Reactivity study on thermal cracking of vacuum residues

A Y León1, S D Díaz1, R C Rodríguez1 and D Laverde1
1 Universidad industrial de Santander (UIS), Bucaramanga, Colombia.

E-mail: yovani_96@hotmail.com

Abstract. This study focused on the process reactivity of thermal cracking of vacuum residues from crude oils mixtures. The thermal cracking experiments were carried out under a nitrogen atmosphere at 120 psi between 430 to 500°C for 20 minutes. Temperature conditions were established considering the maximum fractional conversion reported in tests of thermogravimetry performed in the temperature range of 25 to 600°C, with a constant heating rate of 5°C/min and a nitrogen flow rate of 50ml/min. The obtained products were separated into gases, distillates and coke. The results indicate that the behaviour of thermal reactivity over the chemical composition is most prominent for the vacuum residues with higher content of asphaltenes, aromatics, and resins. Finally some correlations were obtained in order to predict the weight percentage of products from its physical and chemical properties such as CCR, SARA (saturates, aromatics, resins, asphaltenes) and density. The results provide new knowledge of the effect of temperature and the properties of vacuum residues in thermal conversion processes.

1. Introduction

The increase of heavy oil in the diet of the refineries has been paying great attention on the oil industry due to the projected high increases in the production of vacuum residues [1]. These loads are hard to process because of their high content of asphaltenes, heteroatoms and metals. Vacuum residues have elevated equivalent atmospheric points and are classified as the non-distillated fraction in vacuum distillation [2]. To take advantage of the heavier fractions of oil, refineries have been applying and improving their thermic conversion processes to treat the low quality loads and generate lighter products with commercial value [3].

Thermic conversion processes depend of operating conditions as temperature, reaction time and charge nature [4]. Francoise et al. [5] and Jasvinder et al. [6] achieved to establish that the convertible fraction of the heavier fractions of vacuum residues type C14+ and asphaltenes toward distillates, is due to the release of molecules lower in molecular size, but their thermal reactivity increases in structures with a greater degree of aromaticity and content of side chains. Moreover, Marsh et al. [7] and Van Heek et al. [8], proved that the yields of distillate fraction decreases with increasing temperature, resulting in products with orders of yield as ACPM>Kerosene>Nafta>Gases.

In studies of thermal conversion reactivity, the analysis by thermogravimetry has played an important role. Thermogravimetry is a technique that measures the mass changes in function of time and temperature. Also it is widely used in thermal analysis to determine reactivity zones and kinetic parameters that characterize the heavy crude oil, vacuum residues and its derivate [9,10].

The objective of this study consists of determining the reactivity on thermal cracking of vacuum residues in a batch reactor. The research was developed in two stages: the first one consisted in a thermogravimetric analysis (TGA) in order to find the higher reactivity zone. Secondly, thermal
cracking tests were made in a temperature range of 430–500°C and a 120psi pressure. Additionally, predictive correlations of the yield to coke, distillates and gases, were established from physicochemical properties of vacuum residues. Furthermore the purpose of this work is to provide new knowledge related to the effect of the temperature and nature of vacuum residues in thermal conversion processes.

2. Methodology
For this work were selected six (6) vacuum residues from crude oil mixtures. Also the characterization was realized using the ASTM methods for carbon Conradson (CCR) D-4530, simulated distillation D-7169 and compositional analysis SARA D-2007.

2.1. Thermogravimetric analysis
(TA Instruments TGA/2050, Thermogravimetric Analyzer). In trials was analysed approximate amounts of 10mg. The thermal decomposition was performed by increasing the temperature up to 600 with flow 50ml/min of nitrogen at a heating rate of 5/min.

2.2. Thermal cracking tests
The samples of vacuum residues are added to the batch reactor; it is pressurized with nitrogen to guarantee inert atmosphere. Later the reactor is submitted to the tests cracking within a temperature range of 430–500°C. Finally, it is cooled with water and the products are recovered in order of realize mass balances.

3. Results discussion
Table 1 shows the used ASTM methods for the characterization of the two vacuum residues which content of asphaltenes is appreciably different from one another.

| Property             | Method          | FV1 | FV2 |
|----------------------|-----------------|-----|-----|
| Density gr/ml, 15°C  | ASTMD-4052/70   | 1.0 | 1.1 |
| CCR (%wt)            | ASTM D-4530     | 17  | 35  |
| Saturates (%wt)      | ASTM D-2007     | 16  | 13  |
| Aromatics (%wt)      | ASTM D-2007     | 42  | 41  |
| Resins (%wt)         | ASTM D-2007     | 33  | 20  |
| Asphaltenes (%wt)    | ASTM D-2007     | 9   | 26  |
| T<sub>50</sub>, °C    | ASTM D-7169     | 640 | 707 |

3.1. Thermogravimetric analysis
Figure 1 shows the differential curve of the mass derivate respect to the temperature. This curve allows demonstrating the temperature where there is greater loss of mass, approximately to 430°C. The results of the two (2) vacuum residues selected indicate that the higher reactivity zone is in a range of temperatures between 400 to 500°C. Therefore these results allowed to establish the range of temperature for the study of thermal treatment in a reactor batch which was determinate to be between 430–500°C.

3.2. Temperature effect
Figure 2 shows the coke formation, distillates and gases yields for two vacuum residues respectively. It indicates the direct relation between the reaction temperatures and coke yield for both vacuum residues. However, the coke formation depends on its nature.

The asphaltenes content is an important indicator of coke. This allows clarify that the FV 1 shows lower percentages of coke with respect to FV 2. Meanwhile, distillate yield decreases with increasing
temperature due to its transformation to gases and coke. The tendency of gas formation is a result of cracking of the molecules of less to more complexity of SARA fractions.

![Figure 1](image_url1)

**Figure 1.** Differential weight loss for vacuum residues at 5°C/min.

![Figure 2](image_url2)

**Figure 2.** Product yields. (a) FV 1 and (b) FV 2.

### 3.3. Products formation predictions

The correlations for predicting coke yield, distillates and gases were made from the (6) vacuum residues using multivariate analysis with Staggraphic Centurion XVI. Therefore, normalized correlations for prediction of performance of products were made by the following general expression:

\[
\%\text{Coke} = m \cdot T + a
\]  
(1)

\[
a = 523.5 - 0.96 \cdot T_{bp50} - 8.2 \cdot \text{CCR} + 3.5 \cdot \text{SAT} + 10.5 \cdot \text{ASP}
\]  
(2)

\[
m = -1.2 + 0.002 \cdot T_{bp50} + 0.02 \cdot \text{CCR} - 0.008 \cdot \text{SAT} - 0.02 \cdot \text{ASP}
\]  
(3)

\[
\%\text{Distillates} = b \cdot T^2 + c \cdot T + d
\]  
(4)

\[
b = 0.04 + 0.004 \cdot \text{API} + 0.0023 \cdot \text{CCR} - 0.0002 \cdot \text{TB50} + 0.0004 \cdot \text{RES}
\]  
(5)

\[
c = -35.8 - 2.16 \cdot \text{CCR} - 0.38 \cdot \text{RES} - 3.77 \cdot \text{API} + 0.18 \cdot \text{TB50}
\]  
(6)

\[
d = 8008.3 + 855.4 \cdot \text{API} + 492 \cdot \text{CCR} - 41.2 \cdot \text{TB50} + 89.3 \cdot \text{RES}
\]  
(7)

\[
\%\text{Gases} = e \cdot T^2 + f \cdot T + g
\]  
(8)

\[
e = -0.05 + 0.00011 \cdot \text{Tb50} + 0.00001 \cdot \text{API} - 0.00027 \cdot \text{RES} - 0.00051 \cdot \text{ASP}
\]  
(9)
\[
f = 48.6 - 0.144 \times Tb50 - 0.096 \times API + 0.016 \times RES + 0.27 \times ASP \\
g = -11067.2 + 21.9 \times Tb50 + 5.03 \times API - 61.8 \times RES - 106.3 \times ASP
\]

Figure 3 shows coke yield and distillates experimental and calculated. The predictive correlations for coke, distillates and gas production, showed standard deviations between 1.13 y 2.95wt%. The results are satisfactory and can be applied to predict the coke yield, distillates and gas thermal cracking processes.

4. Conclusions
Thermogravimetric analysis is an important tool to determine the operational ranges in the thermal cracking treatment of vacuum residues; therefore favourable results can be obtained from small sample amounts under short periods of time.

The increase in reaction temperature favours the coke and gases production. Compared to the distillates production where it yields decreases with the increase in temperature, as a result from its transformation into gases and coke.

The predictive correlations for coke, distillates and gas production in thermal treatment of vacuum residues are satisfactory, taking into account that the average standard deviation is less than 3%.

Acknowledgments
Special acknowledgments for the Industrial University of Santander (UIS) Chemical engineering faculty, for financial support, scientific and human development of this work, and Corrosion Research Group (GIC), for its attention and cooperation during the experiments.

References
[1] Stratiev D, Dinkov R, Petkov K, Stanulov K 2010 Petroleum & Coal 52 35
[2] Hedrick B W, Seibert K D and Crewe C A 2006 A new approach to heavy oil and bitumen upgrading (Saudi Arabia: 16th Annual Symposium on Catalysis in Petroleum Refining and Petrochemicals (http://www.uop.com/?document=a-new-approach-to-heavy-oil-and-bitumen-upgrading&download=1)
[3] Sanfilippo D 2009 Bottom of the barrel technology within refining extracting additional value from oil feedstocks using EST technology (Italy: WTG Webinar Connected from San Donato Milanese)
[4] Reza Asgharzadeh Shishavan, Mohammad Ghashghaei, Ramin Karimzadeh 2011 Fuel Processing Technology 92 2226
[5] Francoise Behar, Francois Lorant, Laurent Mazeas 2008 Organic Geochemistry 39 764
[6] Javvinder Singh, M M Kumar, Alok K Saxena, Surendra Kumar 2005 Chemical Engineering Journal 108-3 239
[7] Marsh H 1991 Carbon 29-6 703
[8] Van Heek K H 2000 Fuel 79-1 1
[9] AijunGuo, Xuejun Zhang, Zongxian Wang 2008 Fuel Processing Technology 89 643
[10] Alvarez E, et al 2011 Fuel 90 3602