Treatment of vacuum residues in hydroconversion conditions

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Abstract. In this paper the use of a liquid homogeneous catalyst has been studied in reactivity vacuum residues by hydroconversion under different conditions. To cover a wide range of compositions, six (6) vacuum residues were selected from crude mixtures. Hydroconversion test were performed in batch reactor with hydrogen atmosphere at about 2000 psi in a temperature range between 430 and 480°C. The results allowed to establish that the reactivity hydroconversion conditions about coke formation is higher in vacuum residues with higher content of resins and asphaltenes. The reaction conditions promote distillate formation, however, with increasing stringency conditions, the distillate yield decreases due to distillate transformation into temperature range 430 and 460°C compared to the tests performed without catalyst demonstrating that the use of homogeneous catalyst is an alternative to treating vacuum residues and results are satisfactory in the conversion processes. Finally, predictive expressions have been developed in the formation of products depending on the conditions of temperature and physicochemical properties of processed vacuum residue.

1. Introduction

Oil is known as one of the main non-renewable energy resources in the world, is processed for the purpose of generating fuel and value aggregate products. With increased heavy oil production and high demand for fuel, the refineries have been forced to rethink their processes with new diets what it's projected a high increase in the production of vacuum residues with numbers that can range between 35 and 50vol% with respect to oil processed [1]. Oil is considered a complex fluid formed of hundreds of thousands of molecules, with significant differences in their molecular structures and its more complex molecules are concentrated at the vacuum residues [2, 3]. With the high availability of these residues, it has been promoted to the search for processes that allow its transformation as thermal carbon rejection processes and hydroconversion [4, 5]. In hydroconversion processes the hydrocarbon is contacted with hydrogen in the presence of a catalyst under temperature conditions in the range between 300 and 450°C, and the hydrogen pressure between 800 and 2900 psi [6]. In studies oriented to catalytic conversion, the reactivity was evaluated in processes that include the use of middle distillates and streams from heavier fractions. For example, Ortega et al. [7], Fortain et al. [8] and Samina et al. [9] were able to establish that the increased of conversion yields of vacuum residues and heavy crudes is mainly due to increase in temperature. However, with the presence of catalysts were achieved conversions up to 70% of heavy hydrocarbons, with reductions in sulphur and nitrogen content above 60 and 55%, respectively. The objective of this study is to evaluate the effect of a homogeneous catalyst under different temperature conditions in the vacuum residues treatment.
2. Experimental

For the development of this work were selected six (6) vacuum residues from crude mixtures. The characterization was carried out using the ASTM methods for the following properties: Conradson Carbon (CCR) D-4530, simulated distillation D-7169 and compositional analysis SARA D-2007.

2.1. Treatment of vacuum residues by hydroconversion

An amount of vacuum residue and liquid catalyst NM is added to the batch reactor. The react is pressurized with hydrogen to effect the optimal reaction. Then the batch reactor is subjected to severe conditions up to the reaction temperature for 20 minutes. After the reaction, the reactor is cooled in ice water in order to stop the reaction. With the objective to vary the conversion and to determine the performance of the reaction, experiments were performed in the temperature range of 430 to 480°C. Finally, the obtained products are recovered, in order to perform the respective balance mass.

3. Results and discussion

Table 1 shows the characterization of vacuum residues selected for this study.

It is evident from the data selected vacuum funds differ significantly in their properties. The content of saturates, aromatics, resins and asphaltenes vary by a factor of 4, 1.6, 1.9 and 6 respectively.

| Property          | Method         | Min  | Max  |
|-------------------|----------------|------|------|
| Density gr/ml     | ASTM D-4052/70 | 1.01 | 1.06 |
| CCR (%wt)         | ASTM D-4530    | 17.1 | 34.6 |
| Saturates (%wt)   | ASTM D-2007    | 4    | 16   |
| Aromatics (%wt)   | ASTM D-2007    | 34   | 56   |
| Resins (%wt)      | ASTM D-2007    | 20   | 37   |
| Asphaltenes (%wt) | ASTM D-2007    | 5    | 30   |
| T50, °C           | ASTM D-7169    | 638  | 747  |

3.1. Effect of temperature

Figure 1 shows the variation in the reaction temperature significantly modifies the performance of reaction products. As the reaction temperature increases coke formation has an increase which depends on the nature of the sample. Coke formation can be attributed largely to the asphaltenes content. For this reason, the vacuum residue VI with a percentage of asphaltenes of 30% by weight and the vacuum residue I with a percentage of asphaltenes of 5% by weight showed the highest and lowest coke formation during the entire range temperature.

Figure 1. Hydroconversion experimental results: (a) Vacuum residue I and (b) Vacuum residue VI.
Meanwhile, the results show a decrease in the percentage of distillates as the temperature increases mainly due to cracking of the newly formed structures which contribute to the formation of gases and low coke yields. The above allows clarify the formation of gases where the percentage of these increases when increase the reaction temperature.

3.2. Effect of catalyst

To evaluate the effectiveness of the catalyst with the temperature on the inhibition of coke formation, cracking tests were conducted to vacuum residue VI without catalyst. Figure 2 shows that the production of coke for the hydroconversion process with catalyst is lower with respect to the tests without catalyst for vacuum residues I and VI in the range of temperatures between 430°C and 480°C. The results show a consistent effectiveness in inhibiting catalyst coke formation from 79 to 63% by weight and 89 to 35% by weight in the temperature range from 430 to 460°C, for vacuum residues I and VI respectively. However, in conditions above of 460°C the coke conversions are similar with and without addition of catalyst, due to problems of diffusion of hydrogen. The results corroborated that at high temperatures the dominant process is the thermal cracking. Therefore, although the catalyst plays an important role in hydrogenation processes, it has little effect on the control of cracking mechanisms.

![Figure 2](image)

**Figure 2.** Coke yield with and without catalyst: (a) Vacuum residue I y (b) Vacuum residue VI.

3.3. Prediction of product formation

The development of predictive correlations for production of coke, distillates and gas from six (6) vacuum residues was performed by multivariate analysis using Staggraphic Centurion XVI. As mentioned above, the temperature has a predominant effect on the formation of the products obtained in the process of hydroconversion of vacuum residues. Therefore, normalized correlations for prediction of performance of products were made by the following general expression:

\[
\%\text{Products}_i = \alpha_i + \beta_i T
\]  

Where, \(i=\%\) Coke, \% Distillates y \% Gas.

\[
\alpha = 1781.9 - 1451.2\text{Density} + 1.5\text{Saturates} - 0.6T50
\]

\[
\beta = -4.1 + 3.33\text{Density} - 0.003\text{Saturates} + 0.001T50
\]

\[
\alpha = 3604.2 + 38.3\text{CCR} + 1.5\text{Aromatics} - 6.2T50
\]

\[
\beta = -8.1 - 0.08\text{CCR} - 0.003\text{Aromatics} + 0.001T50
\]
% Gas:

\[ \alpha = -5359.8 + 27.9 \text{Saturates} + 16.2 \text{Aromatics} + 6.2T50 \]  \hspace{1cm} (6)

\[ \beta = 12.3 - 0.06 \text{Saturates} - 0.033 \text{Aromatics} - 0.013T50 \]  \hspace{1cm} (7)

Figure 3 shows the percentage values of experimental and calculated for distillates and coke. Correlations for predicting the percentage of coke, gases and distillates showed standard deviations between 1.7 and 2.6% by weight. The results indicate that the correlations obtained are appropriate for predicting the performance of the products obtained from vacuum residue at hydroconversion conditions.

4. Conclusions

Increasing the reaction temperature favours the production of coke and gases. The increase in coke formation at temperatures above 480 °C is due to the decrease of hydrogen diffusion. In the case of gases and distillates it is observed at temperatures above 460 °C the distillate yield decreases and promotes the production of gases.

The inhibition of coke formation produced by the catalyst in the temperature range from 430 to 460°C for vacuum residues I and VI decreases from 79 to 63% by weight and 89 to 35% by weight. However, for temperatures above 460°C to coke conversions tend to be similar with and without addition of catalyst. However, trends in inhibiting coke formation depends on the nature and percentage of compositional fractions SARA of vacuum residues.

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