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Characteristics of slurry-phase hydrocracking for vacuum residue with reaction temperature and concentrations of MoS_2 dispersed catalysts

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ABSTRACT

This study investigated the characteristics of slurry-phase hydrocracking of vacuum residue (VR > 524 °C) at a high conversion (40–95 wt.%) with a change of reaction temperatures and concentrations of the dispersed molybdenum (Mo Conc. 100–2000 wt.ppm) catalyst. Experiments were carried out with an initial hydrogen pressure of 80 bar (at 80 °C) at a reaction temperature from 385 to 440 °C for four hours in a batch reactor. As results, it was found that the sediment formation is mainly dependent on the VR conversion by the reaction temperature and started over 70 wt.% of VR conversion. Up to 70–80 wt.% of VR conversion, the higher catalysts showed the higher asphaltene conversion and prevented the sediment formation at the boundary of its formation, but it didn't show any effect over 80 wt.% of VR conversion anymore. Based on the analysis of the structural change and ξ-potential of asphaltene from the liquid and sediment, and SARA compositional change in the liquid, the reason for sediment formation was explained.

1. Introduction

Asphaltene is known to get surrounded by resin at the initial phase of the refining process causing it to disperse uniformly in micelle form, so it seems that resin can serve as a surfactant to maintain the colloidal stability of asphaltene in petroleum [1]. However, it has been reported that if the residue conversion is over 50% then sediment starts to form that causes problems to the internals, transfer lines and downstream facilities such as heat exchangers, separators and fractionating towers due to the plugging it causes [2]. In addition, sedimentation also causes operability problems, catalyst deactivation, increased catalyst consumption, and decreased residual fuel stability. Prolonged occurrence of any combination of these eventually causes a shutdown of a commercial refinery [3].

Based on previous studies related to sediment formation resulting from hydrocracking, researchers have proposed that this is attributed to the separation that occurs between phases according to the overall composition [4,5]. In other words, low boiling hydrocarbons increase while polar components of high molecular weight start to form as the reaction proceeds so that a solid deposition occurs due to the separation between the light aliphatic and aromatic components. The studies have also mentioned that the formation of sediment accelerates due to the reduced solubility between the asphaltene and maltene that results from the compositional changes caused by the hydroprocessing. Rogel et al. recently reported that the formation of sediment is largely influenced by the concentration of asphaltene in the feedstock and change of solubility of the asphaltene in the middle of hydroprocessing. They pointed out that the main reason why sediment forms is due to the reduced asphaltene solubility that results from the compositional transition it undergoes during the process [6].

Bartholdy and Andersen [7] used Arabian heavy atmospheric residue to investigate the conversion and change of stability of asphaltene by using the flocculation onset titration method at hydroprocessing conditions (360–390 °C, 130 bar H_2, 0.22–0.85 1/h liquid hourly space velocity, 1100 NL/L H_2-to-oil ratio, catalysts functioning hydrodemetallization and hydrodesulfurization). As a result of their experiment, they found that the H/C ratio of the asphaltene decreased as the reaction temperature increased and that at temperatures above 380 °C the product became unstable. Their study explained that the instability is attributed to the changes occurring to the solubility parameters resulting from the compositional transition of the maltene and asphaltene. Ancheyta et al. [8,9] observed the removal of impurities and behavior of the asphaltene constituents during hydrotreating with Maya heavy crude and $NiMo/Al_2O_3$ catalysts at a water pressure of 70 bar, H_2-to-oil ratio of 5000 ft/bbl, temperature of 380–440 °C, and liquid hourly space velocity (LHSV) of 0.5 1/h. Their results indicated

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Table 1
Properties of feedstock for slurry-phase hydrocracking.

Properties of feedstock	ASTM methods	Values
API Gravity at. 15 °C	D 5002-99	5.84
Kinematic Viscosity, cSt	D 445-15	1030 (110 °C)
MCR, wt.%	D 4530-06	20.5
C7 Insolubles, wt.%	D 2007	14.8
Sulfur, wt.%	D 4294-03	6.7
Nickel/Vanadium, wt.ppm	D 4294-03	40/126
Cut point distribution, wt.%	D 7500	
Naphtha (IBP–177 °C), wt.%		0.0
Middle Distillate (177–343 °C), wt.%		1.3
VGO (343–524 °C), wt.%		17.0
VR (524-FBP °C), wt.%		81.8

that as the reaction temperature was increased the nitrogen and metal content in the product also increased but sulfur decreased. This behavior was understood to be the result of the localization of each heteroatom into an asphaltene molecule. In addition, it was found that the aromaticity of the asphaltene increased with time-on-stream and that the number and length of the alkyl chains decreased. It was also found that the metal contents concentrated in the coke that was laid down by the catalyst.

At a higher VR conversion (55 ~ 85 wt.%) in an ebullated bed reactor, Merdrignac et al. [10] investigated the evolution of the asphaltene structure, specifically its size and average structural parameters. The experiments were carried out using Buzurgan VR and Ni-Mo supported by alumina extrudate at 427 °C, 160H_2 bar, and 0.2–0.3 1/h LHSV in a two-staged reactor. The results showed that asphaltene converts faster than that of the residue and the remaining unconverted residue dissociates into smaller aggregates. Also, they found that the asphaltene unit size decreases when conversion increases, and the aromaticity of asphaltene increases due to dealkylation. Using similar conditions to the previous study conducted by Merdrignac et al., Gauthier et al. [11] focused on the continuous evolution of asphaltene with respect to the conversion of residue. They suggested that asphaltene first goes through the dissociation of molecular units then cracks the small polycondensed structure and dealkylates aliphatic chains. Finally, the remaining asphaltene molecules form into a polycondensed structure of several aromatic cycles at high conversion.

Unlike previous hydrocracking methods with heterogeneous catalysts in a fixed bed, moving bed, and ebullated bed reactors, Slurry-phase HydroCracking (SHC) uses a very small amount of a dispersed catalyst which is a nano-scale metal sulphide. In particular, oil soluble types of catalysts can be well dispersed in the feedstock so that its highly dispersed active sites easily access to a high molecular reactants

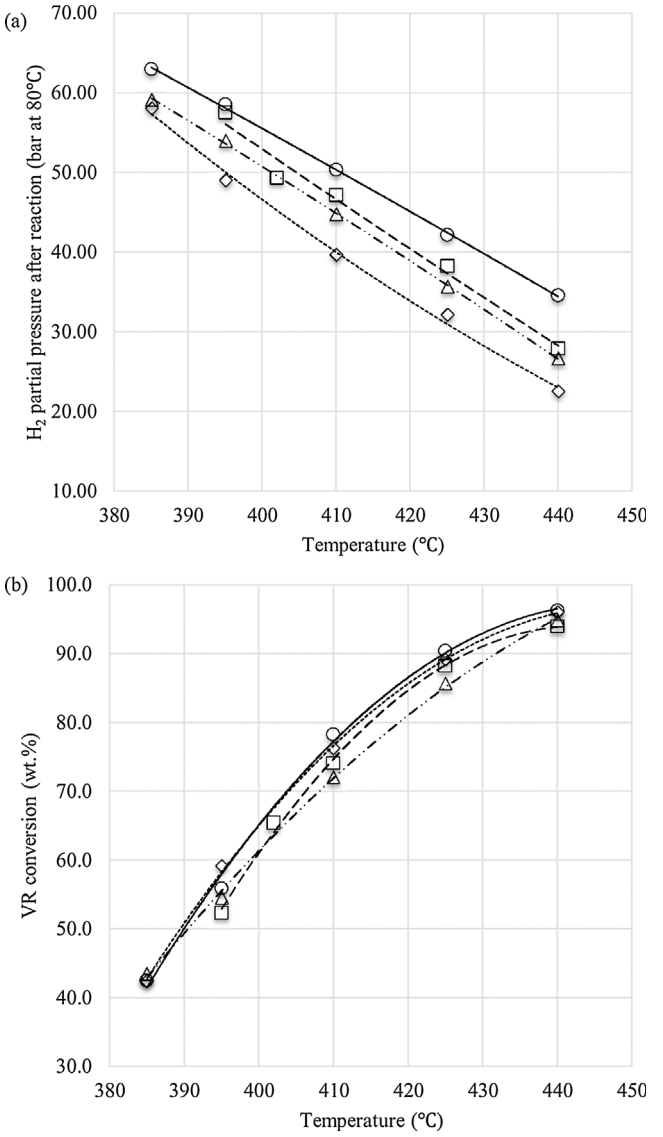

Fig. 2. Effect of reaction temperature and Mo concentration on (a) H_2 partial pressure after reaction and (b) residue conversion, [Mo concentration, wt.ppm: ○100, □ 500, △ 1000, ◇ 2000].

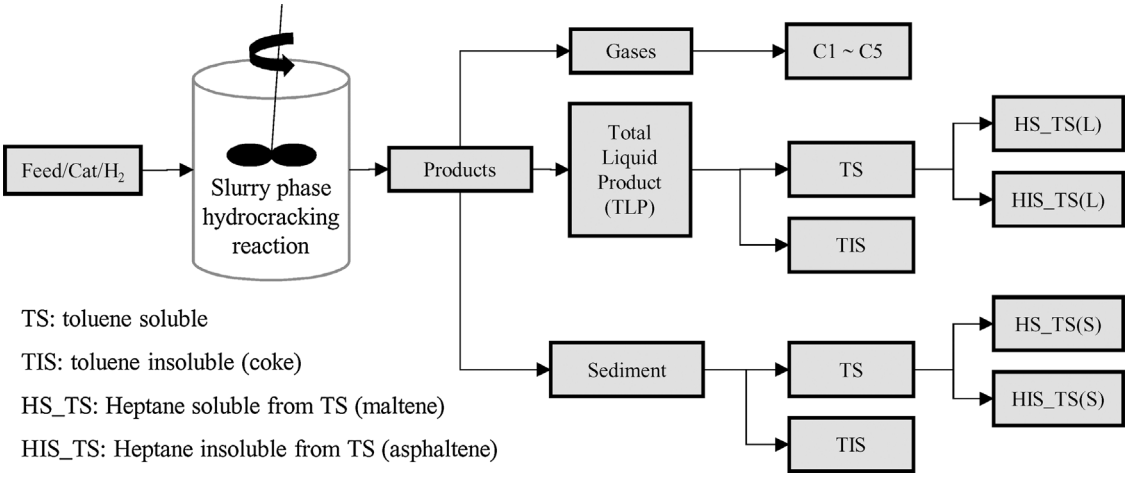

Fig. 1. Product separation procedure for analysis.