Full Length Article

Effect of asphaltene dispersion on slurry-phase hydrocracking of heavy residual hydrocarbons

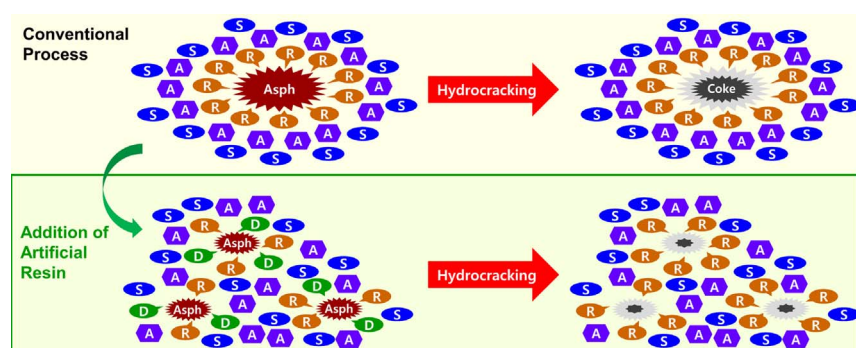Tung M. Nguyen[a,b,1], Jinhwan Jung[a,1], Chul Wee Lee[a,b], Joungmo Cho[a,b,*]

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GRAPHICAL ABSTRACT

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ABSTRACT

Asphaltenes are the heaviest molecular substances that can be found in crude or refined residual oils. It is generally known that irreversible cokes are mainly derived from colloidal macrostructures comprising asphaltenes and resins during the thermal upgrading processes of heavy oils. The addition of artificial resin can significantly alter the colloidal states of the feedstock and affects the rate of coke formation during these processes. In the current study, the effect of the initial asphaltene stability on the hydrocracking performance was investigated by applying chemical compounds containing both polar and non-polar functional groups. Among those chemical compounds tested, polyisobutenyl succinimide (PIB-SI) allowed the most efficient coke reduction irrespective of the type or amount of dispersed catalyst and improved the overall yield of distillable liquid product. The structural changes in the asphaltene molecules during hydrocracking are further investigated in a quantitative analysis based on ^{1}H and ^{13}C NMR spectra associated with the molecular weight distributions for extracted asphaltenes. This analysis shows that considerably smaller molecules can be found in asphaltenes extracted from the liquid product of hydrocracking in the presence of PIB-SI. The results reveal that increasing the dispersion of asphaltenes can be a good strategy for reducing coke formation and improving the yield of the desired liquid products in the hydrocracking process.

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1. Introduction

Heavy oil feedstock contains a significant amount of asphaltenes, which are the heaviest fraction of constituents in heavy oil feedstock and retain the largest portion of impurities. The asphaltene molecule is known to take a non-identical and very complex polymeric structure in which massive blocks of unsaturated polyaromatic hydrocarbons with few outer moieties of saturated cyclic rings and aliphatic side-chains are conjugated for petroleum-derived asphaltene. Impurities of heteroatoms (mostly S, N, and O) and traceable amounts of inorganic heavy metals are also embedded in this structure. The asphaltene molecules themselves induce aggregations [1] due to planar stacking with π-π interactions between the molecules. Mullins [2] has established the modified Yen's model, which rationalizes numerous issues in recent asphaltene science. This model describes that aggregates are composed of 4–10 asphaltene molecules and that a few aggregates, approximately 8, can further form a cluster. In this model, a single asphaltene molecular structure contains 4–10 fused aromatic rings (highest population has 7 fused aromatic rings) and a single plane of polycyclic aromatic hydrocarbon (PAH), contradicting the 'archipelago' model for asphaltene structures; the multiple PAHs are bridged by side alkyl chains. From a molecular structure analysis by using atomic force microscopy (AFM), Schuler et al. [3] has recently revealed that the petroleum-derived asphaltene possesses both of these structures. They observed that asphaltene structures with a single PAH are most common and that the number of PAHs is limited to two, with few exceptions.

Asphaltene has diversely branched aromatics and heteroatoms of high dielectric constants and exerts the highest polarity compared to the other heavy oil fractions; i.e., resins, aromatics and saturates [4–7]. Resin is the second most heavy and polar fraction and is generally composed of a similar molecular compartment as asphaltenes, but resin is soluble in aliphatic solvent, typically n-heptane [8]. Although a contrasting hypothesis that asphaltene aggregations are irrespective of the interactions with resin molecules has been put forward [9], it is widely accepted that the resin content significantly affects the colloidal stability of asphaltenes in heavy oils. In terms of the polarity, resin has an intermediate polarity between that of asphaltenes and other light hydrocarbons (saturates and aromatics) [4,6,7]. In a mixture of such polar and non-polar components, resins are positioned at the outer shell of the asphaltene aggregates, and the resulting asphaltene-resin complexes are isolated from less polar and lighter constituents. There have been numerous efforts to investigate the effect of resins or artificial resin-like materials on the static and dynamic colloidal behaviors by employing several instrumental measurement strategies such as dynamic light scattering [10], small-angle neutron scattering [11], UV–vis spectroscopy [12], near-infrared spectroscopy [13], electrical conductivity [14], and confocal laser-scanning microscopy [15], as well as several others [16]. The colloidal states of asphaltene aggregates in heavy oils, typically deficient in resin compounds, can be dramatically altered by the addition of a third material with both polar and non-polar functional groups that mimic resins. Although applications in heavy oil upgrading has not been extensively investigated, the modification of asphaltene stability in heavy oil has been studied in many fields; for example, studies regarding stabilizers for heavy fuel storage [12,17], viscosity modifiers [18–21], flow improvers [22,23], enhanced oil recovery [24], and a few surface sciences [25–28] have been conducted.

Despite numerous contributions to the design of hydrocracking processes and to the improvement of catalyst efficiency, there has not been a substantial focus on determining the appropriate initial treatment of feedstock, more specifically, the high dispersion of refractory molecules in heavy feedstock, affecting the overall performance of hydrocracking. Since the hydrocracking of heavy residues mainly targets the conversion of heavy fractions, which basically act as a coke precursor with highly aggregated forms, the modification of asphaltene colloidal states in feedstock could affect the catalysis, especially when slurry-phase hydrocrackers are applied to the process. The key feature discerning the slurry-phase hydrocracker from other technologies is the type of catalysts used for the hydrogenation of heavy oils [29]. Dispersed catalysts are designed to have an improved accessibility of the catalytic materials to the heavy residual feedstock, allowing high initial hydrogenation activity. Meanwhile, the other technologies, which employ particularly heterogeneous supported catalysts, are suffering from limited mass transfer, serious coke formation and consequential problems of catalytic deactivation, leading to a short operating cycle. In modern slurry-phase hydrocracking technologies commercially proven or announced to be commercialized, an iron oxide [30] or an organometallic precursor containing molybdenum [31,32] is most widely used as a dispersed catalyst. Iron oxide is inexpensive but its low activity and low dispersion to heavy oils necessitate the high consumption of catalysts and relatively harsh operating conditions, which ultimately require high capital and operating costs. To adjust the operability to more mild conditions, a few technologies have adopted molybdenum-based oil-soluble dispersed catalysts, which have a higher catalytic activity but are fairly expensive, consequently requiring either consuming a minimal amount or recycling a significant fraction of the catalysts. For example, the Eni Slurry Technology (EST) process utilizes molybdenum octoate or naphthenate as a precursor. During the hydrocracking process, the metalorganic precursor is converted into a catalytic form (MoS$_2$ nanoslab) through *in situ* activation by chemical substitution with sulfur impurities originally present in feedstock [31,32]. The key role of organic ligand in precursor molecules is to homogeneously disperse active metals to the targeting heavy molecules. It is generally accepted that a high concentration of the aggregated form of refractory molecules, which typically have a high aromaticity, facilitate the rate of coke formation or impede the conversion to condensable liquid hydrocarbons [33–41]. In this regard, slurry-phase hydrocracking with oil-soluble catalysts are recognized as the most advanced in terms of residual conversion and high selectivity to middle distillates. However, the suppression of coke formation could not be ideally achieved since asphaltene concentrations are sufficiently high to form flocculation, and aggregated asphaltene remains largely unaltered; the catalysts may have a limited mass transfer capacity deep inside aggregated asphaltene clusters or complexes. In this case, full utilization of the active metals could not be anticipated, and the aggregated clusters may follow the dominant reaction pathways to thermal hydrocracking. In addition, the catalysts cannot serve as an active guest for the hydrogenation of targeting heavy molecules during the hydrocracking process.

Based on the aforementioned postulation, we investigated the effect of high asphaltene dispersion in feedstock on the catalysis of slurry-phase hydrocracking. With the disruption of asphaltene-resin clusters, the catalysts are expected to be more available to asphaltene molecules and more efficient. Here, we explored the efficiency of artificial resin compounds in disrupting the asphaltene-resin structures, and the corresponding hydrocracking results were compared with no-additive cases. In addition, the characteristics of hydrocracking behavior are further studied on the basis of the hydrogenation activity of dispersed catalysts as well as the stability of asphaltene molecules in feedstock. In this study, the detailed analysis of hydrocracking products obtained at various reaction conditions helps to elucidate the mechanisms of hydrothermal decomposition and to address how efficient control of the underlying hydrocracking chemistries, including hydrogenation of heavy molecules and the suppression of coke formation, could be achieved.

2. Experiment

2.1. Characterization of heavy hydrocarbon feedstock

For the measurement of asphaltene stability and hydrocracking performance, a refinery vacuum residue (VR), received from Hyundai Oilbank Co., Ltd., was used as the heavy feedstock. Various analytical