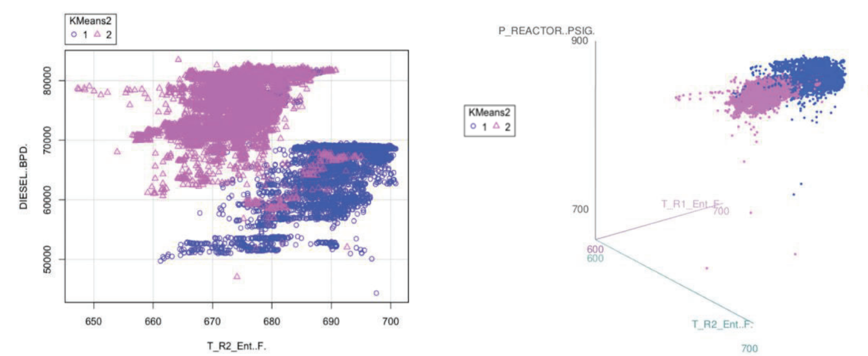

Figure 8: HDT diesel in the operational Modes 1 and 2 vs $TR2_{in}$ (Mode 1 in blue, Mode 2 in fuchsia) (left). Inlet pressure to the reactor vs $TR1_{in}$ vs $TR2_{in}$.

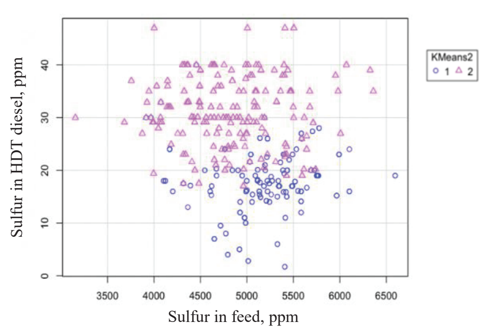

Figure 9: HDT diesel sulfur vs feed sulfur contents (ppm) (Mode 1 in blue, Mode 2 in fuchsia).

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4.3 LCA on Each Operational Mode

4.3.1 Inventory Analysis: In the inventory analysis, the inputs or resources and the outputs or emissions of the unit were inferred from the limits of the variables. The values of the inputs and outputs of the system for the two operating modes of the HDT unit are shown in Figures 2-9 and in Table 1. On the other hand, Table 2 presents the consumption of industrial utilities for the H_2 purification section after the reactors and for the transportation of sour water.

Table 1: Variable statistics; min and max in brackets.

Operating Mode	Feed, BPD	HDT diesel, BPD	Pressure, psig	Compression, kW	Pumping, kW	Heat, kW
1	63110±600 [49400, 73300]	65850±600 [44340, 81790]	870±1.4 [743, 893]	2324±145 [1880, 2690]	6036±220 [4850, 7060]	25530±512 [19910, 30030]
2	60520±330 [49100, 72360]	76350±400 [47060, 83510]	850±0.7 [660, 880]	2053±130 [1570, 2370]	5921±213 [5130, 6850]	22960±531 [17800, 29750]

Table 2: Statistics for the H_2 cleaning section and sour water transport; min and max in brackets.

Operating Mode	Amine solvent, gpm	Air cooler power, kW	Pumping, kW	Sour Water, gpm	Pumping Sour Water, kW
1	187±2 [181, 193]	1948±62 [1249, 2326]	931±22 [650, 1210]	48±0.5 [45, 51]	395±15 [231, 452]
2	186±2 [184, 195]	1975±65 [1525, 2497]	955±31 [589, 1192]	47±1 [44, 50]	386±17 [249, 463]

4.3.2 Impact Assessment: The values of the LCI impact factors of the utilities and pollutant flows in each category were assumed to be those reported in the Eco-Indicator 99 database (Frischknecht et al., 2007). The LCI for damage caused by electricity consumption was taken from the Eco-Indicator 99, as it divides this LCI into pumping and compression. The percentage LCI contribution in each category of the Eco-Indicator 99 is shown in Figure 10. According to this figure, the consumption of H_2 has the largest impact on the "Natural Resources" category. The source "Fossil Fuels" is mainly responsible for this consumption, as steam methane reforming is currently the way to produce H_2. In contrast, H_2 consumption presents the lowest impact factor in the "Human Health" category and "Ozone Layer Depletion" source; various studies support the low impact of H_2 on the depletion of the ozone layer (see Derwent, 2018 and its references; Chandrappa & Chandra-Kulshrestha, 2016). Conversely, SO_2 pollution is in second place with the highest impact factor value (category "Human Health" and "Respiratory Effects" source), and in turn, this pollution presents one of the lowest impacts in the "Decrease Layer of Ozone", as SO_2 emission has not been identified in the mechanisms of ozone layer destruction (Chandrappa & Chandra-Kulshrestha, 2016).

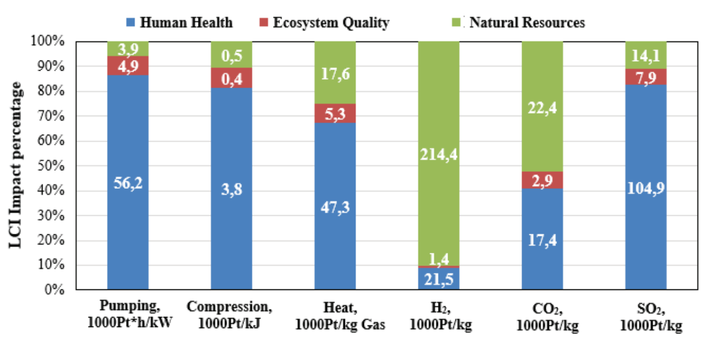

Figure 10: LCI contributions for the impact of industrial utilities and pollution.

On the other hand, the m_u consumptions for the industrial heat energy of the furnaces were found in terms of fuel gas consumption (38 MJ/kg) and furnace efficiency. For CO_2 and SO_2, the m_u were related to gas combustion in the furnaces and the combustion of the products, respectively (Wu & Liu, 2016). Similarly, the environmental impacts of the amine treatment process (Wu & Liu, 2016; Olindo & Vogtländer, 2019) and sour water (Wu & Liu, 2016) were evaluated considering the respective

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requirements of the utilities and the pollution generated (Table 2). Table 3 presents the values of m_u used in Eq. (3) for each mode of operation. According to Table 3, Mode 2 presents the lowest requirements for utilities and the lowest CO_2 pollution, however, it presents the highest SO_2 pollution due to the lower severity of the hydrotreatment (Figure 7). Figure 11 (left) compares the annual environmental damage by category in the two operating modes of the HDT industrial unit, based on the LCI factors, Table 3, and Eqs. (1)-(3). According to this figure, the environmental impact, *EI*, of the HDT unit in Mode 1 is greater than of operation in Mode 2 for each category of the Eco-Indicator 99. The *EI* of Mode 1 is 13.03 MPt/year, while the *EI* of Mode 2 is 12.36 MPt/year. Thus, the environmental damage caused by the annual operation of the HDT unit is equivalent to the annual pollution of 13.03 million and 12.36 million European citizens for operating Modes 1 and 2, respectively. Furthermore, the damages with the highest *EI* value correspond to those related to H_2 ("Natural Resources" and "Fossil fuels" source: 468.74 Pt /h for Mode 1 and 465.34 Pt/h for Mode 2) and electricity consumption (mainly pumping) ("Human Health" and "Respiratory Effects" source: 242.94 Pt/h for Mode 1 and 238.31 Pt/h for Mode 2). As expected, the impact of SO_2 in each category is negligible compared to the impact of industrial utilities and CO_2 pollution.

Table 3: Average flows of utilities or pollutants used in Eq. (3).

	Pumping, kW-h/h	Compression, kW-h/h	Heat, kg/h	H_2, kg/h	CO_2, kg/h	SO_2, kg/h
m_{u1}	6036.0	2324.0	3023.3	2186.6	8314.0	11.9
m_{u2}	5921.0	2053.0	2718.9	2170.7	7477.1	25.1

In addition, Figure 11 (left) shows the *EI* impact values reported by Wu & Liu (2016) for 65 kBPD feed with a sulfur content of 1.3%. This figure shows that the environmental impact reported by Wu & Liu is higher than the impact obtained from the operation of the HDT industrial unit, which is considered in the current work. The largest impact reported in Wu & Liu is due to the higher consumption of H_2 in their process. The feeds considered by these authors report a higher amount of sulfur (between 1.3% and 1.8%) than those treated in the HDT unit (between 0.32% and 0.66%). For the above reasons, the impacts in the "Natural Resources" category in Wu & Liu exceed those calculated for the operating modes of the HDT unit.

Figure 11: Environmental impacts for the HDT unit (Mode 1 in blue; Mode 2 in red; Wu & Liu in green) (left). Intervals for the HDT unit environmental impact (right).

4.3.3 Interpretation of the results: The difference in the conditions and variables between Mode 1 and Mode 2, as mentioned above, corresponds mainly to the severity of the hydrotreatment and, to a lesser extent, to the value of the feed flow. In mode 1, the hydrotreatment is carried out at an average of 15 ºF higher than that specified for hydrotreatment in Mode 2. Consequently, the desulfurization obtained in Mode 1 leads to a diesel with a higher degree of cleanliness (lower sulfur content); *i.e.*, 15 ºF leads to a 13 ppm reduction the sulfur content, although at the expense of catalyst lifetime and increased consumption of utilities (Terán-Alemán, 2016; Ovalle-Orozco, 2020). With this higher degree of desulfurization, the environmental impact derived from Mode 1 is higher by *ca*. 6% of the environmental damage derived from Mode 2 (Figure 11, left). On the other hand, Wu & Liu reported

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an increase of about 0.2 MPt/year in environmental damage from the operation with a 0.1% increase in the feed sulfur content (output diesel sulfur content of about 40 ppm). Using the value of 0.2 MPt/year for each 0.1% sulfur, difference in impact between Mode 1 and Mode 2 due to the feed sulfur content is 0.08 MPt/year (Mode 1: 0.52%, Mode 2: 0.48%). Thus, the remaining difference of 0.60 MPt/year between Mode 1 and Mode 2 (Figure 13) is due to the hydrotreating severity. That is, 0.60 MPt/year corresponds to the increase in environmental damage caused by a 14 ppm decrease in the sulfur content of the HDT diesel (*i.e*. 0.43 MPt/year/ ppm). This increase obtained with the HDT operation agrees with what was reported by Wu & Liu of 2.0 MPt/year of damage with a 31 ppm (from 38 ppm to 7 ppm) decrease in the sulfur content of the output diesel (*i.e.* 0.66 MPt/year/ppm).

It is important to mention that the increase in the environmental impact becomes exponential with the decrease in the sulfur content of the hydrotreated diesel, at values below 40 ppm, due to the increase in fuel gas consumption required for the severity of the reaction (Wu & Liu, 2016; Wu & Liu, 2018). The difference of 0.68 MPt/year between the impacts of the modes 1 and 2 is mainly due to the increase in severity. This increase in severity is reflected in an average elevation of 15 ºF and 20 psi in the operating conditions of the reactors. For this elevation, the HDT unit increases its fuel gas and H_2 make-up consumption, which in turn increases the impacts corresponding to Heat Energy, Compression, and CO_2 in the Human Health and Natural Resources categories. The impact values of the operating modes (Figure 11, left) can be reduced by applying strategies that result in reductions in electricity consumption (pumping), fuel gas consumption (heat energy), and H_2 requirements. These strategies may include:

- Application of steam turbine networks for decreasing electricity demand (Wu et al., 2016).
- Energy integration (pinch analysis) to reduce fuel gas demand (Wu & Liu, 2016).
- Integration of H_2 networks into refinery operations (Wu et al., 2017).
- Implementation of a catalyst with higher efficiency and lower operational severity.
- Application of multi-objective optimization (see Szklo & Schaeffer, 2007; Wu et al., 2018).
- Implement CO_2 capture for the flue gases.

4.4 Variation Intervals for the Environmental Impact

Figure 11 (right) shows the *EI* for each mode at minimum, average, and maximum conditions. According to this figure, the EI obtained from the HDT unit operation was found to be between 8.28 and 15.15 MPt/year. Thus, an increase of about 84% was estimated for the *EI* of the HDT unit in going from the less severe condition to the most severe one. In other words, the higher the values of the operational variables, the higher the resulting *EI* derived from the operation of the HDT unit. Similarly, Figure 11 (right) indicates that the operation of the HDT unit at the maximum or severe conditions of each mode has a comparable *EI*. The difference in the EI of the modes at this condition is 0.1 MPt/year. The impacts on the operation of Mode 2 in its severe condition are close to the respective impacts of Mode 1 due to the increase in the H_2 requirement, which is a consequence of the change in the feed quality. As mentioned above, the type of feed stream in Mode 1 (maximum condition) was mainly high-sulfur diesel, while in Mode 2 (severe condition) a mixture of high-sulfur diesel and LCO was loaded into the unit. LCO has similar characteristics to diesel, but its composition alters the performance of the hydrotreatment, leading to an increase in the requirements of the utilities and, consequently, to a similar *EI* in both operating modes at the respective severe conditions (Figure 11, right). Conversely, the *EI* obtained at the minimum conditions of Mode 1 and Mode 2 decreases to a half of the respective EI at the maximum conditions. The reason for this decrease is due to a drastic decrease in H_2 consumption in both modes at the minimum condition (in accordance with the analysis in Wu & Liu, 2016). The minimum condition in each operating mode refers to the production of diesel with a sulfur content of around 40 ppm (Figures 7 and 9), while the operation at the severe condition can produce diesel with a sulfur content below 20 ppm. According to the international Euro V regulations (Gense et al., 2005), the sulfur content of diesel must be as low as 10 ppm. The *EI* values of the industrial unit increase considerably with the improvement of the diesel quality (increase in the severity of hydrotreatment). Therefore, it cannot be claimed that the *EI* decreases with the use of ultra-low sulfur diesel (below 10

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ppm). In other words, the reduction in the *EI* of the products (lower sulfur diesel) is just the tip of the iceberg, since the production process contributes significantly to the net environmental impact.

5 CONCLUSIONS

An evaluation of the environmental impact derived from the operation of a HDT industrial unit was carried out through the application of the Life Cycle Assessment and the use of operational data. According to the results, the statistical treatment of the operational data using the kmean grouping method led to the identification of two operational modes for the HDT industrial unit. Mode 1 was characterized by a more severe hydrotreating operation (higher consumption of utilities), producing low-sulfur diesel. Mode 2, on the other hand, considered less severe conditions for the HDT unit, resulting in diesel streams with higher sulfur content than those in Mode 1. The LCA with the Eco-Indicator 99 showed that the HDT unit operating in Mode 1 resulted in a greater environmental impact (13.03 MPt/year) than the corresponding impact obtained with the HDT unit in Mode 2 (12.36 MPt/year). This higher environmental impact of operating in Mode 1 was mainly due to a higher demand for industrial utilities as well as a higher CO_2 emission compared to operating in Mode 2. In particular, the H_2 consumption and CO_2 pollution impacts were related to the Natural Resources category, while the electricity consumption impacts the Human Health category. Likewise, the environmental impacts resulting from the operation of the HDT unit in both modes were found to increase with the severity of the operation due to an increase in the corresponding H_2 consumption. An increase in the impact of about 84% was estimated for the operation of the HDT unit going from the minimum condition to the most severe condition. In addition, the environmental impact of the HDT unit was found to be similar for both modes operating at the maximum condition.

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