HYDROPROCESSING HEAVY OILS AND BITUMEN USING UD CATALYSTS: EFFECT OF THE FEEDSTOCK NATURE ON PRODUCT STABILITY

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Introduction

Technologies for upgrading heavy feedstocks can be divided into two general routes: (i) carbon rejection and (ii) hydrogen addition processes.[1] Both routes have important limitations, and considerable effort have been committed to develop new technologies, or to improve existing ones, in order to process these unconventional oils which contain high amounts of coke precursor materials and contaminants. Focusing on in-reservoir upgrading application, the reactivity of full range (non fractioned) heavy oils and bitumen using ultra-dispersed catalysts (UD catalysts) was evaluated using different crude oils. A comparison between both thermal hydrocracking (THC) and catalytic hydroconversion (CHC) processes will be used to define the impact of the UD catalysts on conversion and product stability as a function of the feedstock composition.

Experimental

Four different crude oils were used as feedstock namely: a) Athabasca bitumen; b) Llancanelo and La Paulina heavy oils; and, c) a South-American heavy oil. The compositions of these feedstocks are given in Table 1.

The methodology for preparation and formulation for the UD catalysts is similar to those already reported[2,3], in which aqueous solutions of Ni, W and Mo metal salts are emulsified in the feedstock. An UD catalyst concentration of 1200 ppmw was used for all the experiments. The catalytic emulsion with the metal salt precursors is fed into the reactivity unit, in which the emulsion will be decomposed, leaving the catalytic particles dispersed in the hydrocarbon feedstock ready for reaction. The reactivity of the different feedstock was evaluated for both processes (THC and CHC) in a laboratory scale reactivity unit. The effective volume of the reactor is 20 cm^3. The operational parameters investigated for both processes are: 400 psig (hydrogen), residence time of 8 hours and reaction temperature from 360 to 400 °C.

The limit conversion for both processes was defined as a function of liquid product stability using the P value as reference.[4] Samples with a P value of 1.0 are unstable, i.e., already precipitated. Samples with Pv's near 1.1 are approaching instability with respect to the onset of asphaltene precipitation. The P value of 1.15 was used as reference for the limit conversion.

Hydrocarbon group-type SARA distributions (saturates, aromatics, resins, and asphaltenes) in the feedstock were determined by combining micro-deasphalting with thin layer chromatography (TLC-FID). Details have been covered in a recent publication.[5]

The microcarbon residue (MCR) method (ASTM D-4530) was used to determine the amount of carbonaceous residue formed after evaporation and pyrolysis of petroleum materials under defined conditions, and is intended to provide some indication of the relative tendency to form coke from the studied samples.[6] The coke content in the liquid products after reaction was defined as the amount of material insolubles on chloroform recovered by filtration using a Teflon membrane of 0.2μm.

The simulated distillation (SimDist) analyses were performed in an Agilent Gas Chromatograph Model 6890N used for High Temperature Simulated Distillation (ASTM D - 7169-2005).[7] The results from SimDist are used to calculate the residue conversion, using equation 1.

$$Conv_{545+°C} = \frac{Feed_{545+°C} - \text{Pr}oducts_{545+°C}}{Feed_{545+°C}} \times 100 \quad (1)$$

Table 1. Feedstocks Properties

Feedstock	Athabasca bitumen	Llancanelo heavy oil	La Paulina heavy oil	South-American heavy oil
API	9.5	12.3	14	12
Viscosity @ 40 °C, cP	7300	18,675	> 170,000	2822
MCR	12	12	12.5	12.12
Sulfur, wt %	4.85	2.46	0.2	1.1
HIGH TEMPERATURE SIMULATED DISTILLATION				
IBP-215 °C	2.9	2	0.6	1.52
215-343 °C	15	11.5	7.1	22.65
343-545 °C	32.2	29.7	27.3	46.57
545 °C	50	56.8	64.6	29.27
SARA Hydrocarbon Distribution				
Saturates	12.1	12.4	15.9	39.7
Aromatics	37.8	45.3	17.4	40.2
Resins	39.4	31.8	66	7.7
C_7-Asphaltenes	11.8	10.5	0.7	12.6

Results and Discussion

Athabasca bitumen. The viscosity of the liquid products as function of the residue conversion for both processes (THC and CHC) is plotted in Figure 1. A conversion limit for the THC process around 33% was found at a P value of 1.15. On the other hand, in the presence of UD catalysts (CHC) higher conversion can be reached (around 39%) with a P value of 1.2; further increase in conversion remains feasible. One of the advantages of the catalytic process can be observed in this figure. A product with a lower viscosity can be achieved since a higher conversion with stable liquid products can be obtained for the catalytic process.

The *ΔMCR* (differences between the micro-carbon in the feedstock and the products) as function of conversion for both processes is plotted in Figure 2 for Athabasca bitumen. A lower MCR content in the presence of the UD catalyst with respect to the TC experiments is observed. This result

confirms that the UD catalysts are playing a hydrogenation role during the hydroconversion of both feedstocks.

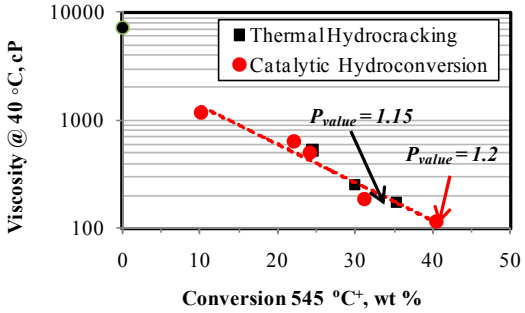

Figure 1. Viscosity upgrading on Athabasca bitumen as a function of conversion for both thermal cracking and catalytic hydroconversion processes.

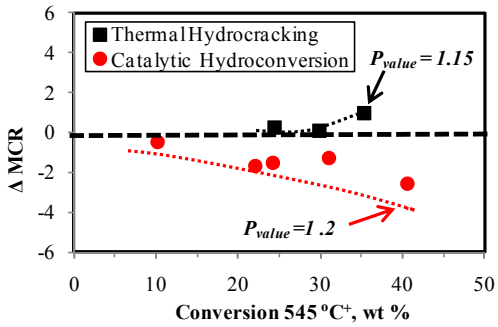

Figure 2. Variation on the MCR content as a function of Athabasca bitumen's conversion for both thermal cracking and catalytic hydroconversion processes.

Llancanelo and La Paulina heavy oils. The effect of conversion (as function of the reaction temperature) on viscosity for both THC and CHC processes for Llancanelo heavy oil is plotted in Figure 3. For the operating conditions explored in this work, the conversion limit for the TC operation was found around 30 wt % with a P value of 1.15. Any increment of conversion above this value leads to unstable products. With the ultradispersed catalysts conversion above, 32 wt % can be reached without any problem on product stability (P value> 1.3). That means that the severity of the system can be increased to achieve more conversion with less problems regarding stability of the liquids products.

The Paulina heavy oil shows the same trend found for the previous feedstocks, as it can be observed in Figure 4. In this particular case the limit conversion for thermal hydrocracking process was not reached, however it is once again demonstrated that for catalytic process' higher conversion (29 wt %) with more stable liquid products (P value >1.3) can be obtained when using UD catalysts.

For both heavy oils (Llancanelo and La Paulina) lower viscosity can be reached in the catalytic process, due to the stability of the liquid products.

The *ΔMCR* as function of conversion for both processes is plotted in Figures 4a and 4b for Llancanelo and La Paulina heavy oils, respectively. Again, the MCR content is lower in the presence of UD catalysts, which agree with the results obtained when processing Athabasca bitumen.

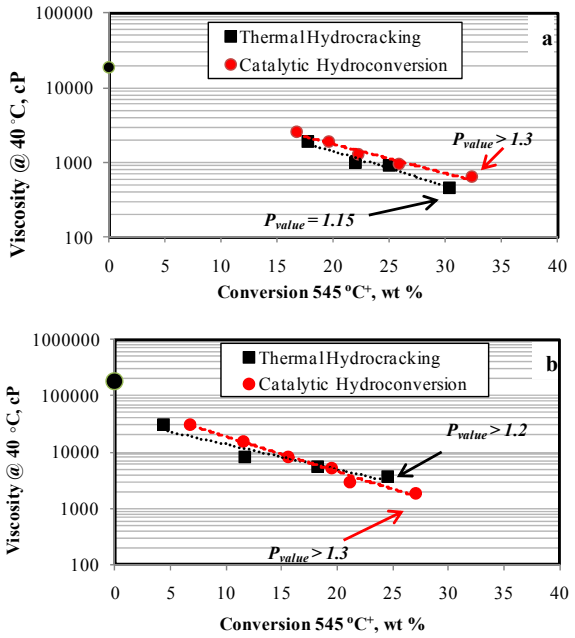

Figure 3. Viscosity upgrading on: a) Llancanelo and b) La Paulina heavy oils as a function of conversion for both thermal cracking and catalytic hydroconversion processes.

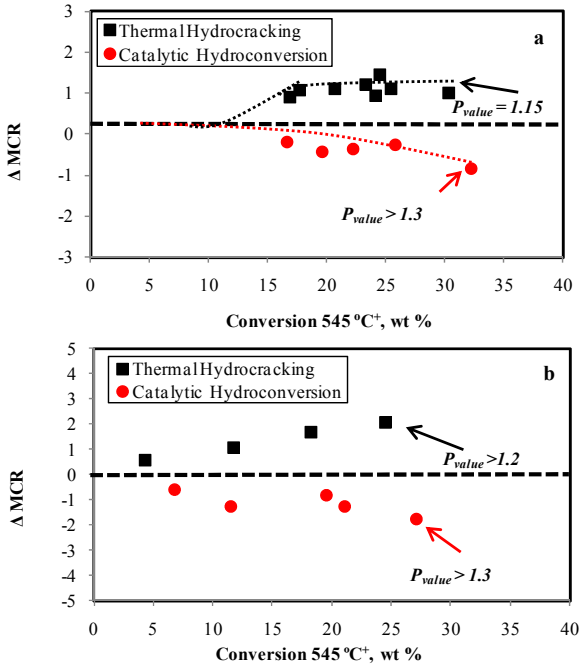

Figure 4. Variation on the MCR content as a function of conversion for both: a) Llancanelo and b) La Paulina heavy oils after thermal cracking and catalytic hydroconversion processes.

Products from Llancanelo heavy oil processing were selected for further evaluation. Thus, asphaltenes content as well as coke production were estimated.

Figure 5 shows the results for asphaltenes content for the Llancanelo heavy oil for both processes, wherein an increment was observed for thermal cracking experiments (above the initial asphaltenes concentration present in the feedstock), than for the catalytic process.

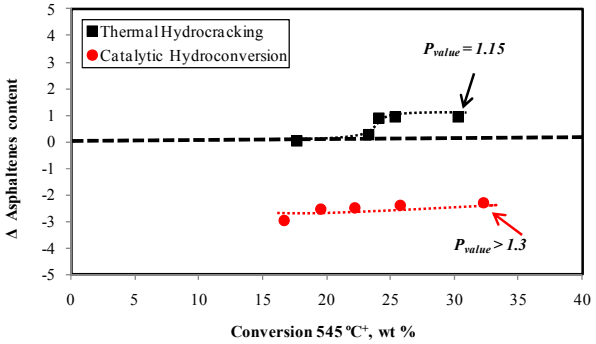

Figure 5. Variation on asphalthenes content as a function of conversion for Llancanelo heavy oil after thermal cracking and catalytic hydroconversion processes.

The results for the rate of coke production show a significant difference between both processes, as can be observed in Figure 6 for Llancanelo heavy oil. In the presence of the UD catalysts the rate of coke production decreases and the trend does not follow the exponential function found for the thermal cracking experiments. This result agrees with the lower MCR content observed for the CHC experiments.

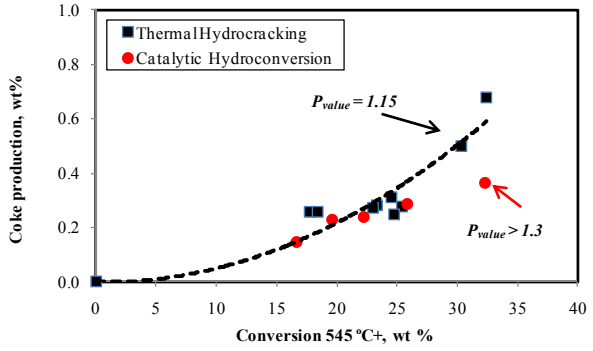

Figure 6. Coke production as a function of conversion for Llancanelo heavy oil after thermal cracking and catalytic hydroconversion processes.

South-American heavy oil. The results for the evaluation of the South-American heavy oil reported in Figure 7 shows that only conversion (with stable liquid products) around 10 wt% for THC and 15 wt% for CHC can be reached. Despite this limitation, higher conversion with stable products can be reached with the presence of the UD catalysts. The characterization of this heavy oil (see Table 1) shows a SARA hydrocarbon distribution with high proportion of saturates and aromatics, feedstocks with similar composition have been reported previously as unstable crude oils.[8] In this graph, due to the instability of this feedstock, is difficult to observe any difference in terms of viscosity between the two processes. However, the presence of the UD catalysts seems to be beneficial for obtaining liquid products with less viscosity.

The ΔMCR as function of conversion for both processes is plotted in Figure 8. For CHC experiments an initial decrease on MCR with respect to the feedstock was found. Once the conversion limit for CHC process was reached an increment of MCR is observed. Since the MCR content decreased further in the presence of the UD catalyst when compared to the thermal cracking experiments (for stable points) one can infer that the UD catalysts are playing a hydrogenation role during the CHC experiments.

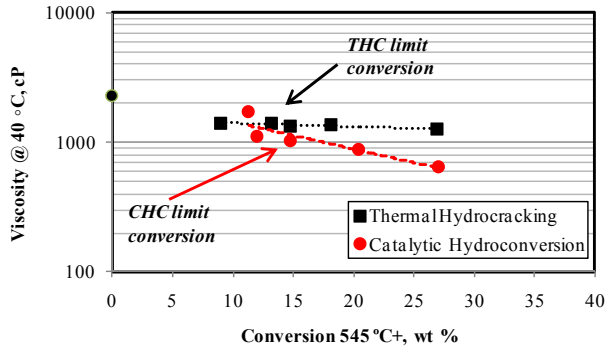

Figure 7. Viscosity upgrading on the South-American heavy oil as a function of conversion for both thermal cracking and catalytic hydroconversion processes.

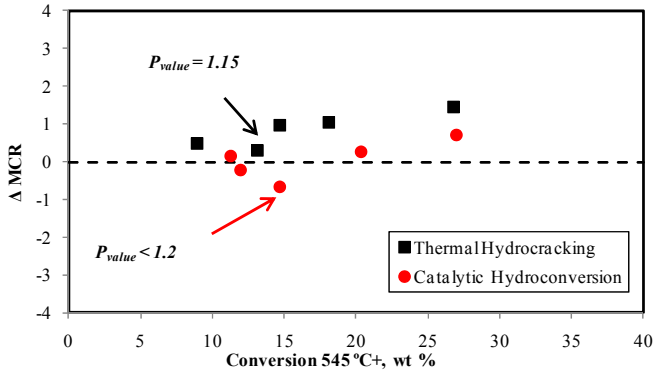

Figure 8. Variation on the MCR content as a function of the conversion of the South-American heavy oil for both thermal cracking and catalytic hydroconversion processes.

Conclusions

These results demonstrate the effect of UD catalysts on liquid product stability and quality. The presence of UD catalysts allows higher conversion than the thermal cracking process both in presence of hydrogen for all the feedstock evaluated. Results have shown that UD catalysts play an important hydrogenation role, since inhibition in coke

formation and decrease in micro-carbon (MCR) and asphaltenes content was found for CHC.

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