Reactivity and stability of vacuum residual oils in their thermal conversion ☆

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HIGHLIGHTS

- Colloidal stability is the dominant factor that affects residue thermal reactivity.
- Asphaltene solubility linearly decreases with thermal conversion increasing.
- Residue colloidal stability is mostly dependent on asphaltene solubility.

ARTICLE INFO

ABSTRACT

Thirteen vacuum residual oils originating from Russia, Middle East, Asia, and South America were thermally cracked in a modified high-temperature–high-pressure batch autoclave reactor. It was found that the colloidal stability of the vacuum residual oils expressed by S-value was the dominant factor that affected the residue thermal reactivity. SARA analysis data of the residual oils were confirmed to contain insufficient information about residue thermal reactivity and colloidal stability. It was found that the higher the colloidal stability of a residual oil the lower residue thermal reactivity and the steeper colloidal stability reduction during thermal conversion. The asphaltene solubility was found to linearly decrease with the increase of the thermal conversion, while the maltene solubility power did not always decrease with the increase of the thermal conversion for the studied residual oils. Having in mind that the ebullated bed residue hydrocracking H-Oil process is also based on thermal conversion the properties of commercial straight run Urals vacuum residue (UVR), visbreaker residue obtained by thermal cracking of UVR (UVBR), and ebullated bed hydrocracking (H-Oil) unconverted residue were investigated. It was found that asphaltene solubility lowered linearly with increasing of conversion regardless of the process: visbreaking or ebullated bed hydrocracking. The maltene fraction average molecular weight seems to decrease with the increase of the residue thermal conversion processes visbreaking and ebullated hydrocracking as the asphaltene average molecular weight does for the same processes. It was found that the atmospheric gas oil fraction from visbreaker has no negative effect on residual oil colloidal stability while the vacuum gas oil fraction has negative impact on residue stability in both visbreaker and H-Oil unconverted residual oils. The data generated in this work study suggest that the asphaltene solubility has a bigger impact on the residual oil colloidal stability than the maltene solubility power.

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1. Introduction

In the time of high crude oil prices [1], worsen quality of supplied crude oil and of oil reserves [2], low refining margins [3], and high differential between prices of transportation fuels and heavy fuel oil [4] the significance of bottom of the barrel upgrading processes becomes very high. The trend of decreased demand of heavy oil products additionally supports the leading role of the

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bottom of the barrel (BOB) upgrading technologies in the refining business [5]. The proper utilization of capabilities of BOB refinery units is vital for competitiveness of any refinery. An increase of 0.7% conversion in a visbreaker unit with a capacity of 25 kbpd is equivalent to 7 million US $ per year [6]. The single variable that has the biggest impact on refinery BOB conversion unit performance is the feed quality. Fig. 1 is an illustration of the impact of residual oil feed quality on the achievable conversion level in an ebullated bed hydrocracking process [7]. The data in Fig. 1 indicate a difference in the conversion level between 10% and 18% when vacuum residues of different origin are hydrocracked. Bozzano et al. reported that by visbreaking of two vacuum residues having different properties (SG_1 = 1.0495, CCR_1 = 24.0%; and SG_2 = 0.975, CCR_2 = 11.8%) at the same operating conditions (coil outlet temperature, coil outlet pressure, and residence time) a difference in conversion of products boiling below 350 °C of amount of 4.0% was obtained [8]. AlHumaidan et al. investigating thermal cracking of three Kuwaiti vacuum residues in Eureka process at different residence times and reaction temperatures reported different conversions and product yields for the different residual feeds [9,10]. The BOB conversion processes thermal cracking and hydrocracking are based on thermal conversion [11,12]. According to data of reactivity of individual hydrocarbons which belong to the classes paraffins, cycloparaffins (naphthenes), and arenes during thermal conversion the reactivity varies in the order: paraffins > naphthenes > arenes [13]. However the data of thermal conversion of vacuum residual oils published by different researchers indicated different order of reactivity of the hydrocarbon groups. For example Guo et al. [14] reported that during thermal cracking of Jinzhou vacuum residue SARA (saturates, aromatics, resins, asphaltenes) fractions reactivity towards volatile compound formation decreased in the order: saturates > aromatics > resins > asphaltenes, while Schucker [15] reported that during the thermal cracking of SARA fractions of Arab Heavy Vacuum Residuum the reactivity of SARA fractions towards volatile compound formation decreased in the order: asphaltenes > saturates > aromatics > resins. Fortain's investigations [11] indicated that asphaltenes from Athabasca bitumen residue were the most reactive of all SARA fractions, while the other fractions resins and saturates + aromatics demonstrated almost the same reactivity in the ebullated bed residue hydrocracking. The investigations of Liu et al. [16] and Yang et al. [17] revealed that conversion of vacuum residual oils cannot be predicted from information of their SARA composition. The investigations of Russell et al. [18] confirmed earlier findings that reactivity of a residual oil in thermal conversion did not correlate with the group hydrocarbon (SARA) composition. The relationship between SARA fractions content of a heavy oil and its reactivity in the processes of thermal cracking and hydrocracking seems to be not so simple and straightforward as in the fluid catalytic cracking (FCC) process. In the heavy oil FCC the feedstock reactivity increases with the increase of saturates and respectively hydrogen content [19,20].
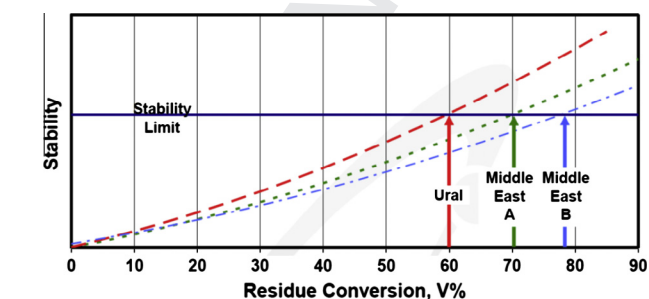
Unlike FCC the thermal conversion based BOB processes did not demonstrate a clear relationship between residual feedstock composition and reactivity. Moreover conversion in the thermal conversion based BOB processes is limited by the colloidal stability of the unconverted product and asphaltene tendency to agglomerate and form coke-like sediment material that settle down on equipment, requiring frequent shutdowns for cleaning [21–28]. When asphaltenes reach their solubility limit in the residue, they would begin to aggregate, so that a new phase, called the mesophase, would separate from the oil phase, which eventually leads to coke formation [27]. The investigations of Stanislaus et al. [25] have shown that sediment formation in residual oil conversion processes is caused by asphaltene insolubility and incompatibility in the product oils. It seems that colloidal stability of a vacuum residual oil may play a more important role in the assessment of residue reactivity in the thermal conversion based BOB processes. Ovalles et al. [29] found out that feed reactivity and asphaltene solubility are linked in resid hydroprocessing. They established that hydrodenitrogenation and the percentage of reduction of microcarbon residue correlate with asphaltene solubility. However they did not investigate the relationship between asphaltene solubility and the feedstock conversion in the residue hydroprocessing. We decided to shed more light on relationship between residue feedstock colloidal stability and residue reactivity and practically achievable conversion in thermal based conversion processes. For that purpose we have performed thermal cracking experiments of thirteen vacuum residual oils from different origin which widely differentiated in their physical and chemical properties. The aim of this work is to investigate the relationship between residual oil colloidal stability and residue reactivity in a thermal conversion based BOB process.

2. Experimental

2.1. Pyrolysis apparatus and procedure

The pyrolysis apparatus used in this study is a modified high-temperature–high-pressure batch autoclave reactor (Fig. 2). The main features include constant pressure operation and distillation of cracked products. Reactor insert material is composed of stainless-steel (SS-304). The reactor is a 100 mL Parr bench-mounted stirred vessel manufactured in Hastelloy C276 and fitted with a high-torque sealed magnetic stirrer drive on the removable head. Feed is added to the reactor once the preweighed micro-insert has been carefully placed inside toward the bottom of the chamber. The reactor is assembled and leak-tested and, if successful, purged with nitrogen. The reactor is then pressurized, and the heater system is turned on. As the temperature increases, the stirring speed is increased, from 440 to 980 rpm. The reactor is further heated to a temperature of 350 °C, where it is maintained for 10 min. This temperature represents the feed temperature prior to entering a typical furnace unit. Furthermore, time at temperature permits feed constituents to equilibrate prior to the cracking onset. The temperature is then increased to 410 °C at a rate of 10 °C min^{-1}. Although pressures may vary from unit to unit, 10 bar was chosen to allow for a direct comparison of cracking distributions. Also for this reason, a temperature of 410 °C was used throughout all characterization experiments. The temperature is maintained at 410 °C for a predetermined length of time. Complete characterization of feed in terms of reactivity and stability of the unconverted product is obtained by performing several pyrolysis experiments of increasing time increments, typically 10, 20, 30, and up to 90 min in duration. Once the predetermined cracking time is completed, the reactor is rapidly cooled back down to 350 °C at 15 °C min^{-1}, thereby quenching any further cracking reactions. The reactor is then drained of pressure through a

Fig. 1. Conversion limits for different vacuum residual feedstocks during their hydrocracking in ebulated bed H-Oil process (Ref. [7]).