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Full Length Article

Promoting asphaltene conversion by tetralin for hydrocracking of petroleum pitch

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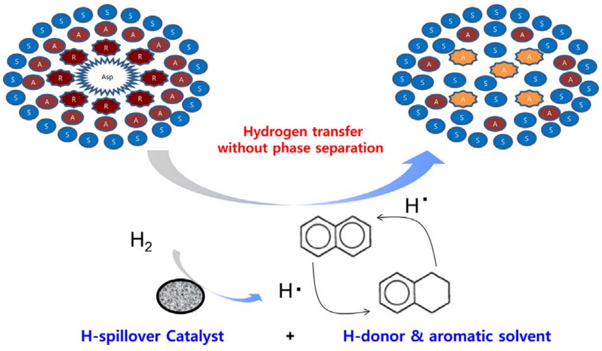
GRAPHICAL ABSTRACT



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ABSTRACT

The effects of tetralin as an H-donor on the reactivity of asphaltenes in a petroleum pitch were investigated under thermal cracking or catalytic hydrocracking conditions at 693 K and 10.0 MPa N_2 or H_2. Reaction temperatures, pressures, and tetralin contents were varied to examine the reactivity of asphaltenes. Thermal cracking of the petroleum pitch led to a considerable amount of coke formation, close to 53.7 wt%, but the addition of tetralin reduced the coke formation down to 23.6 wt%. The coke formation was considerably reduced to 10.3 wt% in the catalytic hydrocracking condition, and was not formed in the presence of tetralin. Kinetic studies on the catalytic hydrocracking of petroleum pitch in the absence or presence of tetralin demonstrated that the addition of tetralin, showing an increase in the hydrogen transfer capacity, contribute to the marked performance of hydrocracking of the petroleum pitch in the presence of dispersed MoS_2 catalyst.

1. Introduction

Declining availability of conventional light crude oils has drawn much research on the upgrading of the extra heavy oils (API ≤ 15) [1,2]. The heavy oils are, however, rich in asphaltenes which are known as a precursor of coke due to colloidal instability and aggregation behavior in refinery processes [3–7]. Much effort has thus been made in the past decades to explore the chemical and physical properties of asphaltene [8–14]. Asphaltenes can be defined as solubility classes that are insoluble in paraffinic solvents (n-pentane or n-heptane) but dissolve in aromatic solvents such as toluene or benzene [15,16]. According to Yen-model, a commonly accepted hierarchical model of asphaltenes, their average molecular weight is considered to be around 750 g mol^{-1} with a majority of molecules in the range 500–1000 g mol^{-1} [17–21], comprising polyaromatic hydrocarbons (PAH) of 4–10 fused benzene rings combined with alkane chains of C8-

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C16 on average. The presence of polyaromatic core in asphaltenes results in interaction among asphaltene molecules through π-π stacking, while alkane chains in asphaltene molecules cause repulsive forces to generate intermolecular interactions, bring a balance between attractive and repulsive forces among asphaltene molecules. If the alkane is decomposed from the core of asphaltenes, the attractive forces are no longer balanced and form coke [22]. For this reason, thermal treatment of heavy oils is accompanied by coke formation [23]. In order to avoid the formation of coke, much research has been done on precipitation of asphaltenes including rheological, structural, kinetical, and catalytic aspects [24–29] In particular, the addition of H_2 with H-donor solvents i.e. polycyclic naphthenic-aromatic or naphthenic compounds, which can reversibly hydrogenate or dehydrogenate in the reacting mixture, has been studied [30,31]. The H_2 transfer via H-donor solvents could reduce the viscosity of heavy oils, and minimize the condensation of the heavy molecules via radical absorption [32–34]. Hart et al. confirmed the residue conversion into distillates with minimizing coke formation using tetralin as H-donor [35]. Our previous study also found beneficial roles of H-donor solvents in catalytic upgrading of vacuum residue [36,37]. In the study, tetralin exhibits higher asphaltene solubility (90.3 g/kg) and H-donor index (0.90) than other solvents like naphthalene, decalin, heptane, and 1-methylnaphthalene, leading to better VR conversion with a minimal coke formation.

Although application of H-donor solvents has been found beneficial in thermal cracking of heavy oils, a detailed understanding of the physical or chemical interaction with asphaltene species with respect to thermal of hydrocracking conditions is still lacking. Indeed, it is noteworthy that hydrogen transfer can be promoted in the presence of catalysts where hydrogen atoms can spill over. The goals of this work are thus to explore hydrogen transfer capacity of in thermal cracking or catalytic hydrocracking of petroleum pitch. In particular, this work seeks to elucidate the nature of hydrogen transfer mechanism of the H-donor in the presence of dispersed MoS_2 catalysts. Measurements were carried out of thermal cracking and hydrocracking at 673 K and 10.0 MPa N_2 or H_2 in an autoclave batch reactor using a petroleum pitch containing C_7-asphaltene of 87.1 wt%. More emphasis will be placed on the kinetic analysis of pitch or deasphalt oil HCK to verify the asphaltene reactivity in the presence of tetralin as an H-donor.

2. Experimental

2.1. Materials

A vacuum residue (VR) as a feed was provided from a refinery in Korea, and the properties of the feedstock are reported in Table 1. The asphaltenes (ASP) were separated from the VR by mixing VR and n-heptane (1:40) at 323 K for 5 h, and the mixture was filtered through a microfilter (5C, Advantec) to separate the asphaltenes from the mixture. This was repeated for three times. The filtercake was then washed in n-heptane for 1 h and was dried in N_2 atmosphere till the weight became constant. The removal of solvent was confirmed by thermogravimetric analysis (TGA). The asphaltene was denoted as petroleum pitch. The feed specifications of VR and pitch are listed in Table 1.

Table 1
Specification of vacuum residue and petroleum pitch.

Feed	VR	Pitch
C-7 Insoluble (Asphaltene) (wt%)	21.0	87.1
C (wt%)	84.41	82.99
H (wt%)	9.69	8.28
Nitrogen (wt%)	0.53	0.99
Sulfur (wt%)	5.14	7.1
H/C (atomic)	1.37	1.19
Ni (wppm)	38.4	150.3
V (wppm)	104.2	407.7
Fe (wppm)	23.2	90.8
CCR (wt%)	23.0	89.9

2.2. Activity tests and characterization

The reaction tests were carried in a 150 ml autoclave batch reactor (Hanwool engineering, Korea) at various reaction conditions. For a standard reaction test, a feedstock of 30 g of asphaltene combined with 15 g of tetralin as an H-donor solvent was loaded with 250 ppm Mo as Mo-octoate into the reactor at ambient temperature. The feedstock was heated to 353 K and the reactor was purged with hydrogen for 15 min. The Mo precursor and vacuum residue were mixed with bubbling H_2 at 1500 rpm. After purging with H_2 the reactor was filled with H_2 to 6.0 MPa. The reactor was sealed up and heated to 673 K with a temperature ramping rate of 10 K/min and hydrogen pressure was increased to 9.5–10.0 MPa. The zero reaction time was defined when the desired reaction temperature was reached. Reaction temperatures were varied at 643, 673, 693, and 703 K. Reaction pressures were varied at 4.0 8.0 and 10.0 MPa at 350 K, corresponding to 7.3, 13.5, and 16.5 MPa, respectively at the reaction temperature 693 K. The amount of tetralin was also varied at 0, 25, and 50% in feed, corresponding to the tetralin to pitch ratios of 0/1, 1/4, and 1/2. Thermal cracking was conducted in the same reaction unit but under nitrogen in the absence of catalyst. After each reaction test, the autoclave was cooled down to 353 K and the gaseous product was vented. The reaction products were collected manually and centrifuged at 4000 RPM for 0.5 h to separate liquid and precipitate [38]. The amount of gas production was obtained by subtracting the amount of liquid and precipitate from the initial amount of the feed. For liquid products, the boiling point distribution was measured by GC-SIMDIS, where the amount of H-donor solvent was excluded based on the boiling point range of each solvent. Asphaltene species were separated from the products by mixing them with n-heptane (1/40, v/v) at 323 K for 5 h, and the mixture was filtered through a microfilter (5C, Advantec) to separate the asphaltenes from the mixture. This was repeated for three times. The filtercake was then washed in n-heptane for 1 h and was dried in N_2 atmosphere until the weight became constant. The asphaltene was denoted as C_7-asphaltene. In the similar manner, the amount of coke formation was measured from precipitate but with using toluene as a solvent for washing and filtering.

$$\mathit{Asphaltene\ conversion}\ (\%) = \left(1-\frac{\mathit{C7\ asphaltene\ in\ product\ (g)}}{\mathit{C7\ asphaltene\ in\ feed\ (g)}}\right)\times 100 \tag{1}$$

Asphaltene conversion, cracking yield, and coke yield were defined as below:

$$\text{Cracking yield } (\%) = \left[1-\frac{\mathit{C7\ asphaltene\ in\ product\ (g)} + \mathit{coke\ (g)}}{\mathit{C7\ asphaltene\ in\ feed\ (g)}}\right]\times 100 \tag{2}$$

$$\text{Coke yield}(\%) = \left(\frac{\mathit{coke}(g)}{\mathit{C7asphaleneinfeed}(g)}\right)\times 100 \tag{3}$$

The amount of total H_2 consumed in the reaction was calculated by the summation of H_2 released from tetralin via dehydrogenation to naphthalene and H_2 consumed in gas phase. The extent of dehydrogenation was measured by the quantitative analysis for tetralin and naphthalene using a gas chromatography (Agilent 6890 N) equipped with a dimethylsiloxane capillary column. Products were diluted with solvent and injected into the GC-FID analyzer. Although tetralin could undergo ring-contraction to form indan-derivatives during hydrocracking [32], they were observed < 1 wt% after reaction. Our previous studies of VR HCK using tetralin also revealed that tetralin is very and decomposition occurs only in trace amounts. Hooper et al. and Benjamin et al. have also shown the stability of tetralin under pyrolysis