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Heavy oil upgrading at moderate pressure using dispersed catalysts: Effects of temperature, pressure and catalytic precursor

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HIGHLIGHTS

- ▶ Thermal hydrocracking improves crude oil but significantly produces gas and solids.
- ▶ Thermal conversion of asphaltenes contributes to the production of gas and solids.
- ▶ The use of low catalyst load (330 ppm Mo) changes little the thermal process.
- ▶ Product distribution can be tuned changing catalyst load and operating temperature.

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ABSTRACT

A study of the influence of reaction parameters (reaction temperature, pressure and catalytic precursor) on the upgrading of Maya heavy oil under low pressure and moderate temperature under slurry conditions is presented. The behavior of the purely thermal hydrotreating system was first characterized to have a basis for distinguishing the effect of incorporating a catalyst in further hydrotreatings. The distillation curves of liquid product were obtained by thermo gravimetric analysis (TGA), ASTM standards were used for evaluation of API gravity and content of asphaltenes and carbenes–carboids. The separated asphaltenes were analyzed by XRD and C^{13} NMR techniques. The effect of temperature, catalytic precursor and pressure (800 and 960 psi) of process were studied. The study of thermal hydrotreating showed that 390 °C and 400 °C were promising temperatures for catalytic hydroprocessing and increasing pressure approximately 100 psi promoted the improvement of light liquid fractions at the expense of the heavy and residua fractions. The use of catalytic precursors at 400 °C in concentrations of 330 ppm of Mo increased gasoline production without producing more solids but did not result in the improvement of the liquid yield in comparison to the homologous thermal hydrotreatment. The liquid yield was improved either hydrotreating at 390 °C or at 400 °C with 1000 ppm Mo as catalyst.

1. Introduction

Today, heavy oil is looked to as a future energy source since its total reserves are estimated in 6.3 trillion barrels. However, its processing is not easy due to its characteristic high content of metals (Ni, V), sulfur and nitrogen, as well as high content of heavy molecules and asphaltenes [1,2]. Heavy oils have been processed in the most varied ways going from solvent processes to fixed and ebullated bed hydrotreatments, slurry phase hydrocracking and their combinations [2–8]. Particularly, the field of slurry phase hydrotreating is attractive because of it is able to process feeds with high content of metals ($V + Ni > 300$ ppm) and high content of sulfur and impurities. Additionally, it presents no bed plugging problems and a wide adaptability to different sources of raw material achieving conversions of vacuum residue (VR) up to 95% [1]. However, slurry technology is still in the development stage due to the difficult operability of the units, high operation temperature (typically 420–460 °C), high pressure of process (10–20 Mpa) and low catalyst recoverability.

Slurry processes use unsupported dispersed catalysts [9]. They have mainly been applied to the processing of residues, coal and tar sands. Typically, there is concomitant gas and coke formation due to the predominantly thermal nature of cracking reactions. To diminish coke formation slurry processes use high hydrogen pressure and dispersed catalysts in any of two modalities: (1) heterogeneous solid powder catalyst: where the active catalytic phase is a solid mixed with the feed from the beginning of hydroprocessing. (2) Dispersed precursors: where the catalyst is added to

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the feed in the form of a precursor (water soluble or oil soluble non-catalytic compound) that transforms into the catalytic active phase after an intermediate step of activation *in situ* or during reaction conditions. Catalytic precursors have the advantage that prior being added to the reaction mixture, a dissolution can be made (in water or in oil according to the water soluble or oil soluble nature of the precursor). Then, the dissolution is mixed with the feed to form a dispersion where the precursor gets well distributed all over the reaction mixture. Heterogeneous solids are commonly added in large amounts (1–5 wt%) while water soluble and oil soluble precursors have been developed to overcome increasing costs of catalyst lost and achieve high conversions with low coke formation. However, since catalyst gets trapped into the produced solids (formation of solids is typically >3 wt% of feed and depends on the amount of asphaltenes), there is still the problem of its recoverability. Thus, much efforts are on the direction of diminishing catalyst concentration, which has lead to research organometallic compounds such as molybdenum, nickel and iron naphthenates, and alkyl thiometallates as oil soluble catalytic precursors [2,10–12]. Nevertheless the use of organometallic precursors is limited to less than 1000 ppm due to their high cost. Hence, the use of water soluble precursors is a good option from the costs point of view. Phosphomolybdic acid (PMA), ammonium molybdates, ammonium heptamolybdate (HM) and ammonium tetrathiomolybdate (TM) have been some of the most popular water soluble catalyst precursors studied for slurry systems due to their ease of synthesis and the relatively low cost among molybdenum compounds [2,13]. Most investigations on slurry catalytic hydrotreatment have been made at the typical conditions stated above to diminish coke formation. Nonetheless, Zhang et al. made investigations on catalytic conversion of coal and tar sands derived asphaltenes in the range from 658 K (385 °C) to 700 K (427 °C) at operation pressure 13.8 MPa (2000 psi) and near 1 wt% metallic load with promising results [14], they found that asphaltenes could be hydrocracked at the investigated conditions to produce mainly oil, gases and preasphaltenes (non-soluble toluene solids; preasphaltene coincide with the definition of carbene and carboids) but they also point the finding that asphaltenes from different sources have different conversion levels maybe due to the pretreatments according to their derivation. Despite previous investigations, the hydrotreatment of heavy oils using thermal or slurry catalytic systems is not well understood. With this in mind, investigating slurry systems for hydroprocessing heavy crudes at moderate catalytic load (<1000 ppm), temperature (<400 °C) and pressure (<2000 psi) is important to achieve a more solid knowledge basis on slurry hydrotreating of heavy crudes.

The aim of this work is to contribute to the understanding of heavy oil hydrotreating at moderate conditions of temperature and pressure using slurry reactors with dispersed catalysts. To achieve such goals the present work is structured in the following manner: (1) characterization of the purely thermal hydrocracking in a batch reactor (350–400 °C). (2) Pressure induced effects (800 and 960 psi) on the non-catalytic system. (3) Catalytic precursor (ammonium heptamolybdate and ammonium tetrathiomolybdate) induced effects at low load at a selected temperature (400 °C) using bulk MoS_2 as reference. (4) Effects of catalytic load and operation temperature.

2. Experimental

Maya crude (175 mL) of was fed into a 300 ml Parr Instruments batch reactor. For catalytic tests the catalytic precursor was added after Maya crude. The reactor was sealed and pressurized at 800 psi with H_2. The reactor was set up on its base and coupled to a 2 litters H_2 container pressurized at the same reactor pressure. Stirring was set to 1100 rpm. The reactor was heated at 350 °C over 1.5 h with a ramp of 5 °C/min, to achieve the sulfidation of the catalyst precursor, and then heated with the same ramp to the desired reaction temperature and kept at this temperature for 4 h. Once the reaction time elapsed, stirring and heating were turned off. The reactor was cooled to room temperature in 1 h, and let to rest during 16 h at 21 °C. The liquid and solid products were collected, quantified and stored in well sealed vessels so loss of mass was avoided. The mass of gas product was obtained from the difference between the fed mass and liquid plus solid mass products.

2.1. Non-catalytic system

For the non-catalytic system, four reaction temperatures were investigated; (350, 380, 390 and 400 °C) at a starting pressure of 800 psi of H_2 (at 20 °C) and a reaction time of 4 h. The initial pressure increased with the reaction temperature to 870 psi, 930 psi, 970 psi and 1020 psi in each case.

An experiment at 400 °C and starting pressure of 960 psi of H_2 (at 20 °C) was made to explore pressure effects. In this case, the pressure at operation conditions increased to 1080 psi.

2.2. Catalytic system

Two different precursors, ammonium heptamolybdate HM (Sigma–Aldrich reactive degree) and ammonium tetrathiomolybdate TM (synthesized according to D. Genuit [15]) were activated *in situ* to obtain MoS_2. The precursor finely pulverized was fed into the reactor after Maya crude. The amount of Mo used in the reaction experiments was 330 ppm. Two temperature stages were established: (1) precursor activation at 350 °C over 1.5 h, (2) reaction stage at 400 °C during 4 h. A complete run (pretreatment time plus reaction time) at 350 °C with each precursor was made to examine if the changes induced by the catalyst at precursor activation conditions were significant. It was found that after 5.5 h operation the conversion of residue ($T = 538^+$) was only 1.1%. Thus, in this work the effect of the activation process on conversion was neglected. An additional run with *ex situ* activated MoS_2 served as catalytic reference. To obtain *ex situ* MoS_2 0.2 g of finely powdered HM was sulfided at 400 °C with a ramp of 1 °C/min in a flow of 10% H_2S in H_2 for 6 h at atmospheric pressure. At the end of the treatment the MoS_2 was cooled to room temperature in N_2, and 0.085 g were transferred to the reactor in N_2 atmosphere. Then the reactor was set to the reaction conditions.

Two tests (at 390 °C and 400 °C) with 1000 ppm of Mo using TM were made to investigate the effect of a higher catalyst load at each temperature. The starting pressure of H_2 was 800 psi. In each case, the operating pressure increased to 930 and 1000 psi at operating conditions.

Liquid and solid products were collected, quantified and stored. Each experiment was coded according to its operating conditions thus T400P800 refers to a thermal experiment at 400 °C and 800 psi of H_2, while 330TM400P800 corresponds to a catalytic experiment using 330 ppm Mo of TM as catalytic precursor at 400 °C during 4 h and 800 psi of H_2.

2.3. Characterization techniques

A summary of the characterization techniques used here appear in the diagram of Fig. 1. The distillation curves of liquid products were obtained by thermogravimetric analysis (TGA) in a Simultaneous DSC-TGA SDT2960 TA-Instruments apparatus. During the TGA experiments N_2 flow of 100 mL/min, heating ramp of 4 °C/min from room temperature to 550 °C, and an isothermal stage at 550 °C during 30 min were used. To correct for the boiling point displacement caused because the evaporation takes place against virtually zero vapor pressure of the boiling component due to

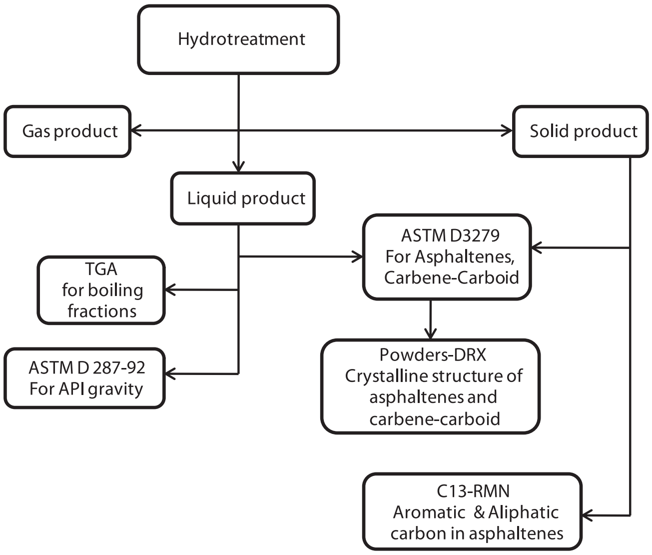

Fig. 1. Diagram of techniques of analysis.

carrying effects of the N_2 flow, a calibration curve was made with organic substances of known boiling point (decane 174 °C, naphthalene 218 °C, fluorene 295 °C, carbazole 355 °C, 4,6-DMDBT 365 °C, pyrene 393 °C, 1,3,5-triphenylbenzene 460 °C, hexatriacontane 497 °C, *n*-tetracontane 522 °C). The API gravity was obtained following the ASTM D 287-92 method. The amount of asphaltenes and the amount of carbenes and carboids produced in samples of solid and liquid products was obtained following the ASTM D3279 method (successive extraction in n-heptane and toluene). To observe structural differences, extracted asphaltenes were analyzed by X-ray diffraction (XRD) using a Phillips PW 1050/25 powder diffraction system operating with Cu Kα radiation and a Ni filter (λ = 1.5406 Å) over the range $10^\circ < 2\Theta < 60^\circ$ with a step of 0.02°. Aromatic and aliphatic carbon was obtained from ^{13}C Nuclear magnetic resonance analysis (^{13}C NMR) of solids in a JEOL Eclipse 300 spectrometer operating at ^{13}C resonance frequency of 100 MHz. The number of aromatic and aliphatic carbon was obtained from the integration of signals in the intervals of [160–110 ppm] and [60–10 ppm] respectively.

The following equations were used to calculate the yields and conversions:

$$\text{Gas (wt\%)} = 100 - \text{Liquid yield} - \text{Solids} \tag{1}$$

$$W_T = (\text{Liquid yield})(M_T/M_{TG}) \tag{2}$$

$$\text{Liquid distillable } (W_{538^-}) = \text{Liquid yield} - W_{538^+\text{product}} \tag{3}$$

where W_T is the wt% of the liquid fraction that distillates either below (T^-) or above (T^+) the temperature T, related to the total mass fed (e.g. W_{225^-} refers to the wt% of liquids having boiling point below 225 °C), $W_{538^+\text{product}}$ the wt% vacuum residue (VR) in liquid product, M_T the mass of a liquid fraction evaporated in a thermogravimetric experiment, M_{TG} the total mass fed into a thermogravimetric experiment, and liquid distillable, and (W_{538^-}) is the sum of all liquid fractions distilling below 538 °C.

$$\%\text{Conversion VR} = (W_{538^+\text{feed}} - W_{538^+\text{product}}) * 100/(W_{538^+\text{feed}}) \tag{4}$$

$$\text{wt\% Total Asphaltenes} = \text{wt\% of Asphaltenes}_{\text{liquid}} + \text{wt\% of Asphaltenes}_{\text{solid}} \tag{5}$$

$$\%\text{Conversion Asphaltenes} = (\text{wt\% Asphaltenes}_{\text{feed}} - \text{wt \%Total Asphaltenes } p_{\text{dproduct}}) \times 100/\text{Asphaltenes}_{\text{feed}} \tag{6}$$

$$\text{Yield}, Y_T = (W_{T\text{product}} - W_{T\text{feed}}) * 100/(W_{455^+\text{feed}} - W_{455^+\text{product}}) \tag{7}$$

$$\text{API-Barrel} = \text{API}_{\text{gravity}} * \text{Liquid yield}/100 \tag{8}$$

$$\begin{aligned}&\%\text{ Converted Asphaltenes not transformed to carbenes or carboids}\\ &\quad = (\text{wt\% asphaltenes in feed} - \text{wt\% total asphaltenes in product}\\ &\qquad - \text{wt\% carbenes and carboids}) * 100/\text{wt\% asphaltenes in feed}\end{aligned} \tag{9}$$

where $W_{455^+\text{feed}}$ is the wt% of fractions in feed having boiling point >455 °C ($W_{538^+\text{feed}} + W_{[455-538]\text{feed}}$), Y_T the production of any fraction related to the total consumption of W_{455^+}, $W_{T\text{feed}}$ the wt% of a fraction in feed (e.g. $W_{225^-\text{feed}}$), $W_{T\text{product}}$ the wt% of a fraction in product (e.g. $W_{225^-\text{product}}$), and API-Barrel is the parameter defined to estimate an optimum with API gravity and liquid yield.

3. Results and discussion

3.1. Thermal hydrocracking

3.1.1. Temperature and pressure effects in non-catalytic hydroprocessing of Maya crude

Fig. 2 shows the changes in liquid fractions, solid and gas products when the operating temperature and pressure are varied. The base line represents the natural fractions of Maya crude; above and below the base line are the produced and consumed fractions respectively. For each fraction, the first four bars correspond to temperature-induced effects and the last column correspond to pressure effects at 400 °C.

No Change in Maya fractions was observed when the hydrotreatment was performed at 350 °C. However, as the hydrotreatment temperature was increased, gasoline (225^-), middle distillates (225–454 °C), gases and solids were produced at the expense of the heavy liquids HL (455–538 °C) and VR (538^+) fractions. Gasoline increased considerably after hydrotreating at 390 °C but no further increase was seen when processing at 400 °C. Solids were significantly produced after hydrotreating at 380 °C and increased even more by processing at higher temperature. The consumption of the HL fraction was observable after hydrotreating

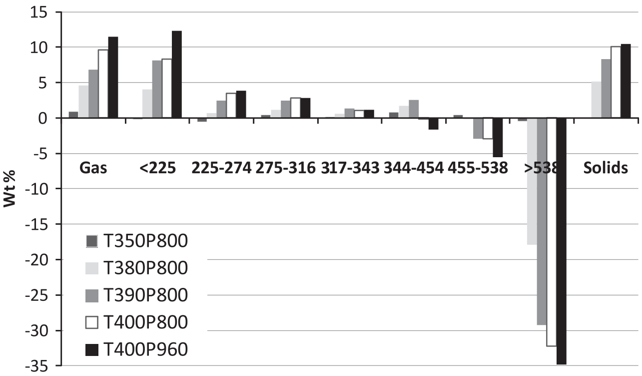

Fig. 2. Temperature effect (first four bars from left) and pressure effect on the product fractions of hydrotreated Maya petroleum. Hydrotreatment at initial pressure *P* = 800 psi and 350 °C (T350P800), 380 °C (T380P800), 390 °C (T390P800) and 400 °C (T400P800). Hydrotreatment at 400 °C and initial pressure *P* = 960 psi (T400P960).

at 390 °C, and processing at 400 °C did not provoke a higher consumption. The most consumed fraction was VR, which diminished 18 wt%, 29 wt% and 32 wt% after hydrotreatment at 380, 390 and 400 °C respectively. Hydrotreating at 400 °C and increasing the starting pressure from 800 to 960 psi increased gasoline production (4 wt% more than T400/800), and higher consumption of HL (455–438 °C) and VR (538$^+$), while the gas fraction was virtually stable (because the uncertainty associated to gas quantification was 5 wt%) and almost no change was observed in the production of middle liquid fractions and solids (see Fig. 2).

The properties of Maya crude and the products obtained at the different thermal conditions appear in Table 1. For simplicity, the liquid fractions in Fig. 2 were grouped in gasoline (225$^-$ °C), middle distillates (225–454 °C), HL (454–538 °C) and VR (538$^+$ °C). The quantitative data confirm that the maximum in gasoline production was reached by hydrotreating at 390 °C and that no further increase was obtained by hydrotreating at 400 °C. Middle distillates showed the same trend, the maximum production was obtained at 390 °C. The amount of HL was virtually constant when hydrotreating up to 380 °C; at higher temperature, 390 °C, HL were transformed to lighter fractions but there was virtually no difference between treatments at 390 and 400 °C. Due to the progressive production of gases and solids the liquid yield decreased with increasing hydrotreatment temperature. Nevertheless, the distillable liquids (W_{538^-}), shown in Table 1, increased until hydrotreatment at 390 °C, where a maximum is observed. The analysis of extracted solids revealed that they were constituted by asphaltenes, carbenes, and carboids only. In Table 1, solids formation continually increased with hydrotreatment temperature from 380 °C to 400 °C. The formation of solids seems to be related to the asphaltenes conversion since the summation of carbenes, carboids and total asphaltenes in Table 1 is always around a value of 11 wt%, which is slightly less than the asphaltenes present in the feed (13 wt%). The difference is explained by the partial depletion of the asphaltene aliphatic side chains since they represent a fraction of the asphaltene mass. Asphaltene conversion to carbenes and carboids in the solid product increased with temperature, indicating that the polycondensed core of the asphaltenes become more condensed at higher operating temperature. It was found that the amount of asphaltenes remains almost constant and that the carbene–carboid component is the one increasing in the solid product. This can be due to two main reasons, the increasing of the aliphatic nature of liquid product with reaction temperature, which diminishes asphaltenes solubility, or the progressive depletion of aliphatic side chains, which besides diminishing asphaltenes solubility, it also diminishes the steric hindrance for interaction of the asphaltenic sheets, allowing them to stack and eventually precipitate. Table 1 also evidences that API gravity increases with the operating temperature, evidencing the progressive transformation of Heavy Maya crude (API = 20) to lighter oil with API = 29 when processing at 400 °C. Since liquid yield and API gravity show opposite trends, a new variable is necessary to quantitatively find the best hydrotreatment conditions to improve the quality of the oil. This variable is, called here API-barrel, is built by multiplying the API gravity, which is related to the quality of the oil, by a measure of the amount of liquid recovered (liquid yield fraction). Therefore, this variable allows comparing the effectiveness of different processes or processing conditions to produce liquids of good quality, and is similar to the concept of "octane barrel" used for gasoline production. In our case, the highest API-barrel was obtained when hydrotreating at 400 °C. For this reason we chose 400 °C as the reaction temperature to investigate pressure effects.

As can be observed in the last column of Table 1, increasing the starting pressure from 800 to 960 psi, caused a considerable increase in gasoline fraction (from 23 wt% to 27 wt% respectively), higher consumption of HL and VR fractions, and virtually no modifications in the middle liquid fractions nor in the amount of distillable liquids. Besides, we observed no change in solids and carbene–carboid production as well as a small increment of total asphaltenes (slight fall of asphaltenes conversion). This means that gasoline and carbene and carboid sources are different and have a dissimilar response to changes in hydrogen pressure.

Fig. 3 shows the residue and asphaltene conversion values for the different operating conditions. In general, an increase in the conversion of VR and asphaltenes is observed in the interval from 380 to 400 °C. Changing the starting pressure from 800 to 960 psi caused the residue conversion to increase from 73% to 79%, but the asphaltenes conversion to diminish from 79% to 73%. Thus, asphaltene and residue conversions behave parallel with temperature but in different way with pressure.

To know how much of VR and HL are transformed to each produced fraction at each temperature, an analysis of the yields related to the consumed fractions (heavy liquids + residue), W_{453^+}, is shown in Fig. 4.

The production of the different fractions does not follow a uniform trend. Two groups of production are distinguished; the middle liquid fractions (225–454) follow a trend of consecutive production in decreasing order of weight. In contrast gas and solid yields move together at each operating temperature. Despite that gasoline belongs to liquid products it does not seem to follow the same behavior that middle distillates, maybe because the production of gasoline besides coming from the middle fractions it has also a significant contribution from the cracking of the heavy

Table 1
Properties of liquid and solid products. Except API and API-barrel quantifications, all the values are reported in mass percent (wt%) on the basis of total mass fed. Repeatability for liquid fractions (gasolines to residue) was determined on the basis of the maximum variation observed in different TGA experiments for the same liquid product (±2 wt%).

	Maya	T350P800	T380P800	T390P800	T400P800	T400P960
Gas (±5.0)	0	1	5	7	10	12
Gasolines (W_{225-})	14	14	18	23	23	27
Middle liquids ($W_{[225-454]}$)	31	32	35	40	38	37
Heavy liquids ($W_{[455-538]}$)	11	9	10	8	8	5
Liquid yield	100	99	90	85	80	78
Distillables (W_{538-})	56	55	64	70	68	69
Vacuum residue (W_{538+})	44	44	26	15	12	9
Solids (±1.0)	0	0	5	8	10	10
Asphaltenes-solid	0	0+	2	2	2	2
Asphaltenes-liquid	13	13	5	3	1	2
Total asphaltenes	13	13	7	5	3	4
Carbenes and carboids	0	0	3	6	9	9
API (±0.2°API)	20	–	24	26	29	29
API-barrel	20	–	22	22	23	23

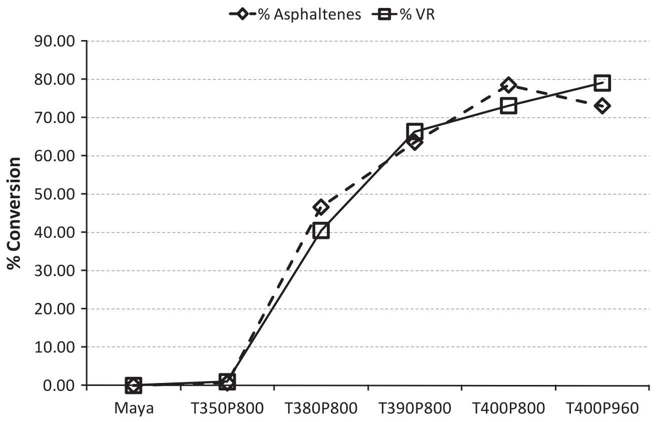

Fig. 3. Residue and asphaltene conversion. Effect of operating temperature and pressure.

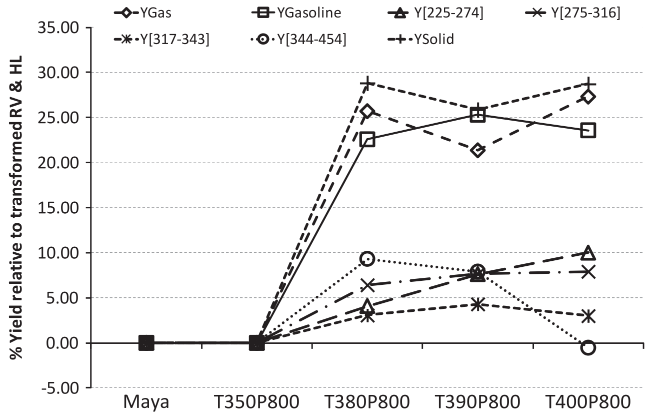

Fig. 4. Yield of liquid fractions, solid, and gas calculated on the basis of HL + VR consumed at different operating conditions ($P = 800$ psi; $T = 350, 380, 390, 400$ °C).

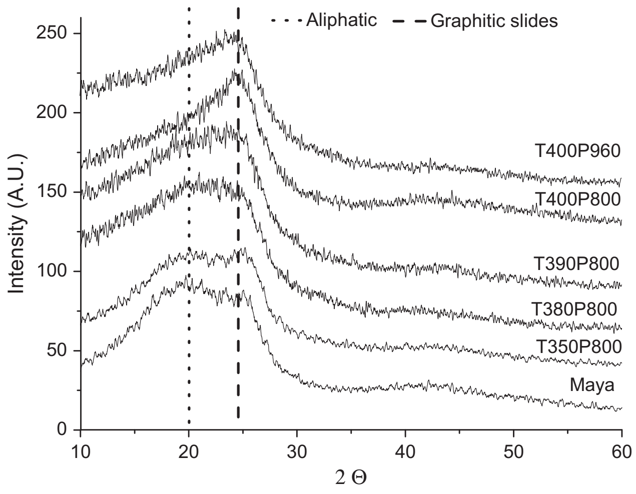

Fig. 5. XRD analysis of solid extracted asphaltenes.

fractions (HL and VR). Fig. 4 shows that gas, gasoline and solids are the main products and that their sum accounts for about the 80% of the transformation of VR and HL.

Asphaltenes conversion must be considered to explain the production trends of solid and gas. Published works of Bartholdy and Andersen [16] and Seki and Kumata [17] report that, in spite of the refractory nature of the polycondensed aromatic skeleton of asphaltenes to hydrotreatment, their alkyl side chains easily crack at relatively low temperature (380 °C approximately). In particular, Seki and Kumata [17] after a methodic NMR analysis found that alkyl side chains crack the first producing C_1, C_2 or C_3 hydrocarbon units until a critic temperature (near 410 °C) and from this point onwards the number of side chains suddenly decrease. In contrast, resins present an almost constant rate of cracking from 380 °C to 420 °C. In our case, the progressive shortening of alkyl side chains seems to contribute to the accelerated production of gases at 380 °C. At higher temperatures the yield of gas remains almost constant. The yield of solid follows a similar trend indicating that the solid comes mainly from asphaltenes conversion. The increasing production of solids with hydrotreatment temperature is the consequence of the cracking of asphaltenic side chains since this leads to the destabilization of the asphaltenic dispersion and its subsequent precipitation. The XRD diffractograms of solid-extracted asphaltenes, shown in Fig. 5, support the above proposal by evidencing the progressive diminishing of the signal attributed to alkylic side chains ($2\Theta \approx 19°$) and the concomitant better definition of the peak attributed to graphitic type slides of polycondensed asphaltenic bodies ($2\Theta \approx 25°$). These results were confirmed by ^{13}C NMR, which showed an important change in the relative amount of aliphatic and aromatic carbon going from 65% aliphatic and 35% aromatic carbon in Maya crude to 44% aliphatic and 56% aromatic carbon after hydrotreating at 400 °C.

The effect of pressure on the structure of the asphaltenes present in the solid is also shown in Fig. 5. The wider nature of the XRD diffractogram of asphaltenes coming from hydrotreatment at 400 °C and 960 psi, reveals the higher importance of aliphatic side chains when compared to those coming from hydrotreatment at the same temperature and 800 psi. The effect of pressure is also observable in the last column of Table 1. Compared to the experiment made at the same conditions ($T = 400$) but at a starting pressure of 800 psi, one can see that higher pressure enhanced the production of gasoline, and diminished the presence of heavy liquid and residue, while the amount of middle distillates was practically constant. It is also evident that at higher pressure (960 psi) the amount of total asphaltenes for T400/960 is higher compared to T400/800, which suggests that asphaltenes and non-asphaltenic heavy molecules contained in the heavy liquid and residue are not affected the same by pressure. Thus, from the results in Table 1, it appears that at the higher operating pressure (960 psi), the cracking of non-asphaltenic heavy molecules in HL and VR increase the production of gasoline. Increasing the initial pressure from 800 to 960 psi preserves more asphaltenes in the liquid (1.7 compared to 1.2 wt%), indicating a diminished depletion of asphaltenes side chains. In line with this, (Fig. 6) shows that there are differences between the X-ray diffractograms of asphaltenes extracted from the liquid (L) and those extracted from the solids (S). In general, asphaltenes coming from the liquid present a greater contribution of the peak corresponding to aliphatic chains; this effect is more visible as hydrotreatment temperature rises.

Summarizing, non-catalytic hydrotreatment of Maya crude improves the properties of the oil, increasing the fraction of gasoline and middle distillates ($W_{[225-454]}$), API gravity, and diminishes heavy liquids ($W_{[455-538]}$), VR, and total asphaltenes. Increasing pressure from 800 to 960 psi improves the production of gasoline mostly at the expense of heavy liquids and vacuum residue, although the conversion of asphaltenes decreases. Asphaltenes considerably contribute to gas production and most of the solid. The study of the product solids allowed to establish that asphaltene and residue conversions behave parallel with temperature (when temperature increases both conversions increase) but dissimilar with pressure (when the operating pressure increases VR conversion increases but asphaltenes conversion decrease slightly). At

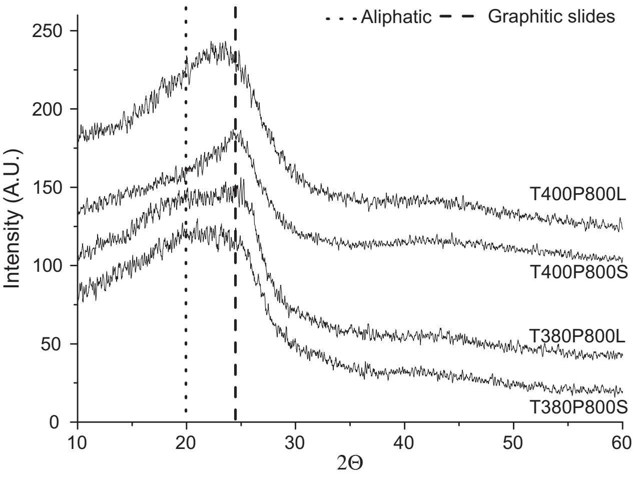

Fig. 6. XRD analysis of liquid (L) and solid (S) extracted asphaltenes.

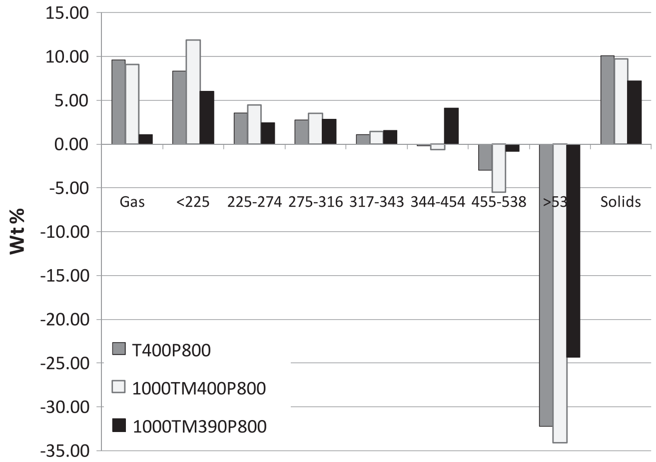

Fig. 7. Effects of temperature (390 vs 400 °C) on slurry catalytic hydrotreating of Maya crude using 1000 ppm Mo.

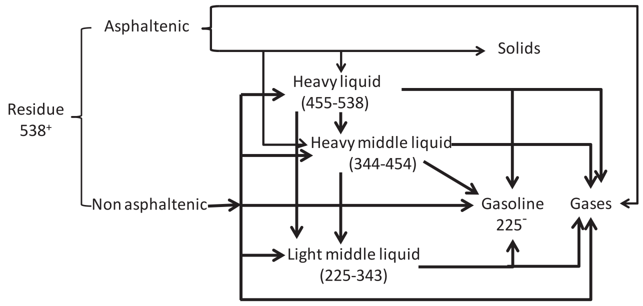

Fig. 8. Reaction routes for the transformation of the different constituents of heavy Maya crude.

Table 2
Comparison of properties of liquid and solid products coming from catalytic hydrocracking at 400 °C and 390 °C with different catalyst load. Except API and API-barrel quantifications, all the values are reported in mass percent (wt%) on the basis of total mass fed. Repeatability for liquid fractions (gasolines to residue) was determined on the basis of the maximum variation observed in different TGA experiments for the same liquid product (±2 wt%).

	T400P800	1000TM400P800	1000TM390P800
Gas (±5 wt%)	10	9	1
Gasolines ($W_{225}-$)	23	26	20
Middle liquids ($W_{[225-454]}$)	38	40	42
Heavy liquids ($W_{[455-538]}$)	8	5	10
Liquid yield	80	81	92
Distillables ($W_{538}-$)	68	71	72
Vacuum residue ($W_{538}+$)	12	10	20
Solids (±1.0)	10	10	7
Asphaltenes-solid	2	1	2
Asphaltenes-liquid	1	2	3
Total asphaltenes	3	3	5
Carbenes and carboids	9	9	5
API (±0.2°API)	29	29	25
API-barrel	23	24	23
% Converted asphaltenes not transformed to carbene or carboid	14	12	23

the operating conditions used here, 400 °C and 800 psi gave the best results in terms of the optimality API-barrel parameter.

3.2. Catalytic hydrocracking

Reaction experiments performed at $T = 400$ °C, $P = 800$ psi with 330 ppm of Mo catalyst obtained *in situ* using different Mo precursors (HM, TM, and MoS_2), showed no great difference in the amount of the different fractions obtained as products from the hydrotreatment of Maya crude during 4 h, when compared to the purely thermal process (T400P800). The main difference was in the wt% content of gasoline, which was 23 for the thermal process and 25, 25 and 26 wt% for MoS_2, HM, and TM respectively. Hereafter we discuss only the results obtained with TM as catalyst precursor.

Increasing the load of catalyst from 330 to 1000 ppm Mo, keeping the operating temperature and pressure at 400 °C and 800 psi respectively, brings about some changes in the product distribution. Total asphaltenes decrease from 3.8 to 2.2 wt%, the amount of distillable ($W_{538}-$) increases from 67 to 71 wt%, where the increase is mainly due to middle liquids, $W_{[225-454]}$, that change from 34 to 40 wt%, leading to an increase in liquid yield from 77% to 81%. No changes are observed in the amount of gasoline that remains at 26 wt% or API gravity that is maintained at 29. These changes are reflected in the API-barrel parameter that improves from 22 to 24 when the catalyst load is 1000 instead of 330 ppm Mo.

Interesting changes in the product distribution are observed when the operating temperature is decreased to 390 °C maintaining 1000 ppm Mo and 800 psi, In other words when we compare 1000TM400P800 with 1000TM390P800 (two last columns in Table 2). In this case the production of gasoline decreases from 26 to 20 wt%, but heavy liquids increase from 5 to 10 wt% and liquid yield also increases significantly from 81 to 92 wt%. The conversion of asphaltenes drop, leading to a total asphaltene content of 5.4 instead of 2.2 obtained at the higher temperature. The amount of gas and solids also decrease significantly from 9 to 1 wt%, and from 10 to 7 wt% respectively. This is in line with the observed decrease in the amount of carbenes and carboids from 9.3 to 4.9 wt%.

It appears then that although decreasing the operating temperature from 400 to 390 °C, using 1000 ppm Mo of catalyst, decreases the conversion of residue ($W_{538}+$), it increases the percent of liquids in the products, in particular middle and heavy liquids. In fact, the percent of asphaltenes not transformed to carbenes and carboids (bottom row in Table 2) increases significantly from 12 wt% (at 400 °C) to 23 wt% (at 390 °C). Therefore, at high temperature (400 °C) the thermal process is dominant whereas at lower temperature (390 °C) the effect of the catalyst benefits the production of liquids and decreases the production of gases. The differences in the product distribution respect to the original Maya crude feed when using 1000 ppm Mo as catalyst, $P = 800$ psi and 400 or 390 °C as operating temperature are shown in Fig. 7, where it is clear that at the higher temperature the product distribution is oriented to the light fractions whereas at lower temperature less gasoline and more middle and heavy liquids appear in the product. It appears then that without considering the effect of the operating pressure, that will be the object of a future study, it is possible to direct the product distribution by changing the amount of catalyst and the operating temperature. Increasing temperature leads to light liquids and gas whereas increasing catalyst load favors the production of middle and heavy liquids. Fig. 8 shows the reaction routes for the transformation of the different constituents heavy Maya crude.

4. Conclusions

From the above results the following conclusions can be drawn: Thermal non-catalytic process:

1. Thermal hydrocracking can be used to improve the properties of heavy Maya crude. However, the benefits obtained from the produced liquid fractions are limited by the significant accompanying production of gas and solids.
2. In thermal processing, hydrocracking of non-asphaltenic heavy molecules contributes to increase the production of middle distillate fractions, gasoline and gas. Thermal conversion of asphaltenes contributes significantly to the production of gas and solids.
3. Asphaltene and residue thermal conversions behave parallel with temperature (when temperature increases both conversions increase) but dissimilar with pressure (when the operating pressure increases VR conversion increases but asphaltenes conversion decrease).

Catalytic hydrocracking

4. The use of low catalyst load (330 ppm Mo) makes almost no difference from the thermal process.
5. The product distribution during the hydrocracking of heavy crude can be directed by changing the amount of catalyst and the operating temperature.
6. In spite of using 1000 ppm Mo as catalyst, at high temperature (400 °C) the thermal effects are important and the production of gasoline and gases are enhanced, and to a lesser extent middle liquid fractions($W_{[225-454]}$). Lowering the operating temperature to 390 °C, the production of liquids is oriented to heavier middle liquids ($W_{[344-454]}$), decreasing gases and gasoline. The conversion of residue also decreases.
7. At lower temperature (390 °C), although the transformation of residue drops, the percent of asphaltenes transformed to products other than carbenes and carboids increases significantly (from 12% to 23%). This indicates that operating longer reaction time at lower temperature (390 °C) might render greater benefits in terms of valuable liquids.

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