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Two stages light gasoil hydrotreating for low sulfur diesel production

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Abstract

In order to study the possibility for production of ultra low sulfur diesel in existent industrial plants, different tests of hydrotreating was developed in plant pilot. Hydrotreating of light gasoil (LGO) in two stages using a commercial catalyst of Co–Mo supported in alumina was made. The LGO was fed twice trough the reactor at operating conditions of industrial plants. The operal conditions for each stage were: pressure 56 bar, LHSV 1.65 h^{-1}, H_2/HC ratio 56 m^3/Bl (hydrogen flow was once trough) and temperatures in the range of 613–653 K. Under the operation in two stages, the global LHSV of the plant decreases one-half.

The performance of the hydrodesulfurization, hydrodearomatization, hydrodenitrogenation and olefins saturation reactions were studied. The obtained results show high removals of pollutants at different operating conditions. Final products with up to 10 ppm of sulfur were obtained. In terms of industrial operation, these results indicate that it is necessary to diminish the space velocity to values of 0.82 h^{-1} with purification of make-up hydrogen to achieve the obtaining of ultra low sulfur diesel.

Keywords: Hydroconversion; Nitrogen; Sulfur; Olefin; Aromatic; Diesel

1. Introduction

The increasing demand of transportation fuels with ultra-low contents of contaminants is one of the largest challenges for petroleum refiners in the world. The world reserves of light crude oil are overcoming and heavier crude oil are being processed; therefore the hydroprocessing represents an even more important challenge [1].

Nowadays, the most of the hydrotreating plants in the world are able to produce diesel with 500 ppmw of total sulfur. The use of improved CoMo/Al_2O_3 catalysts together with the end boiling point fitting of the light gasoil (LGO) have allowed to achieve the diesel with lower sulfur content, less than 250 ppmw [2]. The revamping of existing plants with improvements in the reactor internals and the application of new generation catalysts has been offered as an emerge alternative for the actual refining industry requirements, to produce ultra low sulfur diesel with less than 100 ppmw of sulfur [3].

In order to reduce the diesel sulfur content at levels lower than 100 ppmw, the refiner must face the problem to remove sulfur atoms bounded in complex molecules (refractory compounds). It is well known that in light gasoil (LGO) with end boiling point (EBP) higher than 638 K, the quantity of these refractory compounds is increased, therefore the hydrotreating is not enough to achieve diesel product with content lower than 100 ppmw [4]. The refractory character of the alkyl dibenzothiophenes obeys to the steric constraint present in these molecules. The sulfur atom is surrounded by two aromatic rings and the alkyl groups sterically hinder the sulfur atom reactive. Several studies confirm the mechanism by which they are preferentially desulfurized is different [5]. It involves two different pathways: first the hydrogenation of the aromatic part of the molecule followed by a desulfuration step rather than the direct desulfurization of the sulfur atom (hydrogenolisis). The CoMo/Al_2O_3 promotes the direct desulfurization (hydrogenolisis) in comparison with hydrogenation reaction which is favored using NiMo/Al_2O_3 catalysts. However, when the dibenzothiophene molecule contains alkyl groups either in the 4 or 4 and 6 positions the access to the catalyst site becomes sterically hindered which arouses in the hydrodesulfurization reaction rate

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considerably drops and the sulfur content in the product hardly achieve the specification level.

The global reaction rate equation has been established in terms of the reaction rate from the direct desulfurization and the hydrogenation, respectively [6]. The changes of this global reaction rate are mainly influenced by reaction conditions and also from the content of species such as hydrogen sulfide, ammonia and other reaction products in the reaction mixture. Hence, an increasing of these by-products latter gives a decreasing in the reaction rate, since the concentration terms for these species is included in the denominator of the reaction rate expression. Based on these observations the way to maintain the reaction rate level is either to purify the recycle gas (including the hydrogen make-up) and/or using a multistage hydrotreating reactor, i.e. to decrease the space velocity (LHSV). This scheme provides two advantages: the removing of the by-products using pure hydrogen in the make-up gas and to increase the contact time with the active sites of the catalyst.

Although this approach has been already performed, the main goal of this work is to study in detail, the hydroconversion of the refractory species content in the diesel fuel. Another important feature to include is intent to explain how the reaction conditions affect the sulfur compounds conversion. Thus, the results allow us to suggest some recommendations for the combination of the reaction conditions in each stage in order to achieve the required sulfur contents in the products.

In the experiments we have performed, the feedstock passes twice through the catalytic bed (stages) using pure hydrogen make-up gas at the inlet of each bed. The liquid product from the first stage was stabilized in order to reduce the presence of H_2S at the minimum. Then, for the first stage the "easy" sulfur compounds are removed whereas in the second stage the "hard" sulfur compounds are hydrotreated in better conditions. The reactor LHSV and the active sites competitors decrease allowed an easy access of hindered sulfur atoms from alkyl dibenzothiophenes to the active sites of the catalyst.

2. Experimental

2.1. Pilot plant

The experimental program was performed in a hydrotreating pilot plant (Fig. 1). The set up is provided by automatic control (including valves and mass flow rate controllers), in order to get a reliable operation as well as experimental data. The reactor was manufactured with stainless steel and operates in an isothermal mode. Three independent electric heating units are used to control the temperature of the reactor (Fig. 2). One heating unit is located at the top of the reactor, where the hydrogen and hydrocarbon feed can reach the reaction temperature. This zone is packed with inert material. The second zone includes the catalytic bed, here temperature is carefully controlled. The third zone correlate to the reactor outlet and it is also packed with inert material. A positive displacement pump and a balance (BA-1) is used to feed and register the amount of the liquid hydrocarbon feedstock. The hydrogen flow rate is controlled and measured with an electronic mass flow control. The hydrogen and the liquid feedstock are mixed before go into the reactor. Once the mixture reacts, the effluent is cooled in a heat exchanger and separated in a high pressure flash tank. The liquid product is flashed at room conditions. The light gases in the liquid, are mixed with the sour gas produced from the first separation and are analyzed

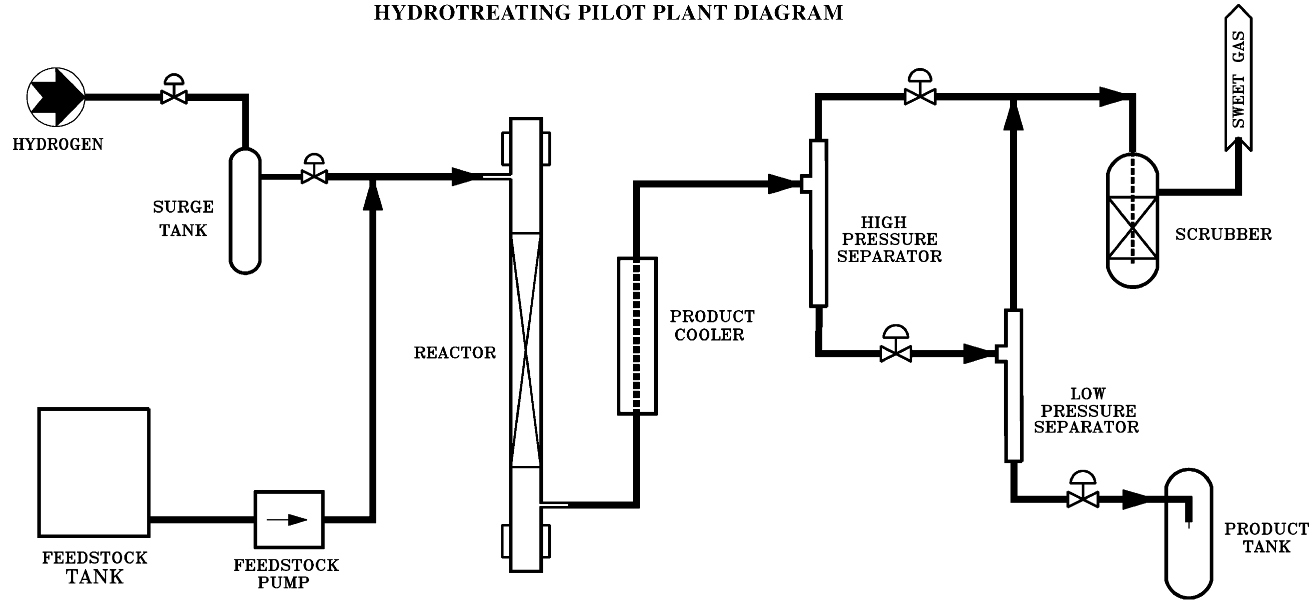

Fig. 1. Diagram of pilot plant.

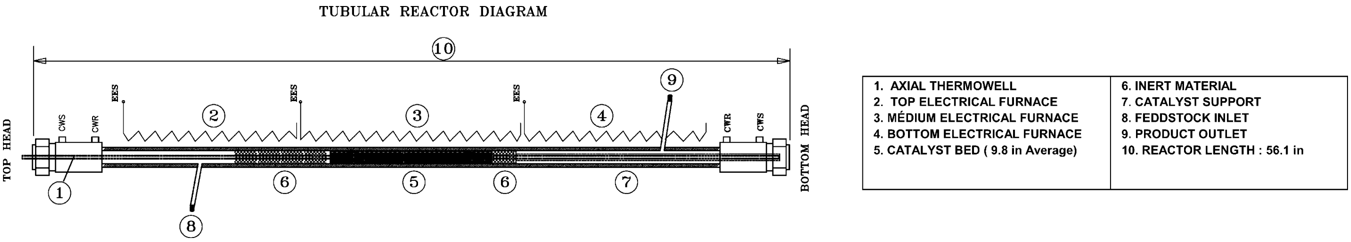

Fig. 2. Diagram of tubular reactor: (1) axial thermowell; (2) top electrical furnace; (3) medium electrical furnace; (4) bottom electrical furnace; (5) catalyst bed (249 mm in average); (6) inert material; (7) catalyst support; (8) feedstock inlet; (9) product outlet; (10) reactor length: 1425 mm.

on-line in a GC HP 5398 to quantify the H_2, H_2S and light hydrocarbons (C_1–C_5). Thereafter they are scrubbed in a sodium hydroxide solution to remove the H_2S. The liquid product is recovered in a tank and analyzed off-line.

2.2. Catalyst

A typical HDS commercial CoMo/Al_2O_3 IMP catalyst containing 14.7 wt.% MoO_3 and 3 wt.% CoO and previously sulfide catalyst was used for the experimental program. The physical properties are: surface area of 238 m^2/g; pore volume of 0.53 cm^3/g. Due this catalyst was already sulfide, it contains 11.89 wt.% of carbon and 10.44 wt.% of sulfur in sulfide oxide form.

Several activities related to the catalyst conditioning were performed during the experimental program: catalysts loading, activation, stabilization and operation. A detail description of these activities is presented as follows.

2.3. Catalyst loading

The catalyst is uniformly loaded and distributed at the central area of the reactor in order to have a homogeneous catalytic bed. A scheme of the catalytic bed is shown in Fig. 2. It can be observed in Fig. 2 that the axial thermocouple length goes from the top to the bottom of the reactor, in order to control carefully the temperature in the catalytic bed. In order to have a reliable flow distribution and temperature profile inside the reactor, the catalyst was crushed to a size between 1.0–1.4 mm and 100 g were diluted with α-Al_2O_3 [7]. Before starting up the set up, reaction section was checked so as to avoid leaks. Nitrogen was introduced until the pressure system reached 67 bar.

2.4. Catalyst activation

The catalyst used in this study was previously sulfide by CRI Company. Nevertheless, during the activation step (transformation of sulfide oxide to metallic sulfide) an additional quantity of sulfur was added to assure the total activation of the catalyst. The activation was made in liquid phase using straight run naphtha doped with a sulfiding agent such as CS_2. This procedure is widely used in our pilot plant set ups and assures that the catalyst is completely activated. The detailed procedure considers the following activities. The pressure in the system is fitted at 56 bar with a hydrogen flow rate matching a GHSV of 1230 h^{-1}. The sulfiding tank is filled with straight run naphtha contaminated with CS_2 (0.5 wt.% of total sulfur content). Therefore, the straight run naphtha doped with CS_2 is feeding into the reactor at a LHSV of 3.3 h^{-1}. Then an increasing of the reactor temperature from ambient to 503 K, at 25 h^{-1} rate. Continuing with adjusting the hydrogen flow rate to reach an H_2/HC ratio equal to 52 m^3/Bl in the reactor. The sulfiding conditions are maintained for 8 h. During the activation stage the temperature must be constant. Once the activation procedure was ended, the record of the different process variables, including H_2S content in sour gas is started.

2.5. Stabilization of the operation

This stage is carried out in order to assure that the catalyst is completely activated and the set up is operating in steady state. The stabilization time accounts for 36 h in total. After this period the experimental reaction conditions are established (see Table 1). The feedstock is changed from doped naphtha into LGO, fitting the LHSV at a value of 1.5 h^{-1} and increasing the reactor temperature at 613 K. The sulfur content in the product is quantified either three times every 12 h or to get a constant value. This procedure allows to obtain a reliable set up operation as well as experimental data. Feedstock properties are shown in Table 2.

2.6. Feedstock and products characterization

During the set up operation, several liquid product samples were collected to be characterized. The following analysis and the respective methods were practiced: content of sulfur (ASTM D-4294-90), total nitrogen (ASTM D-

Table 1
Operating conditions

Feedstock	LGO
Sulfur feedstock (wt.%)	1.4255
Pressure (bar)	56
H_2/HC ratio[a] (m^3/Bl)	52
LHSV[b] (h^{-1})	1.5
Temperature (K)	613–653

[a] Hydrogen flow is once through.

[b] Catalyst volume = 116 ml.

Table 2
Physical properties of feedstock

Specific weight (293/277)	0.8614
ASTM-D-86 (K)	
IBP	471
5%	505
10%	519
20%	534
30%	545
40%	556
50%	567
60%	578
70%	590
80%	605
90%	614
95%	643
FBP	656

4629-91), aromatics (ASTM D-1319) as well as the determinations of specific gravity (ASTM D-4052), the temperature distribution (distillation) (ASTM D-86) and the bromine number (ASTM D-11319). The content of different sulfur and aromatic compounds were determined by ASTM D-5326 and ASTM D-5186, respectively.

2.7. Description of the experiment

Based on the industrial plant operation for the LGO hydrotreating, the set up reaction conditions were selected (see Table 1). It can be observed that the hydroconversion is carried out modifying the temperature.

The experimental program for the first stage starts at 613 K during 24 h. Every 8 h the sour and light gases are analyzed, together with the collection of a liquid product sample to be entirely analysed. The mass balance for the set up was performed with same periodicity. At the end of this point, the temperature is increased from 613 to 628 K and the same activities are repeated. The experimental work of the first stage finishes when the temperature in the reactor reaches 653 K. Thereafter the reactor temperature is decreased at 613 K using fresh feedstock (time on stream 152 h). The hydrotreating set up was running at this temperature in order to take into account the catalyst deactivation (check back point). The operation of the second stage starts using as feedstock, the stabilized products from the first stage. The operation of this second stage continues similarly as first stage with increments of temperature until reach 653 K. Finally, an additional operating point at 613 K (“third stage”) using as feedstock, stabilized product from the second stage at 613 K was run.

3. Results and discussion

The hydrotreated products were also characterized considering the reaction conditions (Table 1) and the experimental program mentioned above. Firstly, the analysis of the specific gravity shows that this parameter is decreasing as the severity of the operation is increased. The specific gravity behavior for the two stages is shown in Fig. 3. The removing of the heteroatoms and the addition of hydrogen to unsaturated hydrocarbons produces molecules with lower density than the feedstock. The initial boiling temperatures (IBP) for the different products were fitted according to the properties of the feedstock in the range from 513 to 519 K. In the same way the final boiling temperature range (FBP) is also in correspondence with that of the feedstock, therefore the values are close to 653 K. All the samples used in the experimentation had shown the typical boiling temperature at 70% of distilled volume (315 K)

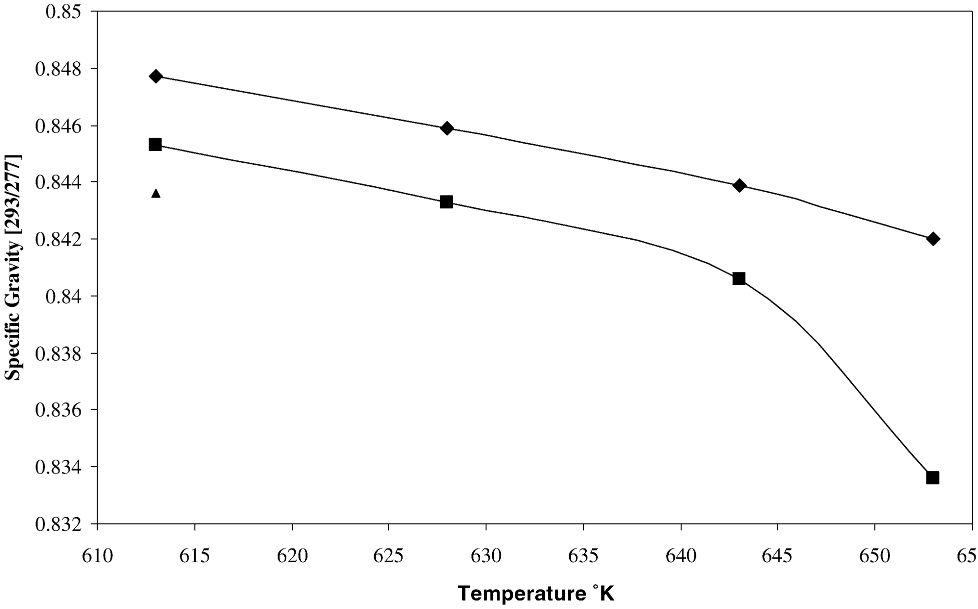

Fig. 3. Effect of hydrotreating on products specific gravity: (◆) first stage products; (■) second stage products; (▲) third stage product.

which makes a feedstock candidate to be hydrotreated. Hence, the feedstock with this characteristic requires an LHSV of 2 h^{-1} maximum, to be hydrotreated with a CoMo commercial catalyst [8].

The catalyst performance was measured as the ability to removal sulfur and nitrogen and the saturation of aromatic and olefin (these latter measured as bromine number). The values were calculated taking into account the liquid yield, which always was higher than 93 wt.% for both stages hydrotreating. For the first stage and check back point, yields were calculated based on the fresh feedstock flow rate, while for the second stage, they were calculated based on the feedstock flow rate for each experimental point.

3.1. Hydrodesulfurization (HDS)

Fig. 4 shows the results of sulfur removal measured as weight percent of hydrodesulfurization. During the period of stabilization an almost sulfur constant conversion is observed. This assures that the catalyst is completely activated and in steady operation. The results of operation in the first stage show high sulfur removal, up to 99.28 wt.% at 653 K. The check back point at 613 K corresponds properly with the ones getting at the beginning of the evaluation (94.82 and 94.84% of HDS, time on stream 56 and 152 h, respectively); indicating that deactivation in catalyst is negligible. From here, the data from the second stage show lower sulfur conversion. This decrease in conversion reaches a minimum at 628 K (58.8 wt.% HDS). This behavior results of different feedstock used for each temperature level on the second stage. At 613 K, the second stage feedstock (product from the first stage) has higher sulfur concentration (736 ppm), therefore, the HDS conversion corresponding to the second stage is higher (71.4). On the other hand, at 628 K, the feedstock to the second stage has 332 ppm of sulfur (less than one half of the sulfur content measured at 613 K), thus the HDS conversion in the second stage is lower at 628 K (58.7). The activity for this reaction is recovered at 643 K and higher temperatures with maximum values of 90.2 wt.% HDS at 653 K. If the activity remains constant (deactivation negligible) then this behavior is consequence of lower content of sulfur in feed. In general, the conversions of sulfur in the second stage are lower to those measured in the first stage. Besides, the remainder molecules in the products from the first stage are more difficult to remove that those in the fresh feedstock, diminishing the removal level in second stage (Table 3). The last point of operation at 613 K (“third stage”, time on stream of 212 h) also shows a very high activity toward HDS reaction (91.6 wt.%). In spite of lower operation severity (temperature) of hydrotreating at this (third) stage, the obtained product has very low sulfur content (62 ppm).

Table 3 shows the contents of the different sulfur compounds in feedstock and products. The feedstock shows the presence of great variety of species that go from the slight and simple as the disulfide, going through naphtothyophenes and alkyl benzothyophenes to the more complex as the alkyl dibenzothyophenes. There is an important amount of dimethyl naphtothyophenes remaining from: (a) its high concentration in feed and (b) as by product of the hydrogenation route of HDS reaction of more complicated species [9]. The products from the first stage do not contain any kind of compounds between disulfides and benzothyophenes and dibenzothyophenes. They are easily removed by the direct HDS mechanism on catalyst active sites. Only the more complex species as alkyl dibenzothyophenes enter to hydrotreating in the second stage. Some of them even remain in the products of the second stage. For the second stage at 653 K the main remaining species is 4,6-

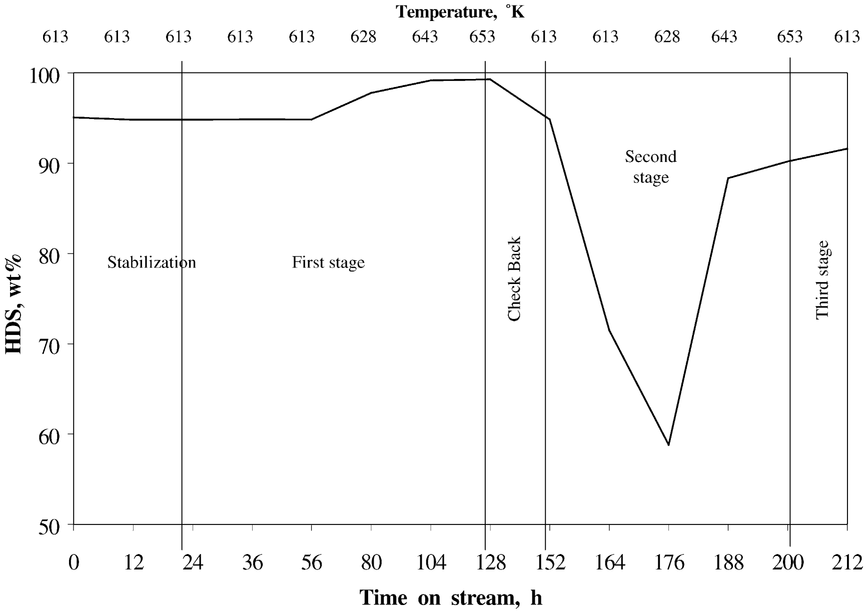

Fig. 4. Catalytic activity for HDS reaction.

Table 3
Sulfur species contained in feedstock and products

Compound (ppmw)	Feedstock	First stage				Check back, 613 K	Second stage				Third stage
		613 K	628 K	643 K	653 K		613 K	628 K	643 K	653 K	613 K
Lights	160	89	28	20	23	81	27	26	0	0	17
n-Butyl disulfide	86	0	0	0	0	1	0	0	0	0	0
Naphtothyophene	224	5	1	0	0	3	0	0	0	0	0
Methyl naphtothyophenes	248	6	1	0	0	9	0	0	0	0	0
Dimethyl naphtothyophenes	100	30	11	2	2	28	7	4	0	0	0
Benzothyophene	56	0	0	0	0	0	0	0	0	0	0
Methyl benzothyophenes	1073	0	0	0	0	0	0	0	0	0	0
Ethyl benzothyophenes	195	0	0	0	0	0	0	0	0	0	0
Dimethyl benzothyophenes	863	0	0	0	0	0	0	0	0	0	0
Propil benzothyophenes	165	0	0	0	0	0	0	0	0	0	0
Ethyl methyl benzothyophenes	417	0	0	0	0	0	0	0	0	0	0
Trimethyl benzothyophenes	1066	0	0	0	0	0	0	0	0	0	0
Butil benzothyophenes	365	0	0	0	0	0	0	0	0	0	0
Ethyl dimethyl Benzothyophenes	221	0	0	0	0	0	0	0	0	0	0
Diethyl benzothyophenes	188	0	0	0	0	0	0	0	0	0	0
Methyl propil benzothyophenes	48	0	0	0	0	0	0	0	0	0	0
Tetramethyl benzothyophenes	261	0	0	0	0	0	0	0	0	0	0
$C_5 + C_6$ benzothyophenes	955	0	0	0	0	0	0	0	0	0	0
Dibenzothyophenes	399	0	0	0	0	0	0	0	0	0	0
4,6-Dimethyl dibenzothyophenes	257	127	86	20	22	143	54	32	6	4	16
Methyl dibenzothyophenes	812	67	30	10	8	66	8	5	0	0	0
Dimethyl dibenzothyophenes	741	98	38	4	4	99	24	10	4	3	7
Ethyl methyl dibenzothyophenes	67	51	26	9	9	48	13	7	2	1	6
Trimethyl dibenzothyophenes	553	130	58	22	21	135	44	23	2	2	11
Ethyl dibenzothyophene	187	16	4	3	2	10	3	1	0	0	0
Butil dibenzothyophene	194	10	1	0	0	9	4	2	0	0	0
Heavy compounds	955	58	23	7	5	57	15	12	1	0	2
Unknown	3399	49	25	9	6	50	12	9	0	0	3
Total	14255	736	332	106	102	739	211	131	14	10	62

dimethyl dibenzothyophene (four of the 10 ppm of total sulfur contained in this product). The product of the ‘‘third stage’’ at low severity (613 K) has a conversion relatively high of 4,6-dimethyl dibenzothyophene. The contents in feedstock are 257 ppm and decreases after the first stage to 127 ppm and in the third stage become as low as 16 ppm, conversions of the 50.6 and 87 wt.%, respectively. This result confirms that the removal of these compounds is highly depending on effects of steric hindrance [10]. In this case, two factors can be considered. On the one hand, the contact time rises, as result of three stages of treatment. On the other hand, there is a lower competition for the active sites since the hydrotreating on stages occurs with flow of hydrogen with high purity. The combination between the increment of the temperature and the decrease of the space velocity produces the highest levels of pollutants removal.

The contents of sulfur in the product always show a descending tendency (Table 3). It is possible to decrease down to 10 ppm at 653 K reactor temperature in a second treatment stage.

In summary, by means of LGO hydrotreating it is possible to obtain products with down to 10 ppm of sulfur in hydrotreated products at 653 K in two stages. It is necessary to diminish the space velocity of the hydrotreating plant to 0.85 h^{-1}. The minimum value of content of sulfur achieved with the hydrotreating in three stages at low severity (613 K) is 62 ppm. This result agrees with those obtained by Cooper and Knudsen [11], in terms of relative reactor volume required to meet different levels of sulfur in diesel. They found that at 54 bar pressure at constant temperature, the relative increase in reactor volume is 1.7 times to go from 500 to 50 ppm of sulfur in product. The volume increase by 2.56 times when try to decrease the sulfur in product to 10 ppm. The obtained results would allow us to suggest different treatment outlines. For example, operate a first stage at low severity (temperature) and the second stage at higher severity in order to reach best results in an economic way.

Obtained results show that two mechanisms for sulfur removal are involved. On one hand, for low molecular weight species, HDS proceeds by direct extraction or hydrogenolysis. For complex molecules as dibenzothyiophenes, sulfur removal took place according to the hydrogenation route. Hydrogenation route has shown progress preferably for dibenzothyophenes desulfurization. The hydrogenation of one of the aromatic rings results in a no longer planar molecule, allowed access to the sulfur atom easier to extraction [12].

3.2. *Hydrodearomatization (HDA)*

The hydrodearomatization results and other reactions were evaluated in the range of 613–653 K, there were no data recovered during the stabilization step.

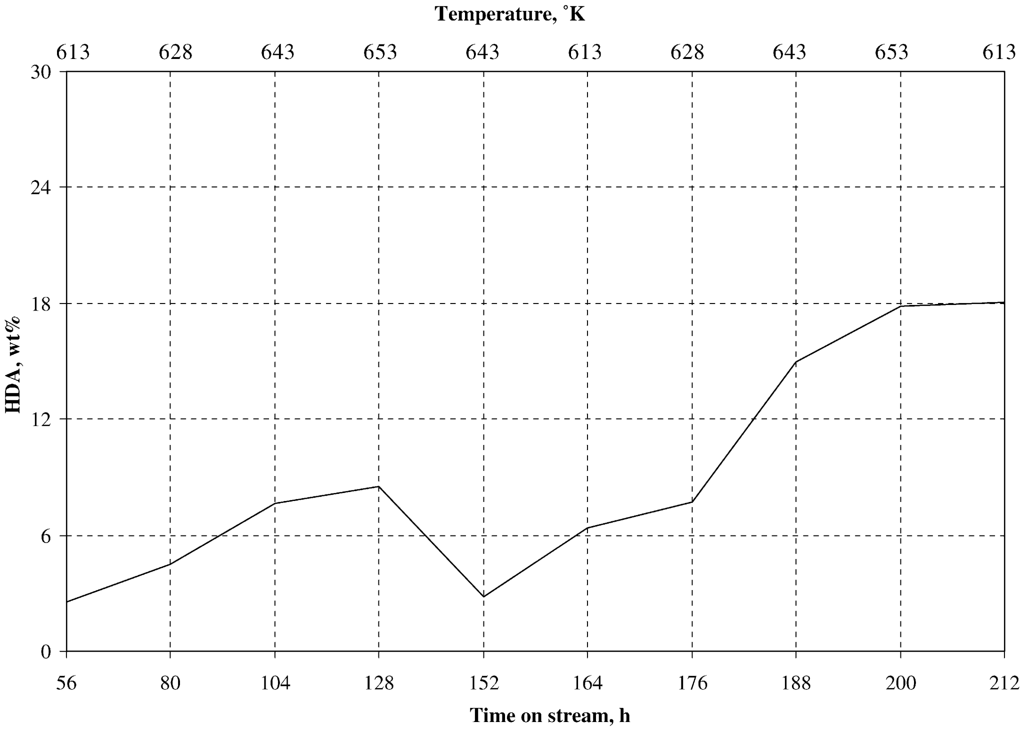

Fig. 5. Catalytic activity for HDA reaction.

Fig. 5 shows the HDA (total aromatics) reaction behavior as a function of time on stream and reaction temperature. The HDA reaction shows a behavior different respecting to HDS reaction. During the first stage, the maximum removal of total aromatics is 7.6 wt.%. For the second stage, the maximum removal is 18.9 wt.%. HDA reaction conversions increase in the second stage. This effect is result of the lower concentration of sulfur in the feedstock to the second stage. That means that exist less competition between HDS and HDA reactions for the active sites of the catalysts. The effect of nitrogen removal is negligible, because its concentration is very low. Besides, active sites of the catalyst where HDS and HDA reactions take place are different respecting those where HDN reaction takes place. For these reasons, the inhibition effect of HDN reaction is lower than HDS or HDA reactions [13].

The contents of total aromatics in the products always diminish respect to temperature increase. This means that our experimentation was carried out always in the kinetic controlled region [14].

Fig. 6 shows the contents of several types of aromatics in the products as a function of time on stream. It is observed that concentrations of mono, di, poli, and total aromatics are always decreasing when increasing the reactor temperature. The decrease in the total aromatic quantity is near to 8.8 wt.%. The aromatic compounds hydrogenation happens from the more complex to the easier molecules, the poli aromatics are saturated to di aromatics and these later to mono aromatics, so the concentration of them is almost constant during the evaluation [15]. Girgis and Gates [16] have proposed with model compounds that naphthalenes and substituted naphthalenes are an order of magnitude more reactive than benzene and substituted benzenes. The rate of hydrogenation of aromatic species increases with the number of aromatic rings. [17]. It is partly due to the low reactivity of the aromatic compounds, due resonance stabilization of the conjugated system and partly due to equilibrium constraints at the pressures and temperatures used [18]. In some experimental data, mono aromatics concentration is higher even than their initial content in feedstock. In the second stage, the aromatic species decreases severely and continues the same sequence of the first stage.

3.3. Hydrodenitrogenation (HDN)

The results of HDN reaction are shown in Fig. 7. HDN and HDS reactions are very sensitive to reaction temperature [14]. For the first stage, it is observed a very high activity for HDN reaction mainly in the range of 613–643 K in which the nitrogen removal goes from 77 up to 97 wt.%. At 653 K, the nitrogen removal is almost total and reaches a value of 99 wt.% (3 ppm nitrogen in product). Increasing temperature from 643 to 653 K only increases in 2% the level of nitrogen removal. In general, the levels of HDN are high in the first operation stage. For the second stage, the conversion of HDN is lower. This phenomenon can be explained because almost the complete removal of nitrogen compounds in the first stage. The concentration of nitrogen in products in one stage is 82 and 3 ppm for 613 and 653 K, respectively. Experimentation made with heavy and light feedstock containing different content of nitrogen com-

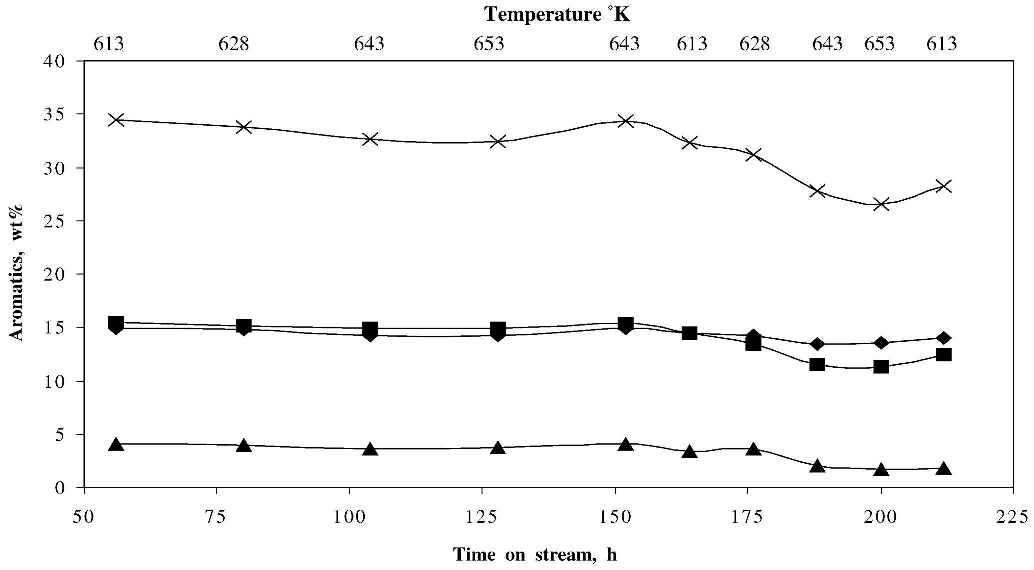

Fig. 6. Removal of different species of aromatics: (×) total aromatics; (◆) mono aromatics; (■) di aromatics; (▲) poli aromatics.

pounds, has exposed that heavier feedstock has higher conversion in the second stage. In spite of the above-mentioned, the nitrogen content in the final product (products of the second stage) is very similar.

3.4. Olefins saturation (OS)

The olefins content, measured indirectly by bromine number of hydrotreated products is shown in Fig. 8. The bromine number decreases as a function of reactor temperature. For one stage, the lowest value obtained was 0.31 mgBr/100 g (approximately equal to 0.7–0.85 wt.% olefins). For two stages, the value of bromine number is 0.28 mgBr/100 g. Comparing both operation stages, single and two, it shows a relatively small decrease of the bromine number and therefore in the olefins content. The differences in bromine number at the same temperature in the two stages, become smaller as the temperature increases. At 613 K, the difference is 0.28 while at 653 K; the difference becomes only 0.03 mgBr/100 g. These results seem to show that exists a competition with other reactions in the process. Besides, it is possible to produce olefins from molecules that contain mainly sulfur and nitrogen, benzo and dibenzothyophenes. It has settled that HDS of thyophene occurs by the

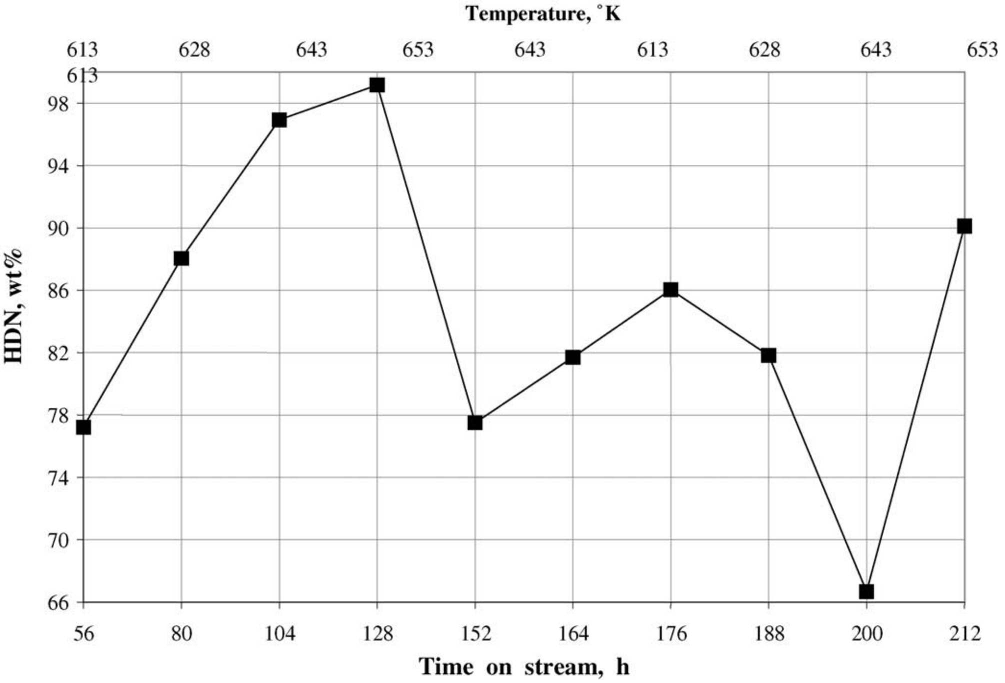

Fig. 7. Catalytic activity for HDN reaction.

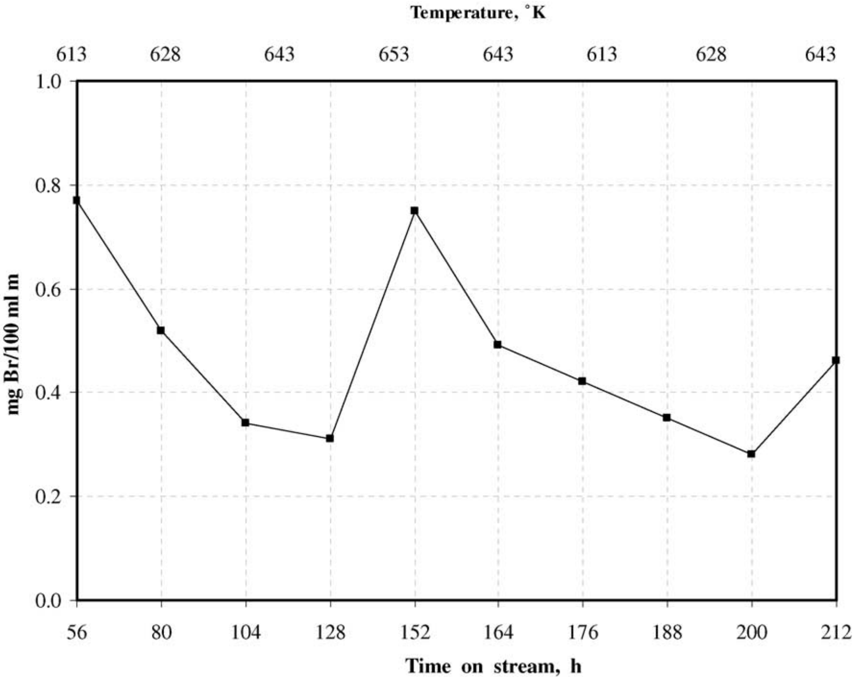

Fig. 8. Bromine number of hydrotreated products as a function of time on stream.

butadiene and butene formation as intermediate products [10]. The HDS of dibenzothyophenes also occurs through the hydrogenation route of the aromatics rings. Therefore, some of the intermediate products are olefins which can contribute to the obtained results.

The behavior of the catalytic activity for different studied reactions shows different profiles. For HDS and HDN reactions, the conversions in the second stage are lower with respect the first stage, mostly due to the previous elimination of the molecules ‘‘easy’’ to remove. For the second stage, the conversion diminishes due the remaining molecules in product are strongly refractory to be hydrotreated. For the removal reactions of aromatic (HDA), the conversion in the second stage is higher than in the first one. This is explained because this reaction proceeds in cascade. Poli aromatics are hydrogenated first to become species di and mono aromatics. The reaction of olefins saturation on the other hand, reaches similar values of conversion in each one of the stages. The olefin contents in the products of the second stage are only lightly lower to those measured in first stage products.

According to Kundsen et al., the effect on catalyst activity of process variables like LHSV, temperature, hydrogen partial pressure, hydrogen sulfide partial pressure, and gas/oil ratio can be predicted by a suitable kinetic expression. It was found that the expression shown below could be used to describe the kinetics on CoMo and NiMo catalysts for deep hydrodesulfurization of diesel [6].

$$-\frac{dC_s}{dt} = \frac{k_D C_s^n P_{H_2}^{\alpha}}{1 + K_{H_2S} P_{H_2S}} + \frac{k_H C_s^m P_{H_2}^{\beta}}{1 + K_F C_F} \qquad (1)$$

We can analyze the experimental results for each one of variables according to Eq. (1).

The effect of reaction temperature in rate constant k_D predicts an increment in reaction rate. This is supported because our experiments were done in the kinetic controlled region. The calculated values of k_D are in the range of 0.043–1.73 ppm$^{-0.5}$ h^{-1} from 613 to 653 K, considering a reaction order of 1.5. The value of k_D at 653 K is 40 times the observed value at 613 K. This data explain why we obtained high sulfur removal conversion at high temperatures.

Other variable that influence favorably the increasing in reaction rate is the sulfur content in feedstock. If sulfur in feedstock is higher, the rate reaction is also higher. For this reason HDS conversion in one stage are higher than HDS conversion obtained in the second stage. Another important factor are the species of sulfur compounds in the feed. Data showed in Table 3 indicated that compounds in the feed to the second stage are considerable more refractive for hydrotreating than sulfur compounds in the feed to the first stage. However, we obtained high HDS conversion in the second stage. This is true because the catalyst activity remains constant and there is less competition of sulfur compounds to the active sites of the catalyst. For this reason, it was possible to obtain low sulfur products in the ‘‘third stage’’ even though the reactor temperature was relatively low (613 K).

An additional factor that favors the low sulfur in products is to use high purity hydrogen flow. There is no recirculation of hydrogen sulfide and ammonia to the reactor, which inhibits the hydrotreating reactions. Besides, the increasing in hydrogen partial pressure favors the pollutants removal.

4. Conclusions

By means of LGO hydrotreating it was possible to obtain products with down to 10 ppm of sulfur in hydrotreated products at 653 K in two stages. It was necessary to diminish the space velocity of a hydrotreating plant until values of $0.85\ h^{-1}$. The minimum value of content of sulfur achieved with hydrotreating in three stages at low severity (613 K) was 62 ppm. This means the diminution of LHSV of the plant down to $0.55\ h^{-1}$. Due to the above-mentioned, it was confirmed that esteric hindrance exists in the hydrotreating of dibenzothyophenes. The variation in the conversion of the different species can also be explained in terms of active sites competition. For the hydrodearomatization reaction, for example, it was possible to obtain higher conversion in the second stage even when the species to hydrotreat were more complex.

The species that remain in hydrotreated products at high temperature are 4,6-dimethyl dibenzothyophene and alkyl dibenzothyophenes, nevertheless they had high conversions in both first and second stages.

High removal of total aromatics was obtained. Poli aromatics compounds were saturated to naphtothyophenes, mono and di aromatics.

The highest conversion of nitrogen compound was obtained in the first stage. In the feedstock for the second stage, nitrogen compounds were almost complete removed specially at high temperatures.

The combination of results would allow us to suggest different treatment schemes at industrial level. For example, to operate two stages at different severity (temperature) in order to favor one or two different reactions: HDS, HDN, HDA or olefins saturation.

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