

An Exploratory Study for Obtaining Synthetic Crudes from Heavy Crude Oils via Hydrotreating

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In this work we present an experimental evaluation about the catalytic hydrotreating (HDT) of Maya heavy crude oil. The study was carried out in a high-pressure fixed bed pilot plant. The HDT reactions were conducted at 54–100 kg/cm² pressure, 0.5–1.5 h⁻¹ LHSV, 380–420 °C temperature, and 5000–10 000 ft³/bbl H₂/oil ratio using an experimental NiMo/Al₂O₃–TiO₂ catalyst. The data showed that API gravity and sulfur, nitrogen, Ramsbottom carbon, asphaltenes, and metals (Ni, V) contents can be improved by direct HDT of Maya crude oil. Values very similar to the Isthmus light crude oil properties were obtained at severe operating conditions. Naphtha, middle distillates, and FCC feedstock fractions yield obtained from TBP distillation of the synthetic crudes increase as the severity of the HDT was increased. Middle distillates showed the greatest yield increase.

Introduction

For various decades, traditional refining operations have been processing light crude oils containing low concentrations of heteroatoms and metals. Significant changes in the petroleum industry have occurred in the past 10 years which have forced changes in refinery operations. Worldwide refineries have undergone a lot of restructuring and revamping units due to changes in petroleum feed properties and demand of more and more environment-friendly products. Middle distillates are emerging as the world's most demanded products, whereas the trend in crude oil supply indicates a growing volume of heavy crudes. To meet this demand a substantial quantity of heavy crude oils has to be upgraded.^{1–3}

Since heavy crudes exhibit high contents of contaminants such as sulfur, nitrogen, metals, and asphaltenes, the refining processes are being modified technologically. A shift to heavier crude oils means that refineries are processing feedstocks with lower API gravity, lower hydrogen-to-carbon (H/C) ratio, and a higher content of sulfur and metals.

Heavier feedstocks produce higher yields of heavy products at a time when demand for such products has been decreasing. In addition, the sulfur content of these products is high.

In response to changing feedstocks and market conditions, the petroleum industry has moved to develop

viable processes which can convert the high-boiling fractions to more valuable products. The purpose of these upgrading processes is to reduce the sulfur and metals contents, reduce the molecular weight, and increase the H/C ratio.

The large molecular size and high heteroatom and metal contents of the constituents of heavy crude oils, which reduce overall reaction rates and decrease catalyst lifetime, present technical challenges for the development of process and catalytic systems.

State-of-the-Art

A wide range of technologies is available for converting residues to light liquids. Some processes include sufficient large-scale commercial experience to be regarded as well-established, mature processes. There are also processes which are in the early stages of commercial use, together with others which have been well tested at the demonstration scale.⁴

The hydrotreating of residues is difficult because of the complex nature of the heteroatom-bearing molecules. Residue HDT processes are strongly influenced by the nature of the catalysts used, the feed to be treated, and finally on the design of the reactors. In hydrotreating processes, catalysts are designed to remove heteroatoms, viz., sulfur, nitrogen, and metals.⁵

Sulfur and nitrogen escape out from the systems as gaseous products and the more refractory compounds remain in the liquid products, while metals get irreversibly deposited on the catalysts causing permanent deactivation.^{6–9}

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Residue HDT processes are also strongly influenced by the method of feed introduction, the arrangement of the catalyst beds, and the mode of operation of the reactors. Hence, proper selection and design of reactors are very important for this. Depending upon the nature of the residues to be treated, hydrotreating of residues are generally carried out in fixed bed, moving bed, or ebullated bed reactors. Sometimes a combination of different reactors is preferred.^{10,11}

In fixed bed reactors, the liquid hydrocarbon trickles down through the fixed catalyst bed from top to bottom of the reactor. Hydrogen gas passes cocurrently through the bed.

A single tailor-made optimum catalyst having high hydrodesulfurization activity and low metal tolerance can handle feedstocks having less than 25 wppm of metal for a cycle length of 1 year. For feedstocks containing metals in the range of 25–50 wppm, a dual catalyst system is more effective. In such a system, one catalyst having a higher metal tolerance is placed in the front of the reactor whereas the second catalyst located in the tail end of the reactor is generally of higher desulfurization activity.^{12,13}

Although an association of up to ten catalysts is claimed in the literature,¹⁴ a triple catalyst system consisting of a HDM, a balanced HDM/HDS, and a refining catalyst are generally used to handle a feedstock having metal content in the range of 100–150 wppm for an average cycle length of 1 year.

For feeds containing metals higher than this range, the HDM catalyst gets quickly exhausted and for getting a cycle length of 1 year, a new swing reactor fixed bed concept has been introduced by IFP. The process includes two swing fixed bed HDM reactors which operate in a switchable mode and the catalyst can be unloaded/reloaded without disturbing the operation of the system. The swing reactors are generally followed by various fixed bed reactors in series containing HDS and other hydrofining catalysts.

To overcome the problems of handling feeds having metal contents higher than 100–150 wppm, besides the concept of fixed bed swing reactors, another system (of moving bed reactor) involving continuous withdrawal of deactivated catalyst and simultaneous addition of fresh catalyst has been introduced.¹⁵

The development of Shell bunker reactor technology is an example of such a system. In this bunker reactor system, fresh catalyst and reacting fluids (both hydrocarbon and hydrogen) move in a cocurrent downflow mode and a special arrangement inside the reactor allows withdrawal of the spent catalyst from the bottom

Table 1. Maya Crude Oil Properties

properties	Maya crude oil	Isthmus crude oil
API gravity	20.99	33.3
sulfur, wt %	3.52	1.80
nitrogen, wppm	3006	1446
Ramsbottom carbon, wt %	11.01	4.23
asphaltenes in <i>n</i> C ₇ , wt %	11.2	3.06
Ni + V, wppm	318.9	99.7
TBP distillation, °C		
IBP	19	10
10 vol %	131	98
20 vol %	201	151
30 vol %	273	201
40 vol %	352	255
50 vol %	430	314
60 vol %	509	377
70 vol %		442
80 vol %		515
vol % distilled at 538 °C	62.5	82.7

of the reactor.¹³ In another design, as developed by Chevron, in their OCR technology, the catalyst moves in a downflow mode while the reacting fluid moves counter-currently from the bottom to the top of the reactor. A similar system has been designed by ASVAHL group but the technology is still at the developmental stage.⁴

In all these cases, a combination of moving bed followed by fixed bed system is used. The moving bed reactor containing the HDM catalyst is placed first which is followed by other fixed bed reactors containing HDS and hydrofining catalysts.

Another alternative for handling metal-rich feedstocks besides the use of swing guard fixed bed reactors and moving bed reactors is the use of ebullating bed reactors. Reactants are introduced at the bottom and product is taken out from the top. The catalyst bed is kept expanded by the upward flow of reactants. The spent catalyst is continuously withdrawn and fresh catalyst is added without disturbing the operation and thereby providing a high on-stream factor.

As can be seen, most of the literature related to the topic of the present work is about hydrotreating of heavy oil fractions, such as atmospheric and/or vacuum residua, and the direct hydrotreating of heavy crude oils has not received too much attention.

This type of research is rather scarce in the literature. For this reason, in this paper we explore this technological option in order to gain further knowledge about the process and catalytic systems.

Experimental Section

Materials. Maya crude oil was used as the feed for hydrotreating studies. Its physical and chemical properties are presented in Table 1. The properties of a light crude oil (Isthmus) are also included in this table as reference.

It can be observed from Table 1 that Maya crude oil is a representative heavy crude oil, since its sulfur, nitrogen, asphaltenes, and metals contents are high, 3.52, 0.30, 11.2, and 0.03 wt %, respectively, and its API gravity is quite low (20.99°).

A NiMo/Al₂O₃–TiO₂ experimental catalyst was used for pilot plant experiments. The catalyst properties are shown in Table 2. Pore size distribution of this catalyst is presented in Figure 1.

Pilot Plant Runs. Experiments were carried out under steady-state operation in a fixed bed high-pressure pilot plant

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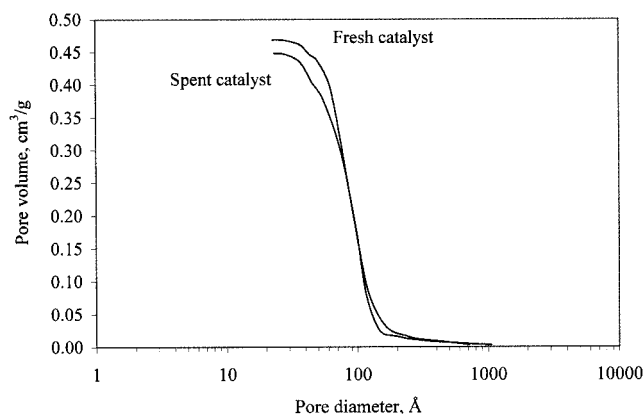


Figure 1. Pore size distribution of fresh and spent catalysts. containing 100 mL of catalyst. A schematic flow diagram of the experimental unit is shown in Figure 2.

The isothermal reactor is designed as a tube with an inside diameter of 2.54 cm and a total length of 143 cm (Figure 3).

The length of the reactor is subdivided in three sections. The first section was packed with inert particles and was used to heat the mixture to the desired reaction temperature and to provide a uniform feedstock distribution. The following section contained the HDT catalyst. The exit section was also packed with inert particles.

To achieve isothermal condition, 100 mL of catalyst was diluted with an equal volume of inert α -alumina, which was considered to be of negligible activity and did not contribute catalytically to the hydrotreating reactions. Such dilution improves the flow pattern by increasing the residence time distribution.

The weight of feed was measured before and after a mass balance period, converted to volume using feed density, and LHSV was calculated.

After loading the catalyst, the reactor pressure was increased from atmospheric to 130 kg/cm² in order to be sure of the airtightness of the system. This condition was kept during 2.5 h.

Table 2. Properties of the Experimental Catalyst

physical properties	fresh catalyst	spent catalyst
size, in.	1/10	1/10
diameter, mm	2.6	2.6
average length, mm	4.25	4.25
surface area, m ² /g	224	174
pore volume, cm ³ /g	0.48	0.44
bulk density, g/cm ³	0.81	
average pore diameter, Å	64	102
pore size distribution, vol %		
< 50 Å	6.8	12.8
50–100 Å	57.4	48.0
100–200 Å	32.4	34.6
200–500 Å	2.0	3.9
> 500 Å	1.4	0.7
chemical properties	fresh catalyst	spent catalyst
molybdenum, wt %	11.5	
nickel, wt %	2.9	
sodium, wt %	0.01	0.05
vanadium, wt %	0	1.75
iron, wt %	0	0.06
carbon, wt %	0	13.95

Once the reactor was verified to be hermetic, the reactor pressure was decreased to 54 kg/cm².

The temperature of the reactor was increased from ambient to 230 °C at a heating rate of 30 °C/h in the presence of hydrogen at a flow rate of 150 L/h.

The temperature of the reactor was increased to the desired reaction temperature and the feedstock and hydrogen were passed at the required rates.

The reactor temperature was maintained at the desired level by using a three-zone electric furnace, which provided an isothermal temperature along the active reactor section. The temperature profile was measured by a movable axial thermocouple located inside the reactor. The greatest deviation from the desired temperature value was about 5–7 °C as can be seen in Figure 4.

Presulfiding Conditions. The catalyst was in-situ activated by sulfiding with a hydrosulfurized naphtha (specific gravity of 0.752, <0.5 wppm sulfur and boiling range

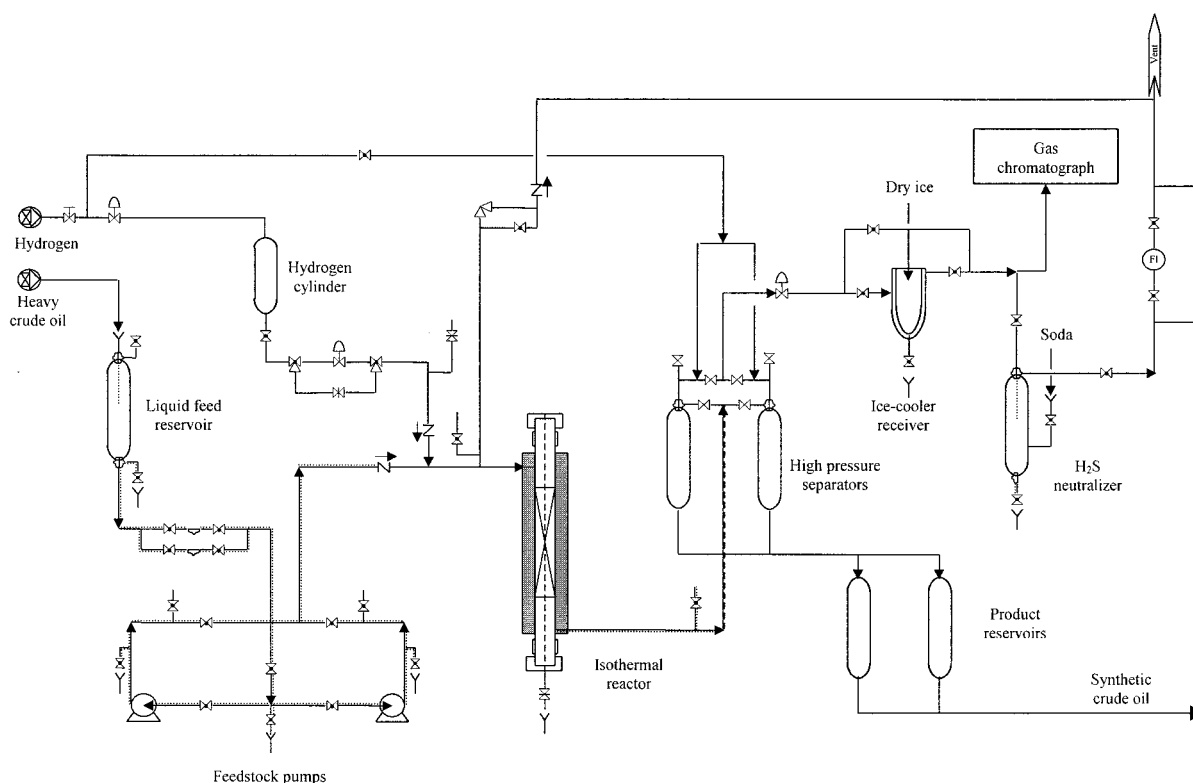


Figure 2. Hydrotreating pilot plant.

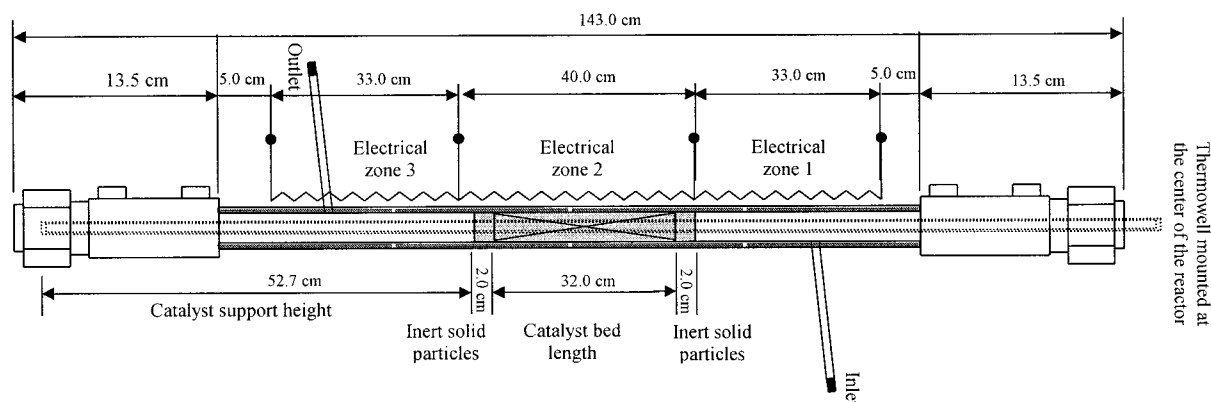


Figure 3. Pilot reactor.

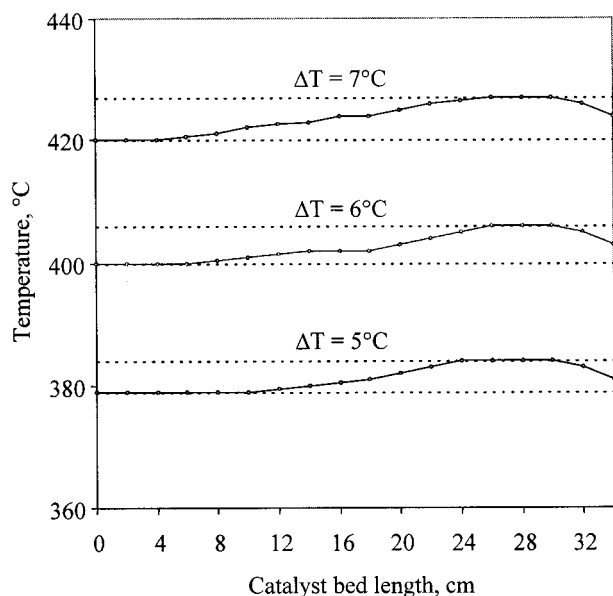


Figure 4. Typical temperature profiles during HDT experiments.

Table 3. Operating Conditions

pressure effect		
pressure, kg/cm ²	54, 75, and 100	
hydrogen-to-oil ratio, ft ³ /bbl	10 000	
LHSV, h ⁻¹	0.5	
LHSV effect		
LHSV, h ⁻¹	0.5, 1.0, and 1.5	
pressure, kg/cm ²	100	
hydrogen-to-oil ratio, ft ³ /bbl	10 000	
hydrogen-to-oil ratio effect		
hydrogen-to-oil ratio, ft ³ /bbl	5000, 7500, and 10 000	
LHSV, h ⁻¹	0.5	
pressure, kg/cm ²	100	

of 96–193 °C), containing 0.8 wt % CS₂ at the following operating conditions: pressure, 54 kg/cm²; H₂/oil ratio, 2000 ft³/bbl; temperature, 230 °C; LHSV, 3.2 h⁻¹.

The time for this test was 18 h in order to ensure complete catalyst presulfiding.

Operating Conditions in the Pilot Reactor. Reactor pressure, space-velocity (LHSV), and hydrogen-to-oil ratio effects were studied in the ranges reported in Table 3. Reaction temperature was varied in the range of 380–420 °C for each experiment.

The hydrotreating was conducted in once-through hydrogen in down-flow. The hydrogen was of 99.8% purity.

Product samples were collected at 4–8 h intervals after allowing a 2 h stabilization period under each set of conditions, and mass balances for each run were in the range 100 ± 5%.

2.5. Analysis of Products. Physical and chemical properties of the feed and products were determined with the following methods:

- API gravity: ASTM D-287
- total sulfur: ASTM D-4294
- total nitrogen: ASTM D-4629
- Ramsbottom carbon: ASTM D-524
- asphaltenes in *n*C₇: ASTM D-3279

Metals (Ni and V) were analyzed by atomic absorption (ASTM D-5863 method). TBP curve was determined by following the experimental distillation described in ASTM D-2892 method.

Results and Discussion

The hydrotreating experiments were focused on studying the effect of important process variables on the extent of heteroatoms and metals and asphaltenes removal from Maya crude oil.

The process parameters included reactor pressure, reaction temperature, space-velocity (LHSV), and hydrogen-to-oil ratio (H₂/oil), and they were selected to clearly define the effect of varying a particular process variable on heteroatoms removal. Each experiment was conducted by changing one variable at a time.

Effect of Reaction Pressure. A series of experiments was conducted to investigate the effect of pressure on the hydrotreating of the Maya crude oil. The reactor pressure was varied in the range of 54–100 kg/cm². Other conditions were 0.5 LHSV and 10 000 ft³/bbl. For each pressure, reaction temperature was studied at 380, 400, and 420 °C.

Experimental results for sulfur, nitrogen, metals, and asphaltenes removals are presented in Figure 5. It can be seen that as the pressure is increased from 54 to 100 kg/cm² the performance of the catalyst also increases significantly. The experimental data show that the increase in reactor pressure improved product quality.

Nitrogen removal was low at 54 and 70 kg/cm² for the three temperatures evaluated (HDN less than 20.2%); this is because this material is typically concentrated in the higher-boiling fractions, and its removal requires more severe conditions. At 100 kg/cm² the rate of HDN reaction increases substantially to values between 56 and 80%.

The most important reduction in sulfur, metals, and nitrogen contents was observed when reactor pressure was increased from 70 to 100 kg/cm². At the most severe pressure and temperature (100 kg/cm² and 420 °C), HDS, HDM, and HDN levels were 92.3, 27.4, and 79.6%,

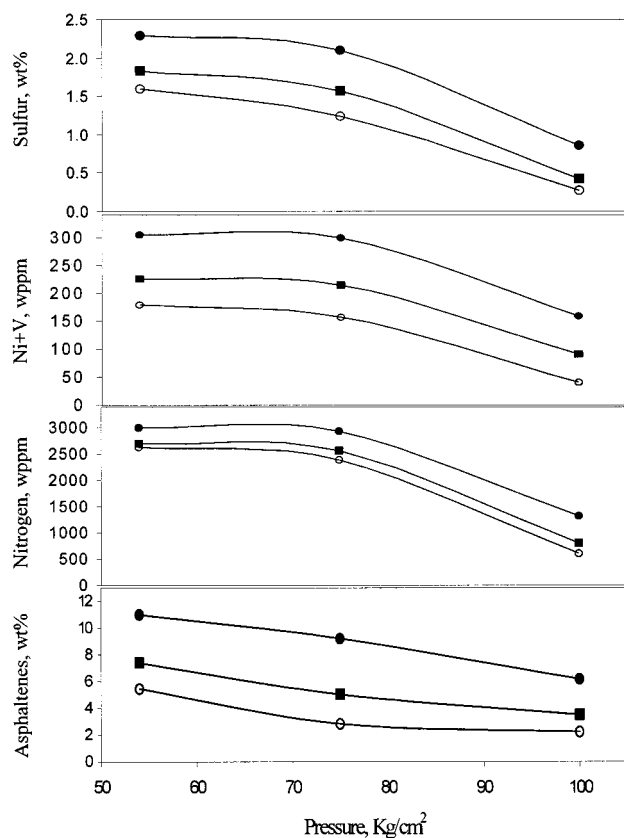


Figure 5. Effect of reactor pressure on sulfur, metals, nitrogen, and asphaltenes in synthetic crudes. (●) 380 °C, (■) 400 °C, (○) 420 °C.

respectively. The reason for this effect of pressure is considered to be that the higher the pressure the better is the contact between the hydrogen and hydrocarbons and the catalyst. However, very high pressures reduce the activity of the catalyst, owing to the adhesion of carbon to its surface.³

Asphaltenes content reduction showed a more or less linear behavior with respect to reactor pressure.

Effect of Space-Velocity. The effect of space-velocity (LHSV) was studied in the range of 0.5–1.5 h⁻¹. Other variables were kept at the following constant values: reactor pressure of 100 kg/cm² and hydrogen-to-oil ratio of 10 000 ft³/bbl. For each LHSV, reaction temperature was also varied in the range 380–420 °C.

Figure 6 illustrates the influence of LHSV on the degree of desulfurization, demetallization, denitrogenation, and asphaltenes removal. It is observed that all these reactions are significantly influenced by space-velocity.

The experimental data show that the decrease in LHSV resulted in improved product quality. The contaminants content of the synthetic crudes are approximately proportional to the LHSV and hence the contact time.

Effect of Hydrogen-to-Oil Ratio. The hydrogen-to-oil ratio was varied in the range 5000–10 000 ft³/bbl keeping the pressure and LHSV at constant values of 54 kg/cm² and 0.5 h⁻¹, respectively. For each H₂/oil ratio, reaction temperature was studied at 380, 400, and 420 °C.

Experimental results for sulfur, nitrogen, metals, and asphaltenes removals are presented in Figure 7. The

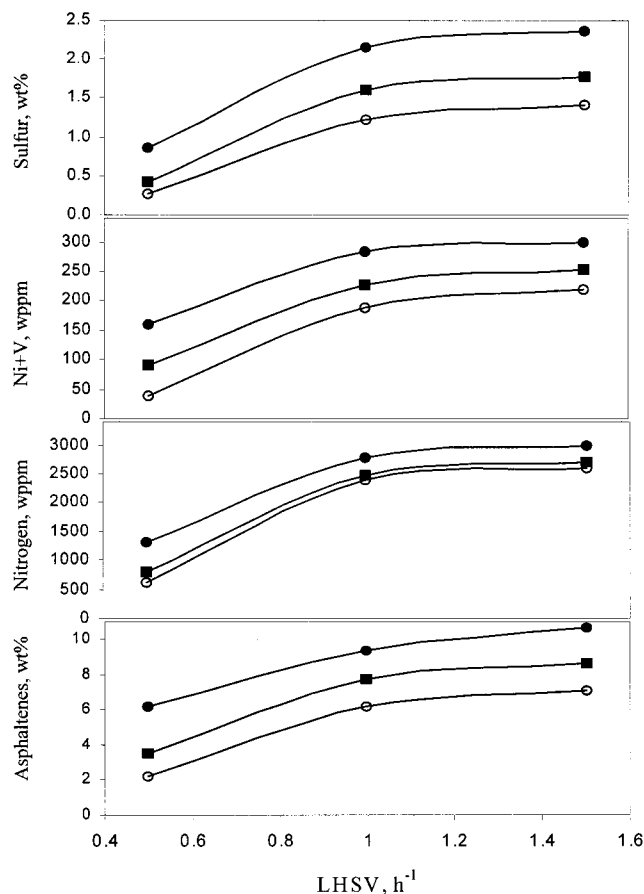


Figure 6. Effect of space-velocity on sulfur, metals, nitrogen, and asphaltenes in synthetic crudes. (●) 380 °C, (■) 400 °C, (○) 420 °C.

H₂/oil ratio has a marked influence on Maya crude oil hydrotreating. The effect is more pronounced as this ratio is increased from 7500 to 10 000 ft³/bbl.

The HDS, HDM, and asphaltenes reduction observed with the increase of this process variable from 5000 to 10 000 ft³/bbl, were in general higher than those obtained when reactor pressure and space-velocity were increased from 54 to 100 kg/cm² and from 0.5 to 1.5 h⁻¹, respectively. Hydrodenitrogenation was very similar when all the variables were changed in the ranges shown in Table 3.

Effect of Reaction Temperature. The effect of reaction temperature on synthetic crudes quality was studied between 380 and 420 °C, and the other variables were modified in the ranges shown in Table 3.

The experimental results presented in Figures 5–7 show that the product quality is improved when the temperature is increased. It means a decrease in sulfur, nitrogen, metals, and asphaltenes contents.

A lower effect of the reaction temperature was observed in HDN reaction compared to other reactions. In general, the temperature effect was higher when this variable was varied from 380 to 400 °C compared to the change from 400 to 420 °C.

Effect of Operating Conditions on Crude Oil Properties and Yields. The results of the presents studies reveal that direct hydrotreating of Maya crude oil is considerably influenced by reaction conditions. Figure 8 shows the relationship between API gravity and sulfur content of the synthetic crudes obtained at

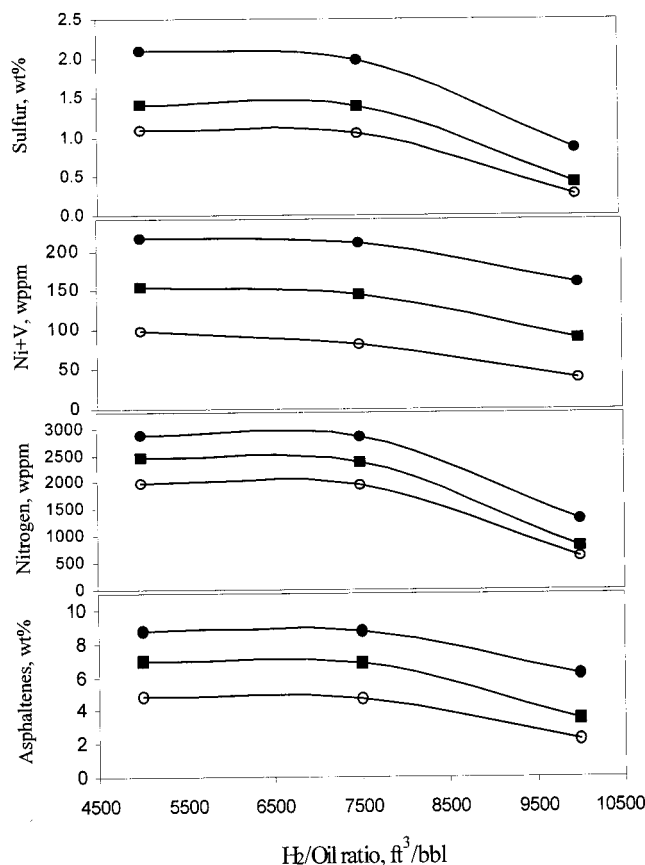


Figure 7. Effect of hydrogen-to-oil ratio on sulfur, metals, nitrogen, and asphaltenes in synthetic crudes. (●) 380 °C, (■) 400 °C, (○) 420 °C.

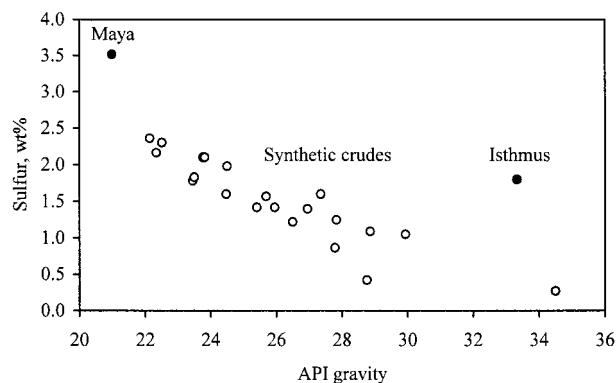


Figure 8. API vs sulfur content. (●) Maya and Isthmus crude oils, (○) synthetic crudes.

the different operating conditions studied in the present work (empty circles). Maya and Isthmus crude oils are also included as reference (full circles).

It can be observed from this figure that crudes follow the general trend of increasing sulfur with decreasing API gravity. Most of the synthetic crudes exhibit less sulfur content as compared to the reference crude oil (Isthmus).

Only one hydrotreated crude presents higher API gravity than Isthmus crude oil (34.5 vs 33.3 API), which was obtained at the most severe operating conditions (100 kg/cm² pressure, 420 °C reaction temperature, 0.5 h⁻¹ LHSV, and 10 000 ft³/bbl H₂/oil ratio). This synthetic crude also showed a very low sulfur concentration compared to Isthmus crude (0.27 vs 1.8 wt %).

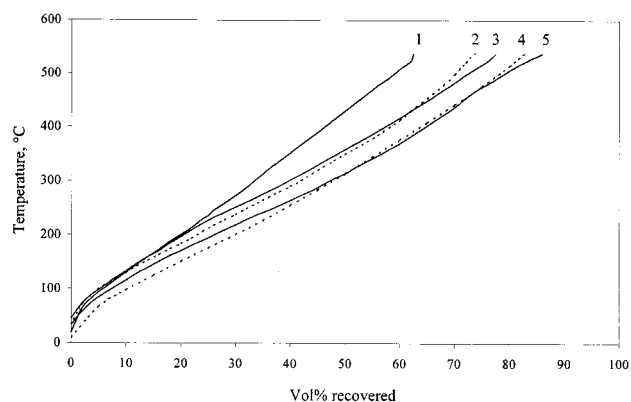


Figure 9. Distillation curves for different crude oils. (1) Maya, (2) synthetic crude at 380 °C, (3) synthetic crude at 400 °C, (4) Isthmus, (5) synthetic crude at 420 °C. Other conditions for synthetic crudes: 100 kg/cm² pressure, 0.5 h⁻¹ LHSV, and 10 000 ft³/bbl H₂/oil.

Table 4. Maya, Isthmus, and Synthetic Crude Oil Properties (HDT conditions for synthetic crudes: 100 kg/cm² pressure, 0.5 h⁻¹ LHSV, 10 000 ft³/bbl H₂/oil ratio)

properties	Maya	SC-1	SC-2	SC-3	Isthmus
HDT temperature, °C		380	400	420	
API gravity	20.99	27.79	29.76	34.50	33.3
sulfur, wt %	3.52	0.865	0.420	0.270	1.80
nitrogen, wppm	3006	1320	810	612	1446
Ramsbottom carbon, wt %	11.01	6.55	3.0	0.75	4.23
asphaltenes in <i>n</i> C ₇ , wt %	11.2	6.17	3.5	2.21	3.06
Ni + V, wppm	318.9	159.3	90.0	39.9	99.7

Typical distillation curves of Maya (line no. 1), Isthmus (line no. 4), and three selected synthetic crude oils (lines no. 2, 3, and 5) are illustrated in Figure 9. The hydrotreated products distillation curves shown in this figure were obtained at the following reaction conditions: 100 kg/cm² pressure, 0.5 h⁻¹ LHSV, and 10 000 ft³/bbl H₂/oil ratio. Each line corresponds to different reaction temperature, 380 °C for line 1, 400 °C for line 2, and 420 °C for line 3.

There are significant differences in the distillations shown in Figure 9. The hydrotreating feedstock (Maya crude) contains 37.5 vol % vacuum residue (538 °C+), while hydrotreated products contain 26.0, 22.5, and 14.0 vol % at 380, 400, and 420 °C reaction temperature, respectively. The reference crude (Isthmus) has a vacuum residue content of 17.3 vol %, which is higher compared to the synthetic crude obtained at 420 °C. It means that distillates obtained by Maya crude fractionation can be considerably increased via hydrotreating.

Table 4 summarizes several properties of the five crudes shown in Figure 9. As this table illustrates, these crudes contain a wide range of contaminant type and quantities depending on the severity of the hydrotreating.

Sulfur content, which is usually a general indicator of the required processing severity, was lower in the three synthetic crudes (SC-1, SC-2, and SC-3) compared to Isthmus crude oil (0.865, 0.420, and 0.270 wt % vs 1.8 wt %). The HDS level in these crudes was in the range 75.4–92.3%.

As stated before, nitrogen is typically concentrated in the higher-boiling fractions. Although its content in petroleum crude is generally low (i.e., Maya crude exhibits 0.30 wt % nitrogen), its effect on refining

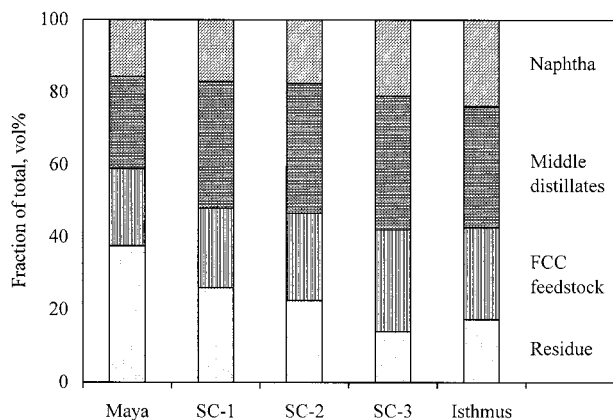


Figure 10. Composition of Maya, Isthmus and Synthetic crude oils API vs sulfur content. (●) Maya and Isthmus crude oils, (○) synthetic crudes.

operations is significant, since it affects both the activity and stability of commercial cracking catalysts.

The reduction of this heteroatom at severe conditions was higher than 56%. The lowest nitrogen content was 0.061 wt % (SC-3), which was achieved at a pressure of 100 kg/cm², space-velocity of 0.5 h⁻¹, H₂/oil ratio of 10 000 ft³/bbl, and a temperature of 420 °C.

Similarly to sulfur content, nitrogen was lower in the three synthetic crudes compared to Isthmus crude oil (0.132, 0.081, and 0.061 wt % vs 0.144 wt %).

Asphaltenes and Ramsbottom carbon contents of a HDT feedstock is directly related to the operating severity necessary to convert these high-molecular weight, hydrogen-deficient materials. The resulting increased coke formation on the catalyst due to the presence of these contaminants in the feedstock affects stability, liquid yields, and the potential for catalyst bed plugging. For the three synthetic crudes shown in Table 4, the levels of asphaltenes and Ramsbottom carbon decrease as the temperature increases. At 420 °C (SC-3), the content of these coke precursors in synthetic crudes is considerably lower than the reference crude oil (2.21 and 0.75 wt % vs 3.06 and 4.23 wt %). Of course, these contaminants concentrate in the heavier fraction of the synthetic crudes.

With respect to metals removal, the nickel plus vanadium content was reduced from 318.9 to 39.9 wppm at 420 °C (SC-3), which corresponds to 87.5% HDM. It should be mentioned that the types and amounts of metallic compounds present in a feedstock play one of the most important roles in determining the complexity and cost of hydrotreating, because metals content dictates both catalyst type and operating cycle length.

Figure 10 shows the composition of Maya, Isthmus, and the three selected synthetic crudes (SC-1, SC-2, and SC-3), which were obtained by using the corresponding TBP distillation curves. The boiling ranges of the crude oil fractions were defined as follow: naphtha, IBP–170 °C; middle distillates, 170–360 °C; FCC Feedstocks, 360–538 °C; and residue, 538 °C+.

It can be observed that naphtha, middle distillates, and FCC feedstock yield fractions increase as the reaction temperature increases, and consequently residue yields decrease. Naphtha and FCC feedstock showed a low increase at 400 °C (from 15.6 and 21.4 vol % to 17.5 and 24.1 vol %, respectively). However, at 420 °C

the increase was considerably improved (up to 21 and 28 vol %, respectively). The greatest yield increase was observed with middle distillates fraction, from 25.5 to 37 vol % for SC-3. Middle distillates and FCC feedstock yield fractions were higher than those obtained with Isthmus crude oil.

These results indicate that the experimental catalyst is more oriented to moderate hydrocracking, since naphtha fraction shows a low increase compared to the higher increase encountered in heavier fractions.

Catalyst Deactivation. The physical and chemical properties of fresh and spent catalyst are given in Table 2. Pore size distributions of these catalysts are also presented in Figure 1. The results reveal that the surface area of spent catalyst decreases as it is expected due to coke deposition. Coke is deposited on smaller pore mouth and hence a decrease of surface area is observed.

It is supported from our observation that the percentage of pore volume having pore diameter 50–100 Å decreases. While surface area of the catalyst decreases, the average pore size increases. This behavior is observed due to an increase in the percentage of pore volumes having pore diameter 100–500 Å. There is no dramatic change of pore volume.

It is also noticed from Table 2 that a considerable amount of coke (14 wt %) is deposited on the catalyst, whereas the deposition of metals is not very high.

It is well known from the literature that HDT catalysts are deactivated rapidly during initial run of reactions. This catalyst deactivation is mainly due to pore mouth plugging by coke. Asphaltenes contained in heavy crudes are the major source of coke. In general, these asphaltenes adsorb on the more acidic sites on the catalyst during initial period of hydroprocessing.¹⁶

The literature stated the requirement of different optimum pore sizes for removal of asphaltenes from different feeds. Shimura et al.¹⁷ reported that the optimum pore size was around 200 Å for initial activity of HDM and asphaltene cracking of Boscan crude. They also reported that the optimum pore diameter for removal of vanadium is smaller than that for asphaltene cracking. Kobayashi et al.¹⁸ observed that the optimum pore size required for removal of asphaltene from Khafji AR was 150 Å.

It is clear that the requirement of optimum pore size of catalyst depends on the average size of asphaltenes contained in the feed. Though we do not know the average size of asphaltenes in Maya crude, the average pore diameter (64 Å) of our catalyst is smaller enough to remove the asphaltene effectively from Maya crude.

Conclusions

The effect of catalytic hydrotreating on Maya heavy crude oil has been investigated over an experimental NiMo/Al₂O₃–TiO₂ catalyst. The most important reaction variables were also studied in the following ranges: reactor pressure, 54–100 kg/cm²; liquid hourly space-

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velocity, 0.5–1.5 h⁻¹; reaction temperature, 380–420 °C; and H₂/Oil ratio, 5000–10 000 ft³/bbl.

The data showed that, in general, synthetic crude oil quality (API gravity, sulfur, nitrogen, asphaltenes, Ramsbottom carbon, metals, and boiling point range) improved as the temperature, pressure, and hydrogen-to-oil ratio increased or space-velocity decreases.

The applicability of these results industrially are mainly restricted by high metals and coke precursor contents in Maya crude oil. However, this exploratory study clearly shows that very low contaminants contents

and high distillates yields of synthetic crudes can be achieved by direct HDT of heavy crude oils. Therefore, more effort needs to be applied in this type of research in order to develop appropriate process and catalytic systems.

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