Model and Simulation of a Hydrotreatment

Reactor for Diesel Hydrodesulfurization in

Oil Refining

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Abstract

One of the most developed industries in the world is the industry dedicated to extraction and treatment of crude oil, due to his economic profitability. One of the equipment more important in any process is the reactor, which is the place where the physico-chemical transformations of the matter are carried out. The hydrotreatment process is used in oil refining, to decrease the level of different contaminants in the crude. Usually, this process is applied to the clearance of sulphur in contaminated streams. The process was modeled and simulated through the Open Source DWSIM software, using hydrogen as reactant and Ni-Mo $\gamma Al_2 O_3$ as catalyst. As product was obtained acid crude. It was chosen the model Chao Seader to predict the main properties of each compound present in the reactor. Through the reuse of hydrogen in the system, it was possible reach a 0.0093% weight of Sulphur in the final crude stream. Furthermore, it was designed the furnace used to warm up the mixture for the reactor and the cooler used to separate the volatile compounds.

Keywords: Heavy diesel, Chemical reactor, Chemical simulation, DWSIM, Chao Seader model, HDS

Introduction

In recent decades, it has been presented an increase in development and innovation of methodologies and processes used in petroleum industry, in order to decrease the

treatment and refining costs in the plant. Furthermore, it is used to rise up the economic profitability and income in the plant   [1], [2]. In addition, the improvement of the actual processes is set out as a reduction of the quantity of waste produce by the whole oil refining plant. Therefore, it drops the final contamination to environment [3]–[5].

The hydrogenation is one of the process more used in industry to drop the concentration of heavy metals, Sulphur and nitrogen present in crude [6]–[8]. This process consist in combine hydrogen with the compounds presents and generating a reaction, to obtain the addition of hydrogen to the target molecules [9]–[11]. These compounds are retired through other processes as settlers of acid water. To carry out these reactions, it requires high hydrogen pressures and the presence of a catalyst [12], [13].

One of the applications more used in petroleum industry is the crude hydrodesulfurization across the hydrotreatment process. In this action the Sulphur molecules react with hydrogen molecules to form hydrogen sulfide, which is blended with water in order to remove a high portion of Sulphur as acid water from the crude [14], [15]. The catalyst in this reaction act increasing the reaction mechanics steps and curb the activation energy from the reaction. Among the most used catalyst for this process are the alloys of Ni-Mo and Co-Mo on an alumina base [13], [16], [17].

In this paper is propose a sulphur removal process for Colombian crude, through high pressure hydrogenation of compounds. In previous phases of the project were obtained the characterizations of the crude fractions from a fractionated distillation column. The hydrogenation process was made for the heavy diesel fraction, which has a high content of Sulphur and a low content of heavy metals, reason why it needs the treatment to accomplish with the laws for Sulphur concentration in fuels.

Methodology

The compound hydrogenation in petroleum industry has as base the design of a hydrogenation reactor. His inlet stream is a high-pressure mixture between oil crude and hydrogen, to obtain an oil crude with low concentration of sulphur for this case. To design the reactor, it is necessary to have the reaction kinetics. For this paper, the kinetic used was adapted from the work made by María A. Callejas and María T. Martínez in 1998 [18]. Where the sulphur concentration was in equation (1), which correspond to a perfect mixed heterogeneous system on steady state.

$$C_0 - C = \frac{K^* C^n P_{H_2}^m}{LHSV} \tag{1}$$

Here C is the sulphur concentration, K* is the kinetic constant, n is the kinetic order, LHSV is the liquid hourly space velocity and m is the dependence order of the hydrogen pressure.

From equation (1) is determined the kinetic reaction for sulphur removal inside the reactor. Besides, it was found the temperature influence with kinetic constants through the Arrhenius equations.

$$-r = K^* C^n P_{H_2}^m \qquad (2)$$

$$K = K_0 \, e^{-\frac{E_a}{RT}} \qquad (3)$$

It should be noted that the catalyst used for this process was Ni-Mo on $\gamma Al_2 O_3$ (alumina). The parameters values for the previous equations were shown on Table 1, in addition, the standard error for the estimated coefficients were estimated.

Table 1: Kinetic parameters adapted from [18].

Parameter	Value	Standard error	Units
Ln [K*]	-11.4	0.4	$\dfrac{L}{ppm \, h \, g_{cat}(MPa)^{0.4}}$
m	0.4	0.08	
n	2		
Ea	68.6		$\dfrac{kcal}{mol}$
LHSV	2.9		$\dfrac{L}{h \, g_{cat}}$

The desulphurization reactions carried out in the reactor were represented by equation (4), where 1 mole of diatomic hydrogen react with 1 mole of methyl mercaptan to remove the tio group from the mercaptan and produce hydrogen sulfide. This reaction can be extrapolated to all species of sulphur present in the crude with a similar reaction.

$$CH_3 - SH + H_2 \rightarrow CH_4 + H_2 S \qquad (4)$$

The characterization for the heavy diesel stream was shown in Table 2 which was the inlet stream to the process. Furthermore, to keep the reaction, it was required a hydrogen stream with a maximum of 1% of water.

Table 2: Inlet oil crude characterization.

Stream	Heavy Diesel	IN	Flux [mol/h]
Tray	48	Methane	0.000
X	0.000	Ethane	0.000
Temperature [°C]	628.7	Propane	0.000
Pressure [kPa]	1378	i-Butane	0.000
Flux [kgmole/h]	2.226	n-Butane	0.000
Flux [kg/h]	601.111	i-Pentane	0.000

Table 3: (Continued): Inlet oil crude characterization.

Std Ideal Liq Vol Flow (m3/h)	0.590
API	7.185
Sulphur (%w)	3.444
Factor K UOP	11.280

n-Pentane	0.001
n-Hexane	0.001
n-Heptane	0.002
n-Nonane	0.549
n-C12	1.429
n-C20	0.048
n-C24	0.001
Sulphur	0.130

The reactor conditions were stablished to achieve an adequate reaction, as shown in parameters in Table 4. These values were taken from literature based on experimental values. They were chosen because they present good results in conversion and in sulphur clearance from the oil.

Table 4: Parameters for the hydrogenation reactor in steady state [18], [19].

Pressure (MPa)	12.5
Temperature (°C)	375.0
LHSV	2.9
H2 / S Volume Ratio	1000

A model raised by K. C. Chao and J. D. Seader in 1961 was used in the system, to model the physico-chemical properties and the compounds presents in design and simulation of the system [20]. This model was developed to predict the hydrocarbon properties, in addition, in order to calculate the liquid-vapor equilibrium, the system is based on semi-empirical parameters. The general form of the method is shown in the equation (5).

$$K = \frac{y}{x} = \frac{v * \varphi}{\gamma} \tag{5}$$

Here "v" is the fugacity coefficient for pure liquid, "φ" the fugacity coefficient for component i for vapor mixture and "γ" is the activity coefficient for component i in the liquid solution. For the vapor phase, the method employ the Redlich-Kwong state equation, while for the liquid phase use the theory of regular solutions of Scatchard-Hildebrand [21].

The hydrotreatment process was model using the Open Source DWSIM made by Daniel Mediros and Gregor Reichert. The reactor was the base of the project. As of this equipment, it was made and connect the sub-process necessaire for treatment the crude with hydrogen and adapt the inlet streams for reactor.

In order to decrease costs in process, it was design a hydrogen separation step through a fast cooling with a flash separator for the reactor outlet stream. Part of this hydrogen was recirculated to the process, so that reduce greatly the quantity of make-up.

The heating and cooling process including in the system was realized across the methane combustion and the flux of water to ambient temperature respectively. For heating, it was used a furnace, for which was determined the quantity of required methane to bring the necessaire energy to the process taking into account the Gibbs free energy for the complete and uncomplete combustion reactions.
The base reactions for the heating process at furnace were base in combustion. For the case of carbon dioxide production from methane were the equation (6).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{6}$$

$$\Delta G_{rxn} = \left(\Delta G_{CO_2} + 2 * \Delta G_{H_2O}\right) - \left(\Delta G_{CH_4} + 2 * \Delta G_{O_2}\right)$$

$$\Delta G_{CH_4 \rightarrow CO_2} = -818.255 \frac{kJ}{mol}$$

For carbon monoxide, the equation (7).

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O \tag{7}$$

$$\Delta G_{CH_4 \rightarrow CO} = -561.048 \frac{kJ}{mol}$$

To consider both reactions for methane, it was assigned an occurrence probability taking as base the Gibbs free energy delta for each reaction (Equation 8), it was obtained the following probabilities.

$$P_{A \rightarrow B} = \frac{\Delta G_{A \rightarrow B}}{\sum(\Delta G_{A \rightarrow \dots})} \tag{8}$$

$$P_{CH_4 \rightarrow CO} = \frac{\Delta G_{CH_4 \rightarrow CO}}{\Delta G_{CH_4 \rightarrow CO} + \Delta G_{CH_4 \rightarrow CO_2}}$$

$$P_{CH_4 \rightarrow CO} = 0.407$$

$$P_{CH_4 \rightarrow CO_2} = 0.593$$

Therefore, 40.7% of the inlet methane to the furnace will produce carbon monoxide, while the other part will react to carbon dioxide.
In the case of cooling with water, it was determined the quantity of necessaire water to achieve the desire cooling, with a minimum temperature delta of 10 K between the fluids.

Results and discussion

The hydrogenation process without separation and recycle of hydrogen was show in Figure 1. The hydrotreatment reactor for hydrodesulfurization was design on an Excel® spreadsheet and linked with DWSIM. For the reactor model, it was used the Tables 1 and 3.

With the actual configuration of the reactor, it was reached a maximum of 83.5% of conversion of sulphur present in the oil crude stream as shown in Table 5. Furthermore, the residence time inside the reactor was 4.3 min. This factor widely depends on the catalyst quantity deposited in the system, such as the void fraction of the catalyst. Also, it should be noted that the flow across the sections with the catalyst produce a drop pressure of 2.5 MPa approximately.
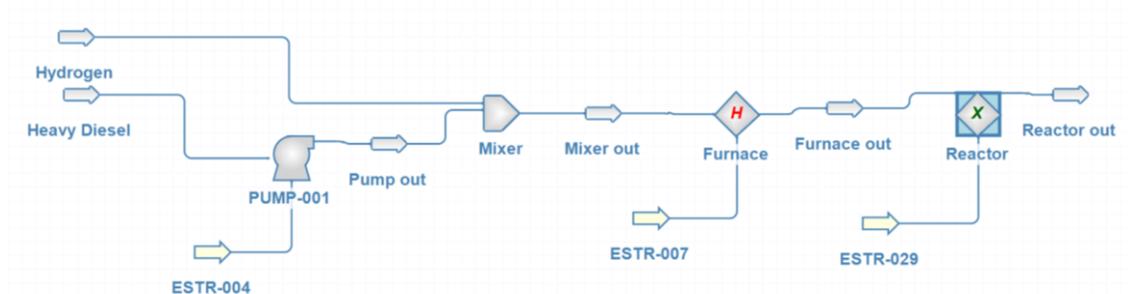

Figure 1: Hydrotreatment process without hydrogen recycle.

Table 5: Reaction without recycle.

Tao (min)	4.295
V (m^3)	2.518
Conversion	83.52
Surface area Cat. (m^2/g)	245
Length reactor (m)	1.2
Length catalyst (m)	0.45 x 2

The coupling zone for the raw material and the reactor was complemented with a sub-process for light gas separation to obtain hydrogen and make a recycle to the system. In Figure 3 was shown the hydrotreatment process with recycle, for which is designed a cooler with a flash separator. The separate hydrogen stream with a 99.8% of purity was compressed to be mixed with the inlet streams.

It should be noted that the stream called Hydrogen whose was the main hydrogen inlet to the system had a specification block which was based on the stream Mixer out. First, the block read the quantity of sulphur in the stream and modify the quantity of hydrogen of make-up in the system, to complete the H_2/S volume ratio. The process had a purge stream coming from the flash separator with a ratio of 1/3 with the recycle hydrogen stream.

The oil crude stream was pressurized until 12.5 MPa, in order to realize the reaction and match with the hydrogen inlet pressure and mix the streams. Subsequently, the mixture was heated until 648.15 K in order to give the energy necessary for reaction in the reactor. To realize these processes, it should deliver 4170 kW of energy approximately.

Table 6: Energy involve in the hydrotreatment process.

Stream	Process	Energy
ESTR-004	Crude pump	1.74561 kW
ESTR-007	Pre-reactor furnace	4169.62 kW
ESTR-029	Reactor	103.224 kW
ESTR-013	Reaction cooler	4041.32 kW

It is worth noting that the reactor had an energy stream commissioned to keep a constant temperature inside the reactor. This, with the purpose of decrease the sulfide and nitrates precipitation in the reactor bottoms. After completing the reaction, the resulting stream was cooled until reach the 310.93 K in order to differentiate and separate the plus volatile compounds. The management of the cooler was made using water with an initial temperature of 293.15 K. The water was boosted with a pump and enter the cooler. It was designed like a shell cooler, following the scheme in
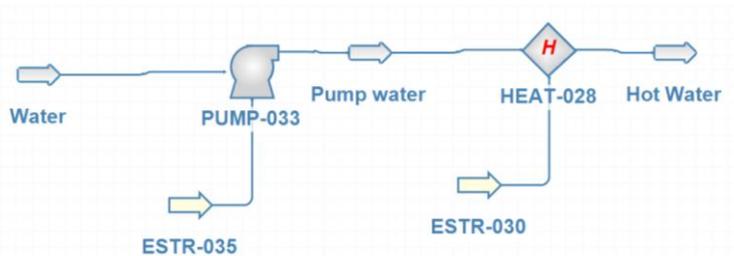Figure *2*.

Figure 2: Quenching react crude with water.

The water let out the cooler with a temperature of 331.21 K while the system works against the current to ensure a delta of temperature capable of keep an energy flux between both fluids. The pre-reactor furnace use methane to increase the temperature. To obtain the required energy flux were used 0.086 kg/s. The quantity of reactants and products from the reaction were shown in Table 6.
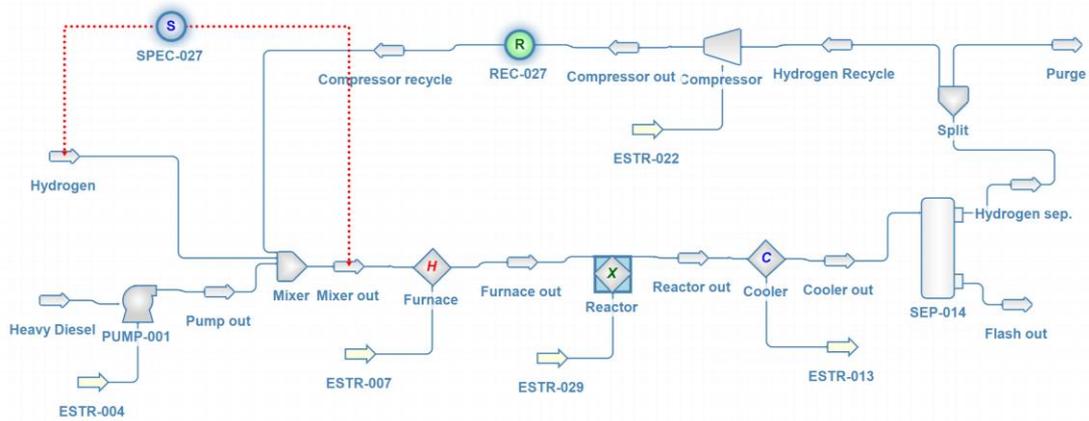
Figure 3: Hydrotreatment process with recycle of hydrogen.

Table 7: Pre-reactor fluxes furnace for heating reaction.

Compound	Flux[kg/h]
Methane (CH_4)	312.69
Oxygen (O_2)	1123.57
CO	222.58
CO_2	510.12
H_2O	703.55
T_1 [K]	298.15
T_2 [K]	680.00

It should be stressed that the methane enter initially with a temperature of 298 K, while the combustion gases from the outlet stream had a temperature of 680 K. The outlet temperature from the gases in relation with the final temperature of the oil crude present a delta of temperature of 22 K with the purpose of allow the temperature exchange.

Conclusions

Nowadays, one of the main utilities in the industry is the software use to model and simulate processes, who involve chemical and physical systems. Reason why, different software had been developed to fulfil the requirements and decrease the calculus time to design an equipment. One of these utilities is the Open Source DWSIM which was used to predict the behavior of a Diesel stream applied for a hydrotreatment process.

The main inlet stream was obtained from a previous process of distillation and was characterized as a heavy Diesel stream with a content of 3.44% weight of sulfur, without the presence of heavy metals. Reason why, the oil crude was subdued to a hydrodesulfurization process to decrease the sulfur content to 0.0093%.

It was developed a hydrogen separation system in order to reuse the no reactant part of hydrogen in the reactor. It was achieved using a cooler to refrigerate the stream

until 310.93 K. Implementing the recirculation system, the conversion arises until 99.3%. In future works, it should be possible to design a separation system to remove the hydrogen sulfide from the final stream.

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