Simulation of Hydrotreating Units of Gas oil and Vacuum Gas oil

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Abstract

With growing need for sulfur removal of oil fractions, the hydrotreating units play an important role which the study and optimization is crucial. The present work consisted in the study of hydrotreating units of Galp Energia, where it was performed the modeling of hydrotreating units of gas oil and vacuum gas oil from Sines refinery, using the simulation software Petro-SIM\textsuperscript{TM}. The simulation of the two units was based on the construction and development of two distinct and rigorous models for each one. For the model of gas oil hydrotreating unit it was obtained a calibration that provides results very close to the real values, allowing to have a good representation of the unit. These, in turn, will contribute to a further appreciation of this new model in study and the currently in use by the company. In the vacuum gas oil hydrotreating unit the model that was constructed approaches almost identically to reality, with the ability to predict good responses for future studies representative of this unit. With the analysis of the answers given by the simulation of the units under study to the impact in the variation of relevant parameters to their operation, reveals that the simulation models correspond to the variation of the operating conditions and they work according to the expected.

Keywords: Sulfur Content, Gas Oil, Vacuum Gas Oil, Hydrodesulfurization, DHTR-SIM\textsuperscript{TM}, VGOHTR-SIM\textsuperscript{TM}

1. Introduction

The oil refining industry is one of the most important industry in the world. This industry faces an evolution of the markets and an increasingly competitiveness, which makes it crucial to minimize operating costs. However, the diversity of the characteristics of the raw material (crude oil) and the demands of petroleum products are constantly changing. This has conducted to the development of computational models that allow predicting and monitoring the treatment that need to be applied to a certain type of crude oil.

Nowadays, the crude oil industry is committed to reducing its sulfur emissions and improving existing processes, to accomplish regulatory requirements, to optimize the crude oil economy and to achieve superior treatment capacity.

For this purpose, the hydrotreating units main function is the removal of sulfur from the different oil fractions, to improve they properties. The relevance of these units in the refining process has increased steadily in recent years in order to achieve the environmental specifications imposed on fuels, as well as the increasing demand for transportation fuels, in particular gas oil.

The purpose of this work was to create rigorous models to hydrotreating units of Galp Energia. For this, it was used a process simulator Petro-SIM\textsuperscript{TM} to develop two distinct models, one for the hydrotreatment of gas oil and the other for vacuum gas oil.

2. Bibliographic Review

2.1. Hydrotreatment

This is a catalytic process with the intent to remove impurities from crude oil fractions, mainly heteroatoms (sulfur, nitrogen, oxygen), metal compounds (nickel, vanadium) and promote the saturation of polynuclear aromatics (PNA) and/or olefins. The concentration of theses impurities...
increases with the boiling point of the crude oil fractions.

The hydrotreatment is not considered a conversion unit, since there is practically no breaking of carbon-carbon bonds (cracking). In a refinery the hydrotreatment is applied in different categories:

- Pre-treatment, step where it’s proceed the hydrotreatment of feed to conversion processes, such as catalytic reforming and hydrocracking;
- Post-treatment, finishing step in order to obtain specifications of transportation fuels within regulated standards.

In refinery industry, the removal of impurities of crude oil fraction are of extreme relevance in order to:

- Improve product properties (color, stability, odor);
- Catalyst protection of downstream units;
- Accomplish environmental targets imposed;
- Reduction or elimination of corrosion during refining.

The hydrotreatment take place in a wide range of operating conditions. The process severity/conditions are adjusted depending on the properties of the feed and the composition of the intended products.

Normally the hydrotreatment is associated to the process of sulfur removal, designated as hydrodesulfurization.

The Galp Energia refining facilities has one vacuum gas oil treatment unit at Sines refinery, three naphtha treatment units (two in Sines and one in Matosinhos) and four medium distillates (jet fuel and gas oil) treatments units distributed two at each refinery (Sines and Matosinhos).

2.1.1. Desulfurization

Sulfur is one of the undesirable compound of crude oil and the higher its content in this, the higher it will also be in petroleum products.

The combustion product of this organic compound, sulfur oxides (SO\textsubscript{x}), are hazardous atmospheric pollutants responsible for acid rain and also by respiratory failure in humans. In relation to the use of transportation fuels, the presence of this sulfur compound acts as a poison to the catalyst in the exhaust control systems of the fuel engines. In the context of refining entails problems of deactivation of the catalyst in process units downstream or even in terms of corrosion in the equipment.

In order to reduce emissions of gaseous pollutants into the atmosphere and health concerns, the authorities have implemented restricted policies at the sulfur limit of transportation fuels, which provides the use of ultra-low sulfur fuels (<10 ppm).

2.1.2. Hydrodesulfurization

Crude oil includes in its composition different types of organic sulfur compounds, which according to their chemical nature are denominated by sulfides, thiophene, benzo thiophenes, alkylated benzo thiophenes and dibenzo thiophenes, these last two are preferably present in the medium and heavy distillates.

Hydrodesulfurization is a chemical method to extract sulfur from hydrocarbons compounds which comprises crude products, in particular in the medium and heavy distillates.

This is an exothermic process with some disadvantages, such as high cost and the fact that some compounds containing organic sulfur are in molecular structural positions of difficult access (refractory compounds) presenting more difficulty in the removal, which demand more specific operation conditions.

2.1.2.1. Hydrodesulfurization Chemical Reactions

The main hydrodesulfurization reaction comprises the catalytic conversion of sulfur from different organic sulfur compounds into H\textsubscript{2}S. In these reaction saturated hydrocarbons are obtained as byproducts. The following reactions occur simultaneously with the main reaction:

- Hydrodenitrogenation;
- Hydrodeoxygenation;
- Hydrodearomatization
- Saturation of olefin and/or aromatics compounds;
- Hydrodemetallization;
- Coke;
• Hydrocracking.

The last two reactions are considered undesired reactions, causing a decrease in catalyst activity. The extent of these reactions negatively affects the yield of gas oil.

2.1.2.2. Catalyst

The hydrodesulfurization catalyst are bimetallic type using combinations of Cobalt and Molybdenum (CoMo) or Nickel and Molybdenum (NiMo) in the form of metallic sulfides (CoMoS or NiMoS) uniformly dispersed in an alumina support. This support has low acidity which limits cracking reactions.[7,8]

Catalyst based on NiMo are selective to hydrogenation reactions, being therefore used in desulfurization reactions involving both the saturation of aromatics and olefins. In the case of catalyst based on CoMo are used when the main objective is the desulfurization reaction.[9,10]

The efficiency of the process and the reliability of its operation depends on a wide extent of the industrial performance of the used catalyst.

3. Modelling the hydrotreating units

The modelling of hydrotreating units for gas oil and vacuum gas oil of Sines refinery uses the KBC Advanced Technologies process simulator: Petro-SIM™ version 6.1.

Two distinct models where develop, one for gas oil hydrotreatment (DHT-SIM™) and the other to vacuum gas oil hydrotreatment (VGOHT-SIM™).

These models where defined using the Petro-SIM™ base model provided by KBC for each hydrotreating units under study, selecting the configuration options of each unit.

Then the development of the models involves two distinct phases: Calibration and Prediction mode.

Calibration mode - the model requires as input, the feeds streams, the products stream and operating conditions. With this information the simulator calculates the calibration factors to represent the functioning of the real unit.

Prediction mode - the feed streams, operating conditions and the calibrations factors (obtained in the previous mode) are known (input). Then the simulator has the ability to calculate the properties and yields of the products streams.

The calibration begins with the selection of complete data sets. These days of data will be calibrated in calibration mode and each one provided a different set of calibration factors. This results in several different sets of calibration factors making it necessary to choose the one that best match the way the unit operate.

In prediction mode each one of calibration factors set obtained in the previous mode will be used to provide results to product streams for all data day, with the intention to choose which of the calibration factors set can provided best results.

Comparing the results of prediction mode with the real values of certain properties of product stream it is possible to determine which set of calibration factors approach better the results with the reality. The set of calibration factors that best predicts these properties in the overall of all the data days will be chosen has the calibration that represents the unit and is the one that will be used as the standard set for future studies of this unit.

This analysis is done considering the following properties of the main treated product (gas oil and vacuum gas oil): density, recovered to 95% (distillation fraction: volume%), mass flow, nitrogen content and flash point. This last property is only considerable in the analysis of gas oil hydrotreating unit.

In the comparison referred above is required to do a qualitative analysis to choose the best set of calibration factors. It was first determined the relative error of the predicted values with each set of calibration factors for each property in analysis. This is determined by the difference between the real value and the predicted value ($\Delta x$) divide by the real value ($x$), as it shows in equation 1.

$$\text{relative error} = \frac{\Delta x}{x}$$

Equation 1

Then the error of each day is given by the sum of the relative error of each one of the property for that same day, equation 2. In this equation it is assumed that all properties in analysis have the same weight.

$$\frac{\Delta x}{x} \text{ day} = \sum \frac{\Delta x}{x} \text{ properties}$$

Equation 2
At last, the sum of the error of all data days predicted with the same set of calibration factors, is termed as objective function (equation 3). This function is the error associated of each set of calibration factors and the calibration that has the lowest value on this function is selected as the best calibration.

$$F_{obj} = \sum_{i} \left| \frac{\Delta x_i}{x_i} \right|_{day}$$ (3)

3.1. Sines Gas Oil Desulfurization Unit (HG)

In the construction of the desired model for the HG unit is necessary to select the options that best defined the configuration of this unit. The configuration of the simulated unit is:

- One reactor with four catalytic beds based on CoMo;
- Distillate Hydrotreater (reactor, high and low pressure separator);
- One splitter and one fractionator column;
- Two feed streams (untreated gas oil and a make-up hydrogen);
- Five product streams (treated gas oil, wild naphtha, fuel gas, H₂S and NH₃).

Thus, the simulated HG unit has the following Process Flow Diagram (PFD), shown in the figure below.

![Figure 1 - Configuration of the unit HG at Sines.](image)

3.1.1. Calibration Data

In calibration it was set 11 days of data for the HG unit, this are days with complete analysis of feed and all product streams. After the simulation model defined it’s now able to simulate all the data days, where each of them will provide a set of calibration factors, as mentioned previously.

3.1.2. Selection of the best calibration set: Results and Analysis

In order to certify that the model of HG unit is working as supposed, it was analyzed the prediction results of two of the mentioned properties, the mass flow and the density of product stream (treated gas oil). The next two figures demonstrate the prediction of this two properties with the 11 calibrations sets, comparing the results with the real value, series "real".

With the mass flow of treated gas oil stream is possible to verify if the unit is performing a significant cracking to achieved the target of sulfur content in treat gas oil.

![Figure 3 - Prediction of the mass flow of the treated gas oil with each set of calibrations factors.](image)

As expected, the mass flow of treated gas oil is correctly simulated with each set of calibrations factors, coinciding with the values of this. So the occurrence of significant cracking is not evident to causes changes in the mass flow.
The refineries of Galp Energia give importance to density of treated gas oil, where it can affect the characteristics of gas oil, namely the cetane index that depends directly on this property, as well as the distillation curve. Density is relevant due to its variation throughout the hydrodesulfurization process. So in the choice of the best calibration the density variation of the gas oil in the process was used instead of the density of the treated gas oil. The following figure shows the density variation of gas oil.

![Density variation of gas oil](image)

**Figure 4** - Prediction of density variation of gas oil for each set of calibration factors.

As it can be seen in figure 4, not all sets of calibration factors provide a very close match result in prediction mode. However, both of this properties confirmed that the model is functioning as intended, due to their proximity to the real values.

The same representation seen in figure 3 and 4 was made for all the other properties mentioned previously. The prediction results were analyzed with the real values of each property by the qualitative analysis defined at the beginning of the chapter.

With this, it was possible to establish that the best calibration factors set is provide by February 17th data. This calibration set is the one that provides results with less deviations of the real data, that is, presents more accurate results with the reality of the unit for all the properties were analyzed. The next figures show the comparison between the value simulated by the set of calibration factors of February 17th and the real value for the properties under analysis.

![Density of treated gas oil](image)

**Figure 5** – Prediction of the density of treated gas oil with the calibration factors of February 17th.

By the analysis of figure 5 the predicted results of density are close to the real values, having a good prediction for this property.

![Mass flow of treated gas oil](image)

**Figure 6** - Prediction of the mass flow of treated gas oil the calibration factors of February 17th.

![95 % Recovered of treated gas oil](image)

**Figure 7** – Prediction of 95% recovered of treated gas oil with the calibration factors of February 17th.

Figures 6 and 7 shows the mass flow and 95% recovered of treated gas oil. As it is seen, the mass flow has predicted values practically identical to the real values. While the 95% recovered have predicted
results that approaches very well the real values. So the PFD of the simulated HV unit was obtained as it shown in the figure below.

![Figure 10 - PFD of the HV unit simulation.](image)

3.2. Sines Vacuum Gas Oil Desulfurization Unit (HV)

The construction of the model for the HV unit begins by choosing the options that best defined the configuration of this unit. The simulated HV unit has the following configuration:

- One reactor with one catalyst bed based on CoMo;
- VGO Hydrotreater (reactor, high and low pressure separator);
- One splitter and one a fractionator column;
- Two feed streams (untreated VGO and a make-up hydrogen);
- Five product streams (treated VGO, wild naphtha, fuel gas, H₂S and NH₃).

3.2.1. Calibration Data

With calibration model defined it’s then possible to select and analyze days with complete data to simulate the model in calibration mode and obtain a several set of calibration factors, where each of them correspond to a day of data.

For the HV unit it was possible to set 9 days of complete data and with the calibration of these days it was obtained 9 sets of calibration factors.

3.2.2. Selection of the best calibration set: Results and Analysis

As in HG unit, its necessary to tested in prediction mode if the model and all the calibration sets are functioning as pretending. For that it was represent the results obtained from prediction mode with the 9 set of calibration factors to the mass flow and density of treated VGO and compared with real values of each of these property.

![Figure 11 - Prediction of the mass flow of the treated VGO with each set of calibrations factors.](image)
in the choice of the best calibration set, instead the density of the treated VGO.

Figure 12 - Prediction of density variation of gas oil for each set of calibration factors.

As it observed in figure 12, not all the calibration set provide an accurate match result in predict mode. However, both properties represented above demonstrated that the unit is working as expected.

The representation in figure 11 and 12 was made for all the other properties in study. Therefore, it was performed the analysis of the prediction results in comparison with the real values of each property to determine which set of calibration factors is the best.

The best calibration set for the HV unit is provided by the February 10th data. In the next figures is observed the comparison between the value calculated by the set of calibration factors of February 10th with the real value to all the properties being analyzed.

Figure 13 - Prediction of the density of treated VGO the calibration factors of February 10th.

Figure 14 - Prediction of the mass flow of treated VGO the calibration factors of February 10th.

With figure 13 and 14 is possible to verify that both properties have prediction results practically identical with the real values, respectively.

Figure 15 - Prediction of the 95% recovered of treated VGO the calibration factors of February 10th.

Figure 16 - Prediction of the nitrogen content of treated VGO the calibration factors of February 10th.

For the 95% recovered and nitrogen content, figures 14 and 15 shows that the prediction results are very close to the real values of this properties.

Thus, the chosen calibration set has shown that in prediction mode, the results are almost similar to the real values, representing very well the real behavior of this unit.
4. Sensitivity analysis

To analyze the functioning of the HG unit it was made a sensitivity analysis to three relevant parameters in the operation of this. The parameters analyzed were as follows:

- Sulfur content in feed stream (untreated gas oil);
- Mass flow of feed stream (untreated gas oil);
- Sulfur content in product stream (treated gas oil).

With the chosen calibration set of the HG unit it was selected six days of data based in their sulfur content and density, either in the feed stream or in treated gas oil stream.

In this paper it only be demonstrated the answer (shown in figures) provided by HG unit to the variation of sulfur content in feed stream (untreated gas oil). The variation of the other two parameters will be only explained the results obtained by the impact of variation from these two parameters in the same properties analyzed below.

4.1. Sulfur content in feed stream: Results and Analysis

In this analysis, the sulfur content in feed stream (untreated gas oil) was varied from 2 000 to 15 000 ppm. The other’s properties have remained constant.

The results obtained from this variation were observed on unit severity (WABT- Weight Average Bed Temperature and ratio of hydrogen consumption per volume of feed) and some properties of treated gas oil, namely density, nitrogen content and mass yield, as it shows on the next figures.

Some figures above have present the “Real 13/jul” point, that represents the real value of the parameter under study (x label) with the real value of each property being analysis (y label). This point has the example day of July 13th and is indicated as a cross with the respective color of the series of this day of data.
Figure 21 - Response of the mass yield of treated gas oil to the variation of sulfur content in the feed.

Analyzing figures 17 to 21 it turns out that increasing the sulfur content in the feed will involve more demanding operating conditions in order to have the product with the desired specifications. So the severity indicators (WABT and ratio of hydrogen consumption per volume of feed) increase with increasing sulfur content in the feed. Thus, the mass yield and the density of treated gas oil decrease, the first is caused by the increase of cracking and the second is due to the removal of the sulfur (impurity). For the nitrogen content it decreases as expected under severe conditions the kinetic reactions are quicker.

4.2. Mass flow in feed stream: Analyze the results

At the mass flow of the feed stream it was made variations between 60 to 100%, where the 100% corresponds to the mass flow nominal value of project (245 ton/h). The other properties have remained constant. The results obtained were observed in the unit severity, density, nitrogen content and mass yield of the treated gas oil. Analyzing the results, as the mass flow of the feed increases will cause an increase in the severity of the operation. Since, the sulfur content increases in the same proportion with the mass flow, as all the components of the feed. The WABT increases to promote the removal of sulfur and the ratio of hydrogen consumption per volume of feed decreases, this last one in first analysis appears to be incorrect. To understand this behavior, the consumption of hydrogen in tons per hour was observed, verifying that this increases as expected. However, the reason why the ratio of hydrogen consumption per volume of feed decreases is due to the higher influence of the denominator (feed) on the numerator (hydrogen consumption), causing a decreasing of this ratio. The density of the product increases because of the insufficient removal of all the constituents (impurities) of the feed. The mass yield of treated gas oil decreases due to increase of cracking during the operation of the unit. The nitrogen content in this analysis will have the same behavior as the sulfur content of the treated product. That is, it will remain constant. If the value of the sulfur content in the product is obtained by increasing severity, it will therefore remove the nitrogen from the product in the same manner.

4.3. Sulfur content in product stream: Analyze the results

In the analysis of this parameter the sulfur content was varied between 1 and 16 ppm keeping all the other properties constant.

The results obtained for the unit severity, mass yield, density and nitrogen content of the treated gas oil were studied. Through the results obtained it is concluded that an increase in the sulfur content in the treated gas oil will caused a decrease in the severity of the operation. Therefore, the WABT and the ratio of hydrogen consumption per volume of feed decrease, this is an indication of the unit due to the decrease in the removal of the sulfur content in the treated gas oil. If sulfur content at the outlet (product stream) increases it will be expected that nitrogen content, density, as well as the mass yield of the treated gas oil will also increase, which was observed.

It's noted that the sensitivity analysis described in current chapter was performed equal for the HV unit, where the same parameters were varied for ranges according to their feed and unit characteristics.

Both models of simulation studied in this work have similarities, since they are hydrotreatment units. However, the results of the sensitivity analysis performed on the HV unit present exactly the same type of behavior in the responses to the variations of the parameters mentioned previously.
5. Main Conclusions

In the present work were intend to develop simulation models for two hydrotreating units of Galp Energia.

In the simulation model of the HG unit the results obtained with the calibration factors by February 17th represent well the real unit. There was particular attention to the density variation of gas oil throughout the process, it was verified that this property is being well predicted with the chosen calibration. This simulation model isn’t part of the basis of the models acquired by the company, as such, the results obtained by this model will be used for a further comparison with the performance of the simple simulation model existed in the company and the possible acquisition proposal.

With the modelling of the HV unit it is concluded that the February 10th calibration is the one that represents results with a performance coincident with reality. The variation of the density during the process is well predicted in the period of data analyzed, with the calibration selected.

In sensibility analysis it is concluded that the simulation models correspond with the variations of the operative conditions and they work according to the expected.

In the two models of simulation developed It is possible to studied and improved some aspects. Both simulation models of this work allow a detailed study that tracks the life cycle of the catalyst. In the model of HG unit is can be study with more detailed some specific characteristics of this model.

6. Main references