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Hydrocracking of Maya crude oil in a slurry-phase reactor. I. Effect of reaction temperature

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ABSTRACT

The effect of reaction temperature in the hydrocracking of Maya crude oil using a slurry-phase reactor was studied. The results indicate that the product distribution is clearly affected by the reaction temperature. In general, the transformation of heavy Maya crude oil into lower fractions follows a parallel-consecutive reaction scheme where vacuum residue converts to smaller fractions, and these fractions in turn, in a consecutive reaction path, are transformed to even lower liquid fractions and gases. Naphtha is the main product and does not seem to contribute significantly to the formation of gases. Solids appear to be formed by two main contributions: coke formation induced by thermal cracking, and precipitation of asphaltenes and other polycondensed aromatics. The precipitation of solids also seems to induce the elimination of sulfur and nitrogen compounds presents in the liquid phase. Increasing catalyst concentration from 300 ppm Mo to 1000 ppm Mo decreases the amounts of solid and gases, and increases liquid yield.

1. Introduction

The increasing demand of energy and the steady decrease in the availability of light crudes has caused researchers to look towards the best means of utilization of the significantly available heavy crude reserves. However, due to the low quality of heavy oils, and the difficulties to transport them, it is necessary to develop technologies, which can upgrade properties such as API gravity.

Hydrocracking is a refining process where the heavy crude oil and heavy fractions are transformed into light products with better quality [1–4]. For performing this process, four main reactor technologies are available: fixed bed reactor, moving bed reactor, ebullated bed reactor and slurry bed reactor. The choice of process type depends mainly on the amount of metals and asphaltenes in the feed, as well as on the level of conversion required [5]. Technologies that use supported catalysts suffer the disadvantage of formation of coke and metal deposits on the surface of the catalyst, and therefore from quick catalyst deactivation.

Previous studies reveal that slurry-phase hydrocracking is a good alternative for the treatment of heavy oil since it is possible to obtain high conversion of vacuum residue (>538 °C) without increasing strongly the cost of fresh catalyst reposition [6–8]. Slurry-phase hydrocracking uses unsupported catalysts in typical amounts from 100 to 10,000 ppm of metal [9]. Normally, these catalysts are sulfides of metals as MoS_2, which provide active hydrogen to the reaction system and therefore, inhibit the formation of coke, improving the selectivity towards intermediate liquid fractions [10,11]. The catalyst precursor can be fed to the reactor either as powder [12], or as a water- or oil-soluble metal salt [13–16].

As in most reactor systems, the effect of the operating conditions is important during slurry-phase hydrocracking. Literature shows that the breakdown of molecules mainly proceeds through thermal cracking, whereas the catalyst participates in the hydrogenation of unsaturated components and hydrogenolysis of compounds with heteroatoms as sulfur or nitrogen [17]. In particular, Panariti [18] and Ortiz [19] reported that the reaction temperature has an important effect in the hydrocracking of heavy oil but they did not report how the properties of the product changed with reaction time, and therefore, the variations of selectivity towards intermediate fractions as the reaction proceeds were not evident.

The aim of the present work is to analyze the behavior of the gas, solid and liquid phases present in the hydrocracking of Maya crude oil. Consequently, the crude oil was hydrotreated at three different reaction temperature (390, 400 and 410 °C), 300 ppm of Mo as catalyst and 1400 psi of pressure. After the reaction, the obtained phases were quantified and, the physical y chemical characterization of the liquid phase was carried out. To complement this work, we explore the possible effect of the catalyst concentration in the hydrocracking of Maya crude oil. Thus, a series tests with 1000 ppm of Mo at 400 °C and 1400 psi of H_2 was carried out.

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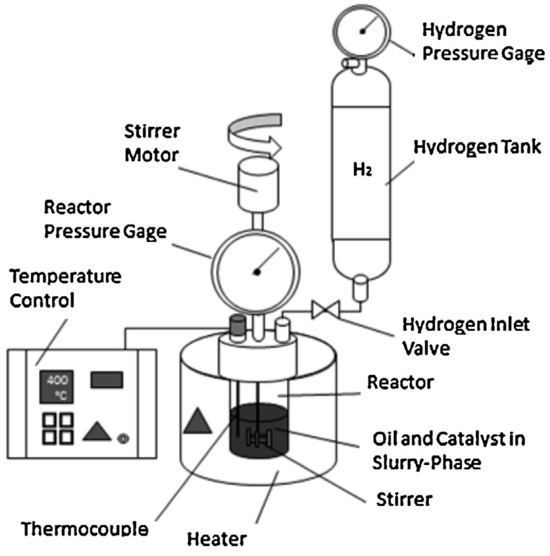

Fig. 1. Slurry-phase reactor used in the hydrocracking of Maya crude oil.

2. Experimental

2.1. Activity

The slurry-phase hydrocracking of Maya crude oil was performed in a Parr batch reactor, which was charged with 175 mL of Maya crude oil and ammonium heptamolybdate as catalyst precursor (300 ppm of Mo). The reactor was pressurized to 1400 psi of H_2 and connected to a tank of 2 L to mitigate the pressure changes due to the thermal expansion and cracking reactions (Fig. 1). Then, the reactor was heated to 350 °C and this temperature was kept constant for 1 h to activate the catalyst in situ. Finally, the reactor was heated to the reaction temperature (390, 400 and 410 °C) and the hydrocracking was carried out isothermally during 2, 4 and 8 h. Additionally, a series of tests with 1000 ppm of Mo at 400 °C was carried out to explore the effect of catalyst concentration in the hydrocracking of Maya crude oil.

2.2. Characterization

The liquid phase obtained from the hydrocracking of Maya crude oil at different reaction temperatures was characterized using the following methods:

- The distillation curve of products that form the liquid phase was obtained by means of thermogravimetric analysis (TGA) in a simultaneous DSC-TGA SDT2960 apparatus. For the TGA experiments, N_2 flow of 100 mL/min, heating ramp of 4 °C/min from room temperature to 550 °C, and isothermal stage at 550 °C during 30 min were used. To correct the boiling point displacement caused by the decrease in the vapor pressure, a calibration curve was obtained.
- The specific gravity at 15.5 °C was determined with a SVM 3000 Stabinger viscometer according to ASTM D7042 method. For each test, 3 mL of sample were fed to the equipment. The repeatability was ±0.1% of the measurement value.
- The molecular weight was quantified using the cryoscopic method in accordance with the ASTM D2224. For each test, 1 mL of sample was solubilized with 10 mL of benzene to obtain the freezing point of the mixture. Then, this value was used to calculate the molecular weight.

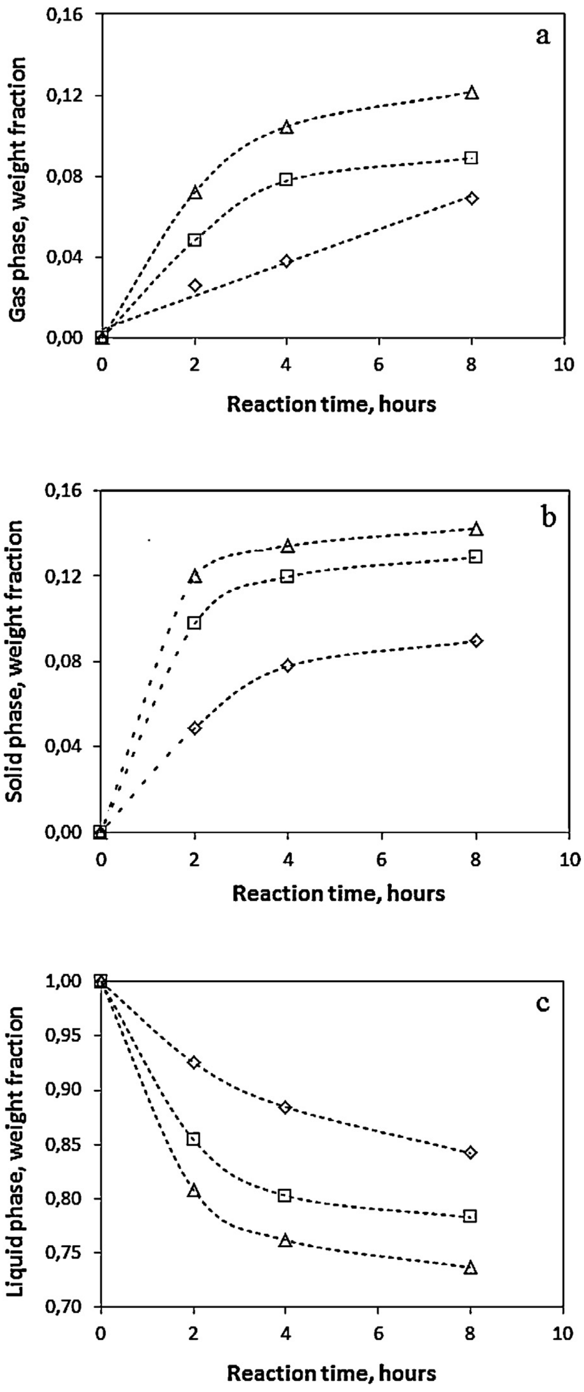

Fig. 2. Gas (a), solids (b), and liquid (c) fractions of hydrotreated Maya crude oil at different reaction temperatures [663 (◊), 673 (□) and 683 K (△)].

- The sulfur concentration was obtained with a Tanaka RX-360SH model analyzer according to ASTM D4294 method. For each test, 10 mL of sample were fed to the equipment.
- The carbon, hydrogen and nitrogen concentration was obtained with a Flash 2000 elemental analyzer according to ASTM D5291 method. For each test, 5.0 mg of sample were fed to equipment.

3. Results and discussion

In general, during hydrocracking, three types of products are obtained: solids, liquids and gases. In our case, after the reaction,

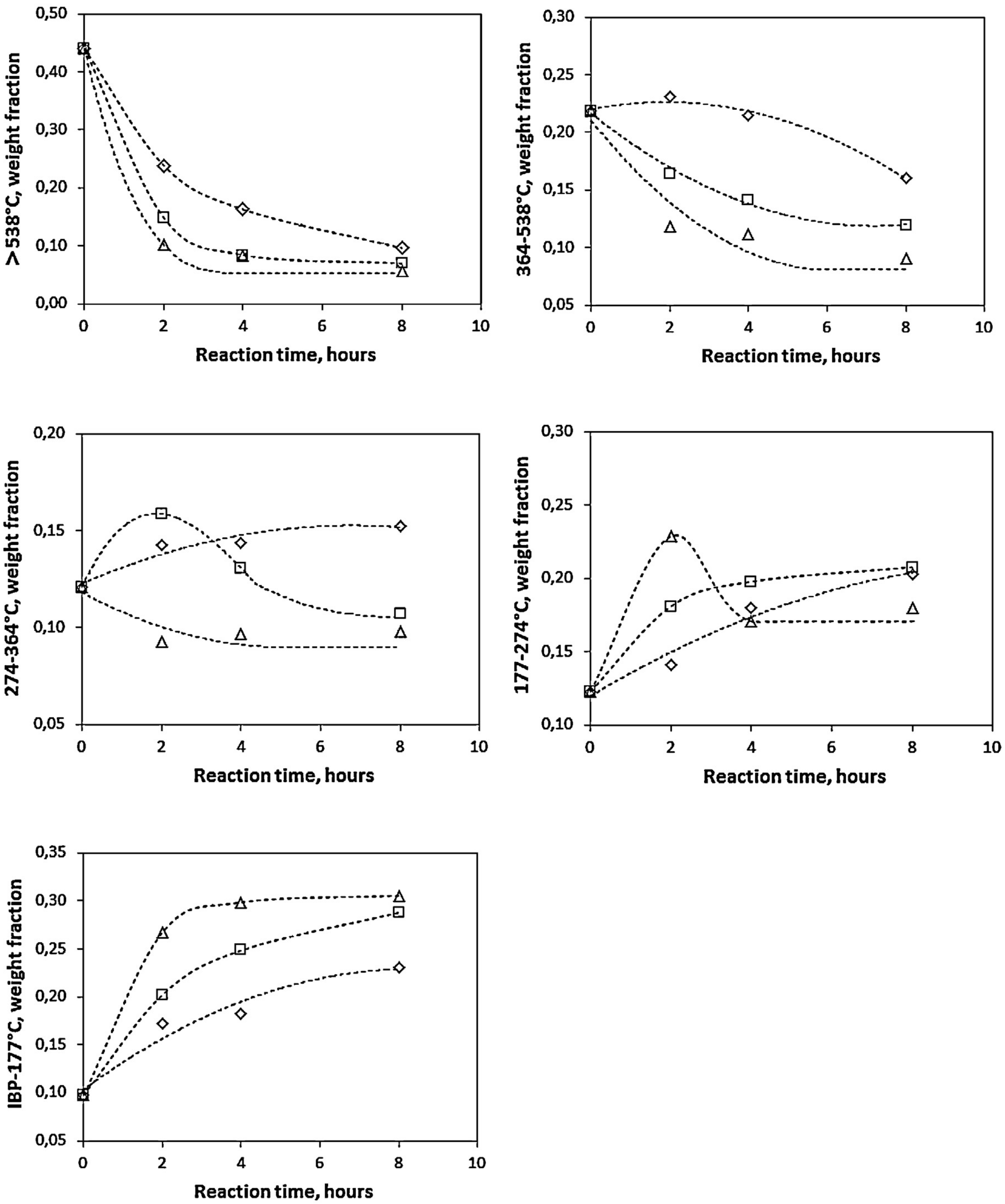

Fig. 3. Weight fraction of components from hydrotreated liquid phase at different reaction temperatures [663 (◇), 673 (□) and 683 K (△)].

the reactor was depressurized and weighted to obtain the mass of gas phase from the difference in weight of the reactor before and after of the reaction. Then, the liquid and solid phases were separated and quantified. Fig. 2 presents the fraction weight related to the initial mass fed to the reactor of these phases as a function of reaction time when Maya crude oil is hydrotreated at different reaction temperatures.

3.1. Gas phase analysis

The results in Fig. 2a show that an increase in the reaction temperature promotes the formation of gas. This formation of gas occurs at a higher rate in the first hours of reaction and then slows down. These two processes could be associated to the cracking of paraffinic chains present in asphaltenes and other large molecules present in vacuum residue in the first stages of the reaction, and to the cracking of smaller molecules in the latter stages of the reaction. At the lower temperature (390 °C), this effect is not observable because of the lower conversion of vacuum residue; in this case, the observed increase in gas production is almost linear.

3.2. Solid phase analysis

The results in Fig. 2b show in the beginning a fast formation of solid phase during the first hours of reaction and then the formation of solids continues but at a lower rate. This behavior may be explained if one considers that the formation of solids has two main contributions, one coming from the formation and further polymerization of coke precursors, and other coming from the precipitation of partially hydrocracked asphalthenes and polycondensed aromatics due to the formation of small paraffins and the hydrogenation of double bonds leading to a more paraffinic system. In a previous work, we demonstrated that the solid product is formed by two different solid phases, precipitated asphaltenes and coke [19]. The formation of these two solid phases has different formation trends and occurs at different rates. The formation of coke occurs continuously through the reaction, whereas the onset of the precipitation of asphaltenes only occurs when the concentration of paraffins in the reaction system reaches a critical value. For this latter process, an S-shaped curve for the formation of solids is normally observed [20]. In our case, since no analysis of the liquid was made in the first stages of the reaction, we can only detect at the second hour of reaction a high formation of solids.

3.3. Liquid phase analysis

The liquid phase is the most important product since it contains the valuable liquid fractions obtained from the hydrocracking process (Fig. 2c). The liquid phase was fractionated to obtain five components with different interval of distillation, IBP-177, 177-274, 274-364, 364-538 and >538 °C, which can be associated to naphtha, kerosene, atmospheric gasoil, vacuum gasoil and vacuum residue, respectively. Fig. 3 presents the weight fraction of these components based on the total mass fed. The results show that the reaction temperature affects the trend of the weight fraction of each component with reaction time, as described below:

(i) The vacuum residue is the main reactant present in the crude oil. This fraction disappeared rapidly when the reaction temperature increased, mainly during the first two hours of reaction.
(ii) At low reaction temperatures (390 °C), a slight formation of vacuum gasoil from vacuum residue is observed in the first stages of the reaction. At this low temperature, the hydrocracking seems to be mainly catalytic, whereas increasing the reaction temperature the thermal cracking reactions take place and the formation of vacuum gasoil is no longer observed since part of this fraction is cracked to atmospheric gasoil and other lower fractions.
(iii) The atmospheric gasoil presents the same behavior that vacuum gasoil. However, the formation of atmospheric gasoil is observed during the four hours of reaction for the experimental at 390 °C. At the higher temperatures (400 and 410 °C), the typical behavior of a consecutive reaction system is observed. This means that atmospheric gasoil is formed from vacuum residue and vacuum gasoil, and that lower fractions are in turn formed from atmospheric gasoil.
(iv) The kerosene fraction also presents the behavior of an intermediate product in a consecutive reaction system. For this fraction, the consecutive behavior is clearly observed only at the higher temperature. At the lower temperatures (390 °C), this fraction does not reach the maximum and show only a steady increase. This is not surprising since the smaller chains are more stable towards cracking.
(v) The naphtha fraction increases in all cases showing that the breaking of these molecules is difficult at the conditions of our experiment. Therefore, the naphtha not contributes in the reaction scheme, or contributes only in a small extent to the formation of gases. In fact, at the higher temperature, the amount of naphtha tends towards a constant value.

An idea of the evolution of the liquid fraction along the reaction time can be obtained from the average molecular weight and the specific gravity of the liquid. Fig. 4 presents the molecular weight in atomic mass units (amu) of the hydrotreated liquid phase. As a results of the above transformations of the different oil fractions, and in particular the disappearance of the vacuum residue and heavy liquid fractions, the molecular weight of the liquid decreases when reaction temperature is increased. The higher decrease in this property occurs during the first hours of reaction. This behavior is in agreement with the observed for the reaction system since during the first hours of reaction the larger molecules present in the reaction medium are easier to crack than the smaller ones present at longer reaction times.

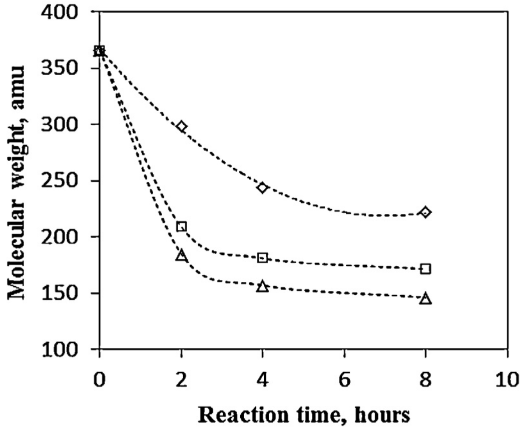

Fig. 4. Molecular weight of hydrotreated liquid phase at different reaction temperatures [663 (◊), 673 (□) and 683 K (△)].

Then, the molecular weight values (M) were used to obtain the average carbon number (Nc) of the hydrotreated liquid phase by means of the Pedersen correlation [21], which is used to estimate the molecular weight of hydrocarbons presenting from 6 to 50 carbon atoms:

$$M = 14\text{Nc} - 4 \qquad (1)$$

Therefore,

$$\text{Nc} = \frac{M + 4}{14} \qquad (2)$$

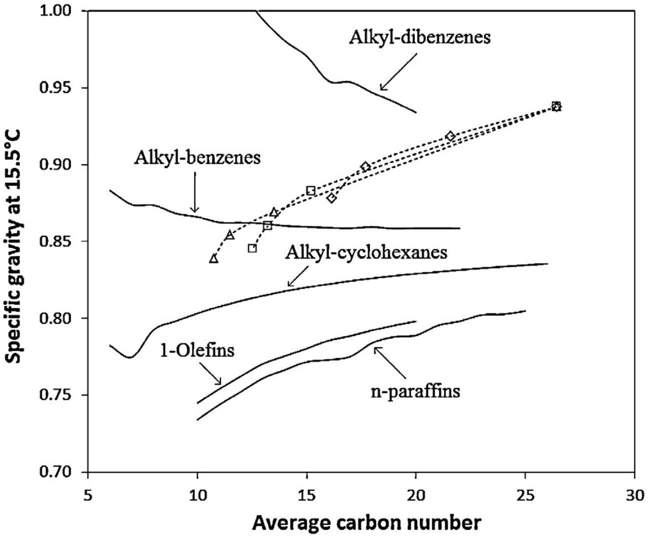

Fig. 5. Specific gravity versus average carbon number of hypothetical mean molecule present in the hydrotreated liquid phase at different reaction temperatures [663 (◊), 673 (□) and 683 K (△)].

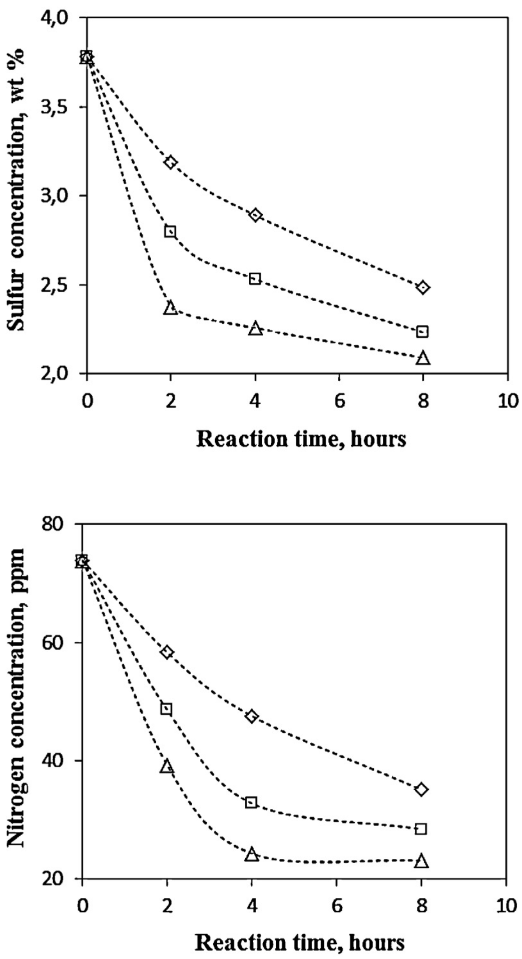

Fig. 6. Concentration of sulfur and nitrogen present in the hydrotreated liquid phase at different reaction temperatures [663 (◊), 673 (□) and 683 K (△)].

Since the Nc values are related to the specific gravity of the liquid, Fig. 5 shows a plot of Nc versus specific gravity. This plot shows that for the experimentally determined molecular weight of Maya crude oil (365 amu) and specific gravity at 15.5 °C of 0.94, the mean hypothetical molecule of Maya oil has ~26 carbon atoms. Then, when the reaction time increases for the different reaction temperatures, the number of carbons diminishes without decreasing at the same rate the specific gravity of the liquid phase. This indicates that thermal cracking dominates the reaction system at longer reaction times leading to an important decrease in the number of carbons. Consequently, the hydrogenation reactions at the conditions of our experiments are not so important, whereas the small molecules obtained from the thermal cracking contribute to the formation of gas.

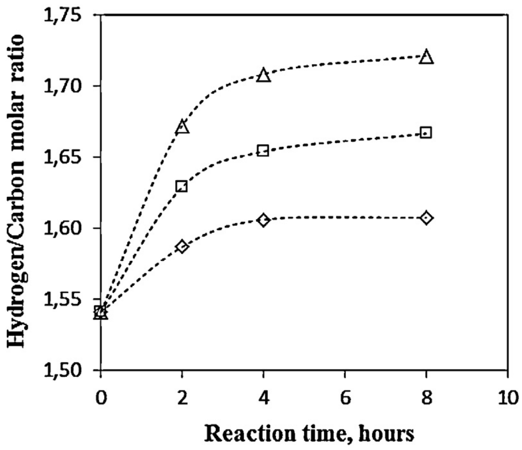

Fig. 7. H/C molar ratio of hydrotreated liquid phase at different reaction temperatures [663 (◊), 673 (□) and 683 K (△)].

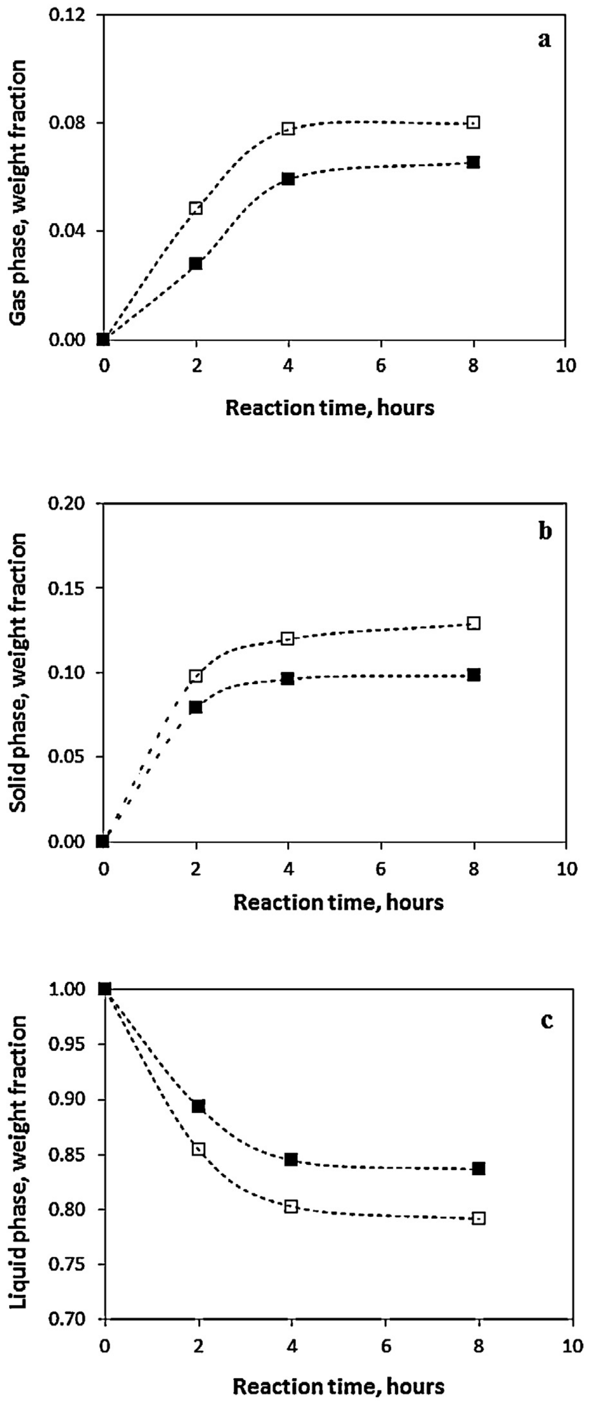

Fig. 8. Gas (a), solid (b), and liquid (c) fractions of hydrotreated Maya crude oil at 400 °C and different catalyst concentrations [300 (□) and 1000 ppm of Mo (■)].

Fig. 6 presents the evolution of the concentrations of sulfur and nitrogen in the hydrotreated liquid phase at different reaction temperatures. The results indicate that the concentration of this impurities in the liquid phase decrease when the reaction temperature is increased. Sulfur goes from 3.78 wt% to less than 2.6 wt%, while nitrogen that in Maya oil has73.9 ppm N, is reduced to 40 ppm N at 390 °C and to 23 ppm N at 410 °C. The increase of sulfur and nitrogen elimination with time and temperature can be associated to the catalytic HDS and HDN reactions but also to the precipitation of solids carrying with them an important fraction of the heteroatom-containing molecules. In fact, Figs. 2 and 6 show the concentration of sulfur and nitrogen follow a mirror-like trend with the production of solids. Therefore, the removal of these impurities can be mainly associated to the precipitation of solids.

On the other hand, the H/C molar ratio of the hydrotreated liquid phase at different reaction temperatures is shown in Fig. 7. In general, the H/C ratio presents a higher value when the reaction temperature was increased. This effect can be associated to the catalytic hydrogenation of smaller molecules and to the carbon rejection induced by the thermal cracking process.

3.4. Catalyst analysis

Previous studies [11,18] show that besides the reaction temperature, other parameters such as catalyst concentration affect the hydrocracking of crude oil. Making a comparison of gas, liquid and solid phases obtained when Maya crude oil is hydrotreated at 400 °C, 1400 psi and different concentration of catalyst (300 and 1000 ppm Mo), gives information on the effect of catalyst concentration. Fig. 8 presents the distribution of gas, liquid and solid phases for these experiments. In general, the formation of gas and solids decreased and the liquid yield increased when the catalyst concentration was changed from 300 to 1000 ppm Mo. This behavior was possibly caused by the hydrogenating ability of the catalyst, which provides active hydrogen and inhibits the typical thermal reactions responsible of the gas and solids formation. However, a more complete study is required to establish the role of the catalyst concentration in the hydrocracking of Maya crude oil.

4. Conclusions

From the physical and chemical characterization of the hydrotreated Maya crude oil at different reaction temperatures, the following conclusions can be pointed out:

(i) In general, the transformation of heavy Maya crude oil into lower fractions follows a parallel-consecutive reaction scheme where vacuum residue converts to smaller fractions, and these fractions in turn, in a consecutive reaction path, are transformed to even lower liquid fractions and gases.
(ii) The gases are formed from the higher fractions but naphtha does not seem to contribute significantly at the conditions of our experiments.
(iii) The formation of solids is significantly affected by the reaction temperature, and is the product of two main contributions, one coming from the coke formation induced by the important contribution of the thermal cracking, and other caused by the precipitation of solids (asphalthenes and other polycondensed aromatics).
(iv) The precipitation of solids also seems to induce the elimination of sulfur and nitrogen compounds present in the liquid phase, mainly in the vacuum residue.
(v) Increasing catalyst concentration from 300 to 1000 ppm decreases the formation of gas and solid phases, and increases liquid yield.

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