ESTIMATION OF VISBROKEN AND SELECTIVE CATALYTIC STEAM CRACKED PRODUCT STABILITY USING IATROSCAN TLC-FID.

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INTRODUCTION

Crude oil vacuum residues are characterized by a high concentration of high-molecular-weight compounds such as asphaltenes. These compounds impart undesirable properties to the residue (i.e. low viscosity) and affect thermal and catalytic conversion processes. In many cases, the efficiency of conversion is related to the formation of insoluble carbon-rich deposits. In visbreaking (VB) and selective catalytic steam cracking (SCSC) processes, severity of the operation is limited by heater fouling and product instability, which is dependent on the asphaltene content of the feed.

An experimental measuring of the stability of the visbroken and selective catalytic steam cracked residues is given by the Shell P-value. This parameter is a measure of the flocculation potential of asphaltenes and their trends to form solid deposits. P-Value is directly proportional to the stability. Its determination involves the visual detection of the flocculated asphaltenes by using a microscope. In consequence, results depend on the operator ability and can vary from an analyst to another. Additionally, the procedure is time consuming.

One approach to determine the instability of heavy oil residues is through the colloidal instability index (CII), which is based on the chemical composition of the residue. The CII is defined as ratio of the sum of asphaltenes and saturates to the sum of the peptizing resins and aromatics:

\[ \text{CII} = \frac{\text{Asphaltenes} + \text{Saturates}}{\text{Resins} + \text{Aromatics}} \]

Calculations of this parameter involve a hydrocarbon group type analysis. Saturate, Aromatic, Resin and Asphaltene (SARA) quantification can be achieved either by High Performance Liquid Chromatography (HPLC) or by Thin Layer Chromatography-Flame Ionization Detection (TLC-FID). The former requires the use of liquid chromatography after asphaltene precipitation and quantification by gravimetry, besides, it is time consuming and needs considerable volumes of solvents.

TLC is becoming increasingly popular in the crude oil industry. This technique is recognized as an efficient, fast and cost-effective way to obtain quantitative information about crude oil composition. For separation and quantification, correct use of Iatroscan TLC-FID offers good precision and accuracy, in addition to rapid analysis and low solvent consumption.

Cebolla et. al 7, Karlset al. 10-11 and Sol et. al 12, are some of the researchers that have used this technique for the analysis of SARA constituents in crude oils and solvent extracts.

In this work, we evaluate TLC-FID as an alternative tool to estimate the stability of visbroken and selective steam cracked residues by CII calculations. Results were compared to the conventional P-Value.

EXPERIMENTAL

The samples studied in this work came from test carried out at a pilot plant of 1 barrel/day capacity, using a short Venezuelan residue operated both visbreaking and selective catalytic steam cracking. The reactions were stopped when the bottom (350°C+)

Table 1. Conversion and P-values of feed and products

<table>
<thead>
<tr>
<th>Feed</th>
<th>VB</th>
<th>SCSC-1</th>
<th>SCSC-2(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (wt.%)</td>
<td>2.7</td>
<td>2.9</td>
<td>5.2</td>
</tr>
<tr>
<td>Of 500°C+</td>
<td>28.2</td>
<td>28.5</td>
<td>36.3</td>
</tr>
<tr>
<td>P-Value</td>
<td>2.7</td>
<td>1.15</td>
<td>1.45</td>
</tr>
</tbody>
</table>

(*) SCSC-2 refers to severe conditions in SCSC process (5°C over the fixed temperature)

SARA TLC-FID Analysis. An Iatroscan TH-10 instrument (Iatron Labs Inc.), equipped with a flame ionization detector (FID) and interfaced with a computerized acquisition system (DIONEX AI 450 Optimize) was employed. This instrument was calibrated for quantitative SARA analysis. Pure hydrogen (190 mL/ min, supplied by a hydrogen generator) and pure air (2.0 l/min, supplied by an air cylinder) were used for the detector. Two sets of 10 silica rods, type Chromarod-SIII ( pore diameter 60 Å, particle size 5µm) were used: One for the saturate and aromatic quantification and the other one for asphaltene quantification. Samples were prepared by dissolution in a mixture of toluene: chloroform 1:1 vol:vol to obtain a final concentration of 25 mg/mL. Before sample application, Chromarods were passed twice through the FID to remove contaminants, and to obtain constant activity of the silica layer. Each rod was spotted by 1.0 µl of the sample solution, applied dropwise by using a 1.00 µl syringe. For saturate and aromatic determinations, Chromarods were developed in n-heptane for 40 min; air dried (3 min) and developed again in toluene for 20 min. For asphaltene determinations, the second set of Chromarods was developed in n-heptane/ isopropanol 95:5 vol. % for 20 min. Each set of rods was dried for 3 min and then, pyrolized at a scan speed of 0,32 cm/s.
Figure 1. SARA distribution of the studied 350°C+ residue and the 350°C+ VB and SCSC products.

It is known that during VB, asphaltene formation increases with conversion. This is a consequence of thermal cracking reactions that follow a free radical mechanism, causing asphaltene condensation and formation of heavier products and coke. On the contrary, the mechanism proposed for SCSC suggests the saturation of these free radicals by the incorporation of hydrogen free radicals formed by the catalytic dissociation of water. Thus, asphaltene formation is avoided as well as the early appearance of condensed products potentially unstable.

Figure 1 shows TLC-FID SARA distributions of the feedstock studied and its VB and SCSC 500°C+ products. It is interesting to note that the addition of steam and catalysts to VB produces a residue with higher resin content and less quantity of asphaltenes. This observation indicates that, while asphaltenes are normally produced in VB, they are converted in SCSC. This particular behavior of SCSC favors the quality of the final product.

Some authors have pointed out that the nature of asphaltenes seem to play an important role in the stability of residues regardless of their content; however, others factors such as the content of asphaltenes, the presence of resins and the quality of the oil media must be taken into account.

Considering the crude oil residues as colloidal systems, resins and asphaltenes comprise the dispersed phase while saturates and aromatics form the continuous phase. The interaction among both phases and their influence on the stability of the system is related to the peptizing power of the resins, the solvent effect of the aromatics, the precipitant properties of saturates and the flocculation tendency of asphaltenes.

Lower values of CII indicate higher asphaltene stability due to the dispersant effect of aromatic and resins. CII exhibits an inverse trend to the one showed by P-Value, giving surprisingly a mirror image. As can be seen in Figure 2, higher CII’s correspond to lower P-Values. It is amazing the excellent correlation found between a chromatographic method such TLC-FID and the titration method (P-Value). This interesting correlation offers a potential tool to evaluate product stability in a very fast and accurate way.

Figure 2. Comparison of CII values calculated from TLC-FID data and the P-Value of the VB and SCSC products of the studied 350°C+ residue.

On the other hand, an identical behavior was found when the P-Value was compared to the Theoretical Distribution of Solubility Parameter of these pure asphaltenes obtained by n-heptane precipitation. These findings confirm that asphaltene nature plays an important role in the stability of the residues.

CONCLUSION
Stability of VB and SCSC products was evaluated by calculation of CII, using TLC-FID SARA distribution. Results obtained by this fast and accurate method are in total agreement with the conventional P-Value. Additionally, the CII showed the same trend found in the theoretical studies of the solubility parameter.

CII is proposed as a potential alternative parameter to obtain a rapid evaluation of the bottom product stability during VB and SCSC processes. However, a higher number of samples are being considered to confirm the results shown in this work.

REFERENCES

Fuel Chemistry Division Preprints 2002, 47(2), 657


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