Thermogravimetric description of visbreaker streams in an oil refinery

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ABSTRACT

Chemical characterization of heavy oil fractions is impractical because of their complexity. As an alternative, thermogravimetric analysis (TGA) provides fast and valuable information about composition of streams entering and leaving visbreaker unit in oil refineries. Deconvoluting thermogravimetric curves allows thermal-based composition of visbreaking streams to be elucidated by using pseudo-components: four for visbreaking feed and seven for visbreaking residue. In both cases, some pseudo-components explains volatilization of light substances (viz. naphtha or gasoil) under $350\,°C$, and three explains cracking of heavy molecules (viz. resins or asphaltenes) around $380\,°C$, $411\,°C$ and $453\,°C$. Obtained results make it possible to define a thermogravimetric index that characterizes composition of visbreaking samples (feed and residue). This index is higher in feed than in residue, and it is higher in light samples than in heavy samples. Deconvolution of TGA curves was improved by using autocatalytic kinetic based on extended Prout–Tompkins equation.

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1. Introduction

According to the Oil Market Report (International Energy Agency, http://www.iea.org/), the estimated global oil demand for the fourth quarter of 2016 is 96.8 mb/d (million barrels per day). Such an enormous demand will coincide with an increasing shortage of oil supplies. In this scenario, oil refineries are expected to be able to process increasingly heavier crudes, and so are bottom-barrel upgrading technologies to gain increasing importance in their economic balances [1]. Coking and visbreaking are among them the most successful technologies for this purpose [2].

Coking and visbreaking are based on the thermal cracking of heavy molecules. The main difference between the two processes is the extent of the cracking reaction. In coking, the reaction develops to completion and produces substantial amounts of middle distillate and coke; in visbreaking, however, the reaction is halted to obtain valuable fuel (fuel-oil) from vacuum residue and other heavy slops of oil refinery [3]. Visbreaking can be understood as soft thermal cracking in a liquid phase, a process that is optimized by maximizing middle distillate production without compromising quality in the resulting fuel-oil. Fuel-oil stability depends on asphaltenes deposition after the cracking reaction.

Overcracking due to an excessive temperature or residence time causes asphaltenes to precipitate from their colloidal suspension and form carbonaceous residues in tubes, as well as poor combustion in the boiler burner [4–7].

The visbreaking process has evolved over time. Initially, the cracking reaction was allowed to develop in the furnace coil for a short time and the resulting products were separated in a flash distillation chamber. Subsequently, a soaker drum was inserted behind the heater to decrease the coil temperature and increase the residence time during the cracking reaction [8,9]. Nowadays, monitoring the visbreaking process involves measuring density, viscosity, asphaltenes, sulfur, residual carbon and flash point [10,11] in each two major streams, namely: visbreaking feed (VF) and visbreaking residue (VR). Some of these determinations (e.g., asphaltene measurements) are slow and detract from throughput. Also, these analyses provide process engineers with little information about chemical transformations occurring in the visbreaking unit.

In addition to chemical analysis, thermogravimetric analysis (TGA) has been used to analyze crude oil and other fossil fuels [12–14]. In TGA, a small amount of sample is heated on a thermobalance in a controlled environment (usually nitrogen or air). During heating, samples undergo mass losses that are used to identify specific components or chemical structures present in them. Under thermogravimetric conditions, thermal degradation of oil derivatives in air shows three phases [15]: below $350\,°C$ light components vaporize, between $350\,°C$ and $475\,°C$ heavy components undergo

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cracking, and above this temperature carbonaceous residues oxidize.

In a previous work, we proved that significance of thermogravimetric analysis applied to oil refining monitoring increases when experimental data are supplemented with mathematical treatment that allows deconvoluting TGA curve by using pseudo-components which degrade according to autocatalytic kinetics [15]. On this basis, this work was undertaken with one main purpose: to describe chemical characteristics of visbreaking streams by means thermogravimetric study of their thermal degradations.

2. Material and methods

2.1. Samples

Over a period of 6 months, the visbreaking unit of La Rábida-CEPSA Refinery (Huelva, Spain) was monitored by analyzing a total of 32 samples of visbreaking feed (VF) and residue (VR) both chemically and thermally. The characteristics of visbreaking feeds differ markedly with the properties of the crude being refined (see Table 1). Thus, 30% of the samples processed during the time span of this work were heavy feeds of a high sulfur content, asphaltenes content and viscosity (viz., 3.7 wt%, 8.7 wt% 2155 cSt, respectively, on average); the remaining 70% were light feeds with a low sulfur content, asphaltenes content and viscosity (viz., 0.8 wt%, 1.8 wt% and 1455 cSt, respectively, on average).

2.2. Physicochemical analyses

Physicochemical analyses of the samples were performed according to the following standards: ASTM 4052 [16] for density; ASTM-D445 [17] for viscosity; ASTM D-4530 [18] for carbon residue; ASTM D-4294 [19] for sulfur; ASTM D6560 [20] for asphaltenes.

2.3. Thermogravimetric analysis

All thermogravimetric analyses were performed on a TA Instruments, TGA Q5000IR balance, using a sample mass of ca. 5 mg under nitrogen for pyrolysis runs, and a 4:1 mixture of nitrogen and oxygen for combustion runs. The temperature was raised from 25 to 900 °C at three different rates (5, 10 or 20 °C/min). Carrier gas flow was 100 mL/min.

3. Results and discussion

3.1. Visbreaking unit

Fig. 1 depicts the visbreaking unit. As can be seen, visbreaker feed (VF, mainly vacuum residue) is pumped through a furnace where it is heated at the cracking temperature and subsequently passed to the soaker for cracking. The soaker effluent is quenched before the reaction completes and passed to the fractionator for separation into VR (typically 85% of the initial feedstock), gas (mainly methane, ethane and propane), naphtha and gas-oil (9%). Basically, the visbreaking unit converts a highly viscous component (visbreaking feed VF) into valuable fuel (visbreaking residue VR) with a relatively high content in asphaltenes.

Table 1 characterizes visbreaking feeds over the studied period. In it, data has been grouped according the asphaltenes and sulfur contents of samples in agreement with the modus operandi of the process engineers who usually differentiate between heavy and light visbreaking feeds to adjust cracking severity. The first (heavy feed) are very viscous (2155 cSt) and show high asphaltenes (8.7%wt) and sulfur (3.7%wt) contents. The second (light feed) are
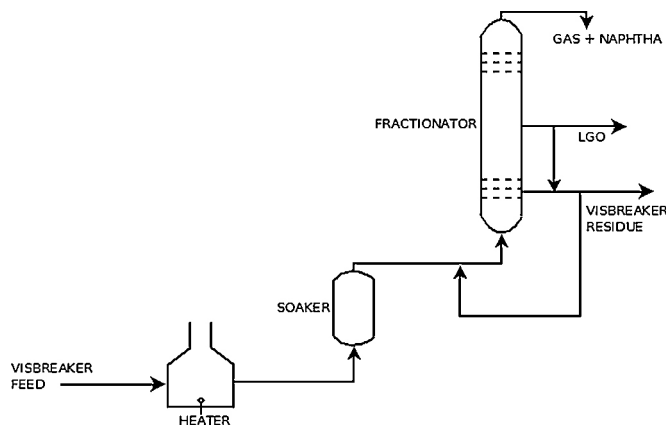

Fig. 1. Scheme of the visbreaking unit.

less viscous (1455 cSt) and show lower values for asphaltenes and sulfur contents (1.8% wt and 0.8% wt, respectively). Throughout the time that the study has lasted, the largest part of samples were light feeds (70%).

For its part, the Table 2 compares average properties for VF and VR. As can be seen, as average, visbreaking unit dramatically reduces viscosity from 1785 cSt to 229 cSt, and increases asphaltenes content from $5.0 \pm 4.5\%$ wt to $10.9 \pm 1.9\%$ wt. For feeds, asphaltenes show a wide range of variation between 0.1% wt and 14% wt, but for residues the range is narrower, between 8% wt and 14% wt. Thus, visbreaking process increases the average level of asphaltenes but significantly reduces the asphaltenes variability in residue (maximum value remains constant but minimum value increases).

3.2. Thermogravimetric characterization of visbreaking streams

Fig. 2 compares the thermal degradation paths for three representative feeds in inert and oxidative environments. These feeds were selected in terms of their asphaltenes content (high, medium or low): HVF (12.8%), MVF (7.5%) and LVF (1.0%), where HVF denotes heavy visbreaking feed, MVF medium visbreaking feed and LVF light visbreaking feed. As can be seen, VF (obtained from vacuum residue) is a refractory material exhibiting different degradation paths depending on the environment used in its thermogravimetric analysis. In nitrogen (Fig. 2a), thermal degradation started above 250 °C, peaked near 450 °C and finished above 500 °C. The derivative of mass loss (DTG curve) was a smooth line with a strong peak at 450 °C and a smooth shoulder near 350 °C. By the end of the analysis (near 600 °C), the thermobalance detected a carbonaceous residue (char, coke) amounting to 6% of LVF and 13% of HVF. The presence of oxygen complicated the thermal degradation path for VF (see Fig. 2b). In an oxidative atmosphere, the DTG curve comprised three distinct zones: i) below 350 °C, ii) from 350° C to 475 °C and iii) above 475 °C. Below 350 °C, the curve exhibited a small, smooth peak due to mass losses caused by vaporization of light components. In the intermediate temperature zone (350–475 °C), the DTG curve exhibited three sharp peaks due to cracking events [3] around the characteristic temperatures (viz., 393 ± 5 °C, 419 ± 4 °C and 451 ± 1 °C). Above 475 °C, the curve exhibited a sharp peak due to char oxidation, the shape and position of which was correlated with the asphaltenes content of the sample (522 °C for HVF and 541 °C for LVF). This result suggests that the reactivity of char obtained after VF pyrolysis depends on their asphaltenes content [21]. Apparently, VF with a high asphaltenes content gives especially reactive char that is easily oxidized over a narrow temperature range.