Hydrocracking of Maya crude oil in a slurry-phase batch reactor. II. Effect of catalyst load

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HIGHLIGHTS

- Slurry Maya oil hydrocracking evolves differently above and below 50% VR conversion.
- Catalytic hydrocracking does not produce solids below 50% VR conversion.
- Sulfur elimination is highly correlated to asphaltene conversion.
- Catalytic hydrocracking increases production of naphtha and decreases coke and gas.

GRAPHICAL ABSTRACT
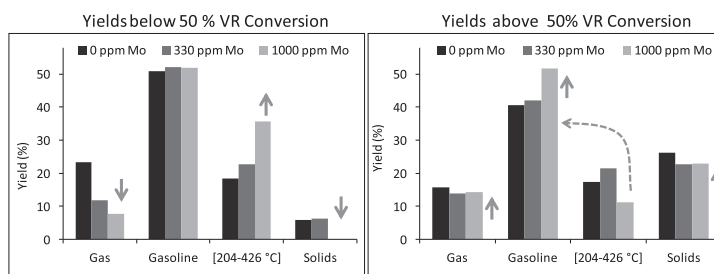
ABSTRACT

The effect of the catalyst load in slurry hydrocracking of heavy Maya crude oil was investigated at mild conditions (390 °C and 1400 H_2 psi). The catalyst load and operating time were varied in the intervals 0–1000 ppm Mo and 0–11 h respectively. The results allowed to establish the transformation routes of the different fractions under thermal or catalytic conditions. Under thermal conditions, the contributors to gas formation were found to be: Asphaltenes ≫ resins > vacuum gas–oil and the use of catalyst inhibited the contributions of resins and vacuum gas–oil. It was found that catalytic slurry hydrocracking evolves in two general reaction stages: the first, dominated by the catalyst-induced reactions, from zero to 50% VR conversion, and the second, above 50% VR conversion, dominated by thermal reactions leading to high production of coke. During the first stage the naturally occurring asphaltenes of Maya crude were effectively transformed to liquid fractions and the formation of coke and new asphaltene-like components were catalytically inhibited. Moreover, the production of middle distillates was enhanced. The second reaction stage in catalytic hydrocracking approaches thermal behavior likely because part of the catalyst is lost when the crude mixture above 50% VR conversion departs from physical equilibrium and forms asphaltenic aggregates that precipitate entrapping some catalyst. During the second reaction stage, middle distillates are transformed to light ends, which are end products because no declination was observed in its production. The use of catalyst improves API gravity and viscosity of the liquid product. In all cases the API gravity increased with naphtha production. The hydrodesulfurization results indicate that most of the eliminated sulfur was of asphaltenic nature, presumably associated to the aliphatic lateral chains of asphaltenes. A qualitative estimation of the importance of the different reaction routes is proposed on the basis of the results of this work.

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1. Introduction

Slurry hydrocracking of heavy crudes is a technological area with increasing attention due to its capability to process feeds with high contents of contaminants (S, N, Ni, V) and large amounts of asphaltenes. In recent years, different hydroconversion processes using slurry reactors have been proposed [1]. Most of the process schemes are once through, although the ENI Slurry Technology proposes the recycling of the heavier fractions to achieve higher conversions. In any case the economy of the different technologies is adversely affected by the fact that most of the catalyst is not recovered from the liquid and solid products [2]. The process typically operates at severe conditions of temperature and pressure ($T \geqslant 420\,°C$ and $P \geqslant 2000$ psi), and uses a finely dispersed transitional metal sulfide catalyst, which minimizes the formation of coke, while the cracking reactions are mainly thermal [2–4]. However, such operating temperatures are associated to large productions of solids and gases with the concomitant reduction in the production of valuable liquids [5,6]. Thus the benefit of heavy feeds hydrotreating technologies is limited by the amount of solids and gases produced, and these two byproducts are depending on the proportions between liquid fractions, resins and asphaltenes as well as their qualities [5,7–10]. Particularly, asphaltenes are highly polycondensed aromatic macromolecules responsible for most of the coke formation during hydrocracking [10–13]. In fact many refinery processes include an initial or intermediate deasphalting stage to avoid poisoning and deactivation of catalysts by coke and metals deposition. Since world availability of light crudes is decreasing while large asphaltenic petroleum reserves are worldwide available the necessity to deal with asphaltenes transformation to valuable and more qualified products becomes evident. It has been demonstrated that asphaltenes are stabilized in the crude oil matrix by resins and that there is a minimum amount of resins as well as a maximum dilution proportion in aliphatic phase to avoid precipitation [14–16]. Resins crack more easily than asphaltenes because of their lower aromatic nature. Therefore equilibrium between resins and asphaltenes cracking must be achieved in order to transform most of the heavy fractions to liquid valuable products. Four main groups of reactions have been reported to occur in oil hydrotreatment above 400 °C: (a) free radicals formation from C–C homolytic scissions, (b) hydrogen rejection by C–H heterolytic or homolytic scissions, (c) hydrogen addition reactions and (d) condensation reactions between free radicals. It is important to say that free radicals formation include β-scission decomposition reactions from which short hydrocarbon molecules (gases) are successively formed from larger molecules. Naturally the equilibrium between the mentioned groups of reactions is temperature dependent and several works report that can be controlled by the addition of hydrogenation catalysts [6,17,18]. However, just a few reports have investigated hydrotreating of heavy feeds at temperatures below 400 °C [19] and the relationship between the different fractions during processing is still unclear since much experimentation as well as characterization and analysis are required. In a previous work we showed that operating at 400 °C the thermal effects were so fast that the catalyst made only small differences in gasoline production and middle distillates with the same level of coke production, while operating at 390 °C more intermediate and heavy liquid fractions were produced with lower associated coke in the catalytic hydrotreating which implied the asphaltenes transformation to liquid fractions [20]. In the present work the temperature of 390 °C was chosen since it is low enough to make distinguishable the catalytic effects but high enough to maintain the importance of thermal effects. Thus the aim of this work is to analyze the changes induced during hydrotreating of heavy Maya oil in slurry reactors when the load of molybdenum, used as catalyst in the form of MoS_2, was varied from 0 to 1000 ppm Mo. To this end, a series of hydrocracking tests using different loads of catalyst (0, 330 and 1000 ppm Mo) and varying operating time (0–11 h) were performed at $T = 390\,°C$ and 1400 psi.

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 0, 330 or 1000 ppm of Mo, introduced as finely ground ammonium heptamolybdate powder solid, used as catalyst precursor for MoS_2. The reactor was pressurized to 1400 psi H_2 and connected to a tank of 2 L to mitigate the pressure changes due to the thermal expansion and cracking reactions. Before and during the reaction, the catalyst particles were dispersed in the Maya crude stirring at 700 rpm. Then, the reactor was heated at a rate of 5 °C/min, from room temperature to 350 °C and this temperature was kept constant for 1 h to activate the catalyst in situ with the sulfur present in the feed. It was estimated that less than 2% of the sulfur present in Maya crude was required to transform the maximum load of catalyst precursor to MoS_2. In previous tests, it was observed that at these activating conditions thermal cracking was not significant but high enough to ensure H_2S formation to transform the precursor to MoS_2. Finally, the reactor was heated to 390 °C and the hydrocracking was carried out isothermally during 1, 2, 3, 4, 5, 8 or 11 h. Concerning the extent of catalyst sulfidation, a comparative experiment using MoS_2 activated ex situ, showed similar vacuum residue conversion, liquid yield and formation of gases than those obtained with the in situ activated catalyst, indicating that most of the Mo in the catalyst precursor was converted to MoS_2. Moreover, in the TEM micrographs of the solid produced in the reactor after hydrotreatment during 5 h, particles of about 30 nm showing fringes of MoS_2 with an interlayer distance of 0.62 nm were observed, suggesting catalyst encapsulation by the produced solid. However, the results from EDX analysis of zones of the solid produced in the reactor were not conclusive since revealed a non-uniform atomic distribution of the S/Mo ratio, which fluctuated from 1.09 to 6.77.

2.2. Characterization

The composition of the Maya crude used as feed is reported in Table 1. Gases, solids and liquids were generally produced from hydrocracking. The gas production was evaluated by mass

Table 1
Maya heavy oil properties.

Fraction (wt%)/property	Maya crude
Gasoline (−204)	13
Kerosene, jet fuel (204–271)	9
Diesel (271–343)	10
AGO (343–426)	11
VGO (426–538)	13
VR (538⁺)	44
S (wt%)	3.78
N (wt%)	0.35
V (wt ppm)	204
Ni (wt ppm)	36
API gravity	19.43
Viscosity (ctS)	824
H/C atomic ratio	1.54
Asphaltenes n-C₇ insol. (wt%)	13

Note: API gravity and viscosity measured at 15 °C.