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Effect of slurry phase catalyst and H_2 pressure on hydrocracking of SDA (solvent de-asphalting) pitch

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Abstract−Hydrocracking of solvent deasphalted (SDA) pitch was performed in batch and semi-batch systems, at different reaction temperatures (380-430 °C) with varying amounts of Mo-octoate precursor (0-1,000 ppm Mo) under 70-130 bar of H_2 pressure. The reusability of the catalyst was also examined. Coke formation was unavoidable in the hydrocracking of the asphaltene-rich feed. The coke induction period was prolonged when the catalyst was introduced. Increasing the Mo catalyst concentration decreased the coke yield and improved the product quality. The catalytic hydrocracking of the SDA pitch under high H_2 pressure suppressed coke formation, promoted desulfurization, and increased the H/C ratio of the liquid products. At least 500 ppm of Mo catalyst and H_2 pressur above 110 bar were required for the hydrocracking of SDA pitch with controllable coke generation in the semi-batch system. Sufficient hydrogen supply and moderate catalyst concentration were essential for the slurry-phase hydrocracking of asphaltene-rich feedstocks to enhance the product quality and suppress coke formation.

Keywords: Slurry-phase Hydrocracking, SDA Pitch, Asphaltenes, Coke, Reaction Conditions

INTRODUCTION

Crude oil has long been the most common source of energy, particularly as a source of liquid fuels. With the reduced availability of light crude oil, the exploration and exploitation of heavy oils has increased in recent decades. These scenarios have promoted the upgrading of heavy oil to meet market demands [1-3]. However, heavy oils contain a large number of impurities, complex chemical structures, and poor characteristics, which are critical issues in the refinery industry [3-6]. This necessitates a variety of processes to produce valuable liquid fuels by upgrading heavy oils.

Asphaltene, considered the most massive fraction of heavy oils, has a highly aromatic structure that is difficult to convert to valuable light products because it is well-known as a coke precursor [7-9]. According to previous studies, asphaltenes are soluble in aromatic solvents such as benzene or toluene and insoluble in light n-alkane solvents, such as n-pentane or n-heptane [7,10,11]. Asphaltene molecules have been proposed to contain approximately seven fused rings in the core system, several alkyl side chains, alicyclic groups, and heteroatoms [8,12]. Owing to this complicated structure, the alkyl side chains are cleaved at high temperatures, leading to the precipitation of the core polyaromatic rings, which reduces the coke induction period under severe conditions. Therefore, research on upgrading asphaltene-rich oils will contribute to the heavy oil refining industry.

The purpose of upgrading heavy oils is to improve physical properties, remove impurities, generate higher-value products, and decrease coke precipitation. The heavy oil upgrading process can be divided into three types: the separation process (solvent deasphalting (SDA)), carbon rejection process (thermal cracking, coking, and visbreaking), and hydrogen addition process (hydrocracking and hydrotreating) [1]. The SDA process is normally used to separate the asphaltene fraction from heavy oil. The asphaltene-rich SDA pitch is removed after filtration and deasphaltene oil (DAO) is considered a suitable feed for further hydrotreating [13-15].

Hydroprocessing has gained recognition as a strong method in heavy oil upgrading [16]. Hydrocracking technologies, which are flexible in modifying catalysts and conditions, generate valuable products with low coke formation. The hydrocracking process in a slurry-phase reactor has shown impressive performance in heavy oil treatment [3,17-19]. For example, a slurry-phase reactor can handle feeds with higher metal content compared to other reactors [3]. Dispersed catalysts used in slurry-phase reactors are reported to be stable and active even under severe working conditions [20, 21]. Dispersed catalysts have been widely applied to the hydrocracking of various feedstocks, such as vacuum residue (VR), petroleum pitch, asphaltenes, and DAO [21-25]. MoS_2 formed from Mo-octoate has been reported to suppress coke formation, reduce the asphaltenes in the liquid products, and conserve a high DAO yield [23]. Thus, the slurry-phase hydrocracking using oil-soluble catalyst precursor was considered in this study.

Coke is an unavoidable by-product of hydrocracking. Coke formation has been reported to be caused by asphaltene polymerization/condensation [4]. During the reaction, the asphaltene solubility is not balanced between the solvent oil and the solute asphaltene. Moreover, the Mo catalyst prohibits coke formation under 50%

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VR conversion, and the catalytic effect is reduced with an increase in precipitate aggregation [18]. Using a slurry-phase hydrocracking system operating at a high conversion of residue, the formation of sediment started at approximately 70% of VR conversion, and most of the asphaltenes and metals were concentrated, which led to the properties of asphaltenes changing linearly with respect to the VR conversion [19]. It has been reported that an excess of catalyst does not contribute to hydrogenation reactions or decrease coke formation [26,27]. A large amount of asphaltenes induces higher coke formation, and the high molecular weight and impurities of asphaltenes are the limitations of upgrading heavy oil [26]. Furthermore, changes in the asphaltene chemical structures have been reported to affect their aggregation [12]. The increase in aromaticity and ring condensation in heavy oil leads to coke formation.

The aforementioned studies were mostly conducted using VR or crude oil. To meet the need for increased heavy oil utilization, research on asphaltene-rich oil such as SDA pitch has been conducted. In this study, the effect of reaction conditions on the hydrocracking of SDA pitch was investigated. The effects of reaction temperature, catalyst load, and reaction pressure were examined using a Mo-octoate catalyst precursor and a semi-batch reactor. The reusability of the catalyst was also considered. Additionally, various analysis techniques have beeen adopted, such as GC-SIMDIS, ICP-AES, and elemental analysis, which delivers a broad overview of heavy oil hydrocracking in terms of several aspects, such as coke yield, asphaltene conversion, product distribution, and H/C ratio of products. This makes it possible to better understand the reaction results. The outcome of this study provides additional databases for the heavy oil upgrading process, specifically the hydrocracking of high asphaltene content feeds.

EXPERIMENTAL

1. Materials and Procedure

SDA pitch from Hyundai Oil Bank was employed as a feedstock; its detailed properties are listed in Table 1. Numerous processes are used to manufacture petroleum pitch. For example, it can come from the SDA unit, the separated aromatic by-product from the lube oil process, or the bottom residues from the vacuum distillation unit [20]. Notably, each of these processes creates a different pitch with distinct physical and chemical properties [28]. In this study, the petroleum pitch separated from VR by the SDA process was considered, which contains mainly asphaltenes (approximately 60%), a low hydrogen to carbon (H/C) ratio, and a high content of impurities such as sulfur, nitrogen, metals (nickel and vanadium), and micro carbon residue. Micro carbon residue (MCR) is a laboratory test that has been widely used and accepted as a standard method for determining the amount of carbonaceous residue remaining after evaporation/pyrolysis processes (ASTM D-4530) [29].

The catalytic hydrocracking reactions in this study involved a molybdenum octoate precursor from Shepherd Chemical (with 15.4 wt% Molybdenum). Toluene (99.5%) and n-heptane (99.5%) purchased from Samchun Chemical and Duksan Chemical were used to separate coke, asphaltenes, and DAO. The hydrocracking process was executed in a semi-batch reactor (Parr Model 4566) with a 100 ml vessel. Pitch (20 g) was loaded into the reactor with various Mo catalyst amounts, such as 50, 250, 500, and 1,000 ppm Mo concentrations, calculated based on the weight of the feedstock. Hydrogen was purged into the reactor, and thereafter, the H_2 flowed steadily inside the reactor through an MFC (Model F-221M, EL-FLOW from Bronkhorst Company) to pressurize to 80 bar at 80 °C. When the temperature reached 80 °C the mixing rate was increased gently to 100 rpm, and when it reached 200 °C, the stirrer speed was increased to 1,200 rpm. The temperature increased to 380-410 °C. Based on previous results obtained from the same experimental apparatus [22,26,30] and the reaction results in this work, 410 °C was chosen as the reaction temperature because it can cause both hydrogenation and thermal cracking during the reaction. The catalytic and non-catalytic hydrocracking reactions were run in semi-batch and batch modes, respectively. The reaction pressure was controlled from 70 to 130 bar in presence of the catalyst. Each set of reactions was carried out from 0.25 to 12 h. After the reaction, the temperature decreased to room temperature and the gaseous product was collected. The liquid and solid products were collected and then separated to coke, asphaltenes, and DAO.

Table 1. Composition of SDA pitch feedstock

Composition	Values
Naphtha (IBP-177 °C) (wt%)	0
Middle distillate (177-343 °C) (wt%)	2.1
Vacuum gas oil (343-524 °C) (wt%)	19.8
Residue (524 °C-FBP) (wt%)	78.1
S (wt%)	5.6
N (wt%)	0.6
Ni (wppm)	210
V (wppm)	1,000
Mo (wppm)	N.D.
H/C ratio	1.4
n-C_7 asphaltene (wt%)	58.5
Micro carbon residue (MCR) (wt%)	44.6

2. Characterization of SDA Pitch and Products

The hydrocracking reactions produced gas, liquid, and solid products, which were characterized by the following methods. Gaseous products such as light hydrocarbons and hydrogen sulfide were determined by YL6500 GC, which has both TCD and FID detectors. SIMDIS analysis is an excellent method for determining the details of hydrocarbon composition. SIMDIS gas chromatography with an Agilent GC 7890 followed ASTM 7169. The liquid and solid products were dissolved in carbon disulfide (CS_2) at a content of 3.33%. Each test resulted in a simulation distillation curve, and the distributions of the products were divided into fractions according to their boiling points. The naphtha fraction contains hydrocarbons with boiling points below 177 °C, the middle distillate fraction includes hydrocarbons boiling from 177 to 343 °C, the vacuum gas oil (VGO) cut boils between 343 and 524 °C, and the rest is VR. H_2 consumption of each reaction was calculated by the following equations [31].

$$H_2\ \text{consumption} = \frac{M_{H_2} - M_{H_2'}}{M_{pitch}} \times 100\% \tag{1}$$

$$M_{H_2} = \frac{2.016V}{22.41} \times \frac{P_1 + 0.1013}{0.1013} \times \frac{273.15}{T_1 + 273.15} \tag{2}$$

$$M_{H_2'} = \frac{2.016V}{22.41} \times \frac{P_2 + 0.1013}{0.1013} \times \frac{273.15}{T_2 + 273.15} \times R_{H_2} \tag{3}$$

Here, M_{H_2} and $M_{H_2'}$ are the mass (g) of hydrogen before and after the reaction, respectively, and M_{pitch} is the weight (g) of SDA pitch in each reaction. V is the volume (L) of the reactor. P_1 and P_2 are the pressure (MPa) in the reactor before and after the reaction, respectively. T_1 and T_2 are the temperature (°C) in the reactor before and after the reaction, respectively, and R_{H_2} is the hydrogen content in the gaseous products.

The liquid and precipitate products were collected and treated for further analysis. Coke, asphaltenes, and DAO were separated by an extraction method with toluene and n-heptane [30]. First, 2 g of liquid and solid products were mixed in equal proportions to the overall product distribution. 250 ml of toluene was then added to the mixture and sonicated in 15 min. After filtration, the toluene insoluble component (coke) was separated from the mixture and washed with toluene in Soxhlet extraction at 120 °C for 20 h to remove the remaining toluene soluble compounds. Toluene in the liquid obtained from the filtration and washing steps was removed by rotary evaporator. To separate the n-heptane insoluble component (asphaltene) from the toluene soluble fraction, 250 ml of n-heptane was added, sonicated, and filtered. The filter cake was collected and washed to remove completely the remaining n-heptane soluble compounds by Soxhlet extraction at 110 °C for 20 h. Finally, n-heptane was removed from the n-heptane soluble fraction using the rotary evaporator to obtain n-heptane soluble component (DAO). A Thermo Scientific Flash EA-2000 Organic Elemental Analyzer (EA) was used to determine the amounts of C, H, N, and S in asphaltenes and DAO. A Thermo spectrometer (ICP-AES) was used to determine the Ni and V concentrations. Transmission electron microscope (TEM) analysis was conducted by a Talos F200S microscope to discover the Mo catalyst active phase between fresh and recycled catalysts. The average MoS_2 slab length was calculated by selecting randomly 50 slabs from different parts of the coke samples using ImageJ software.

RESULTS AND DISCUSSION

1. Effect of Reaction Temperature

To examine the effect of temperature on catalytic hydrocracking of SDA pitch, a series of reactions were conducted at 380, 410, and 430 °C as a function of reaction time (0.25-4 h); the product distributions are summarized in Table 2.

Gas formation rate is highly dependent on the reaction temperature. Gas yield gradually increased at 380 °C, while the gas formation increased at a high rate from the start of the reaction at 430 °C. This indicates that the formation of gaseous products was mainly due to cracking of the alkyl side chains [17] and thus was promoted at high temperature. Coke formation rate and coke yield also increased with increasing the reaction temperature. Coke induction period was reduced when the reaction temperature increased. Then, the maximum coke yield increased significantly with increasing the temperature. These results imply that catalytic hydrogenation is favored at lower reaction temperatures so that asphaltenes can be converted to progressively lighter liquid products. On the other hand, at high reaction temperatures, thermal cracking was accelerated, so that asphaltenes and DAO were rapidly reduced, and a large amount of coke and gas was formed.

The effect of reaction temperature on the liquid product distributions is also listed in Table 2. At 380 °C, a slow conversion of the residue to lighter fractions was observed. At this temperature, light fractions such as naphtha or middle fractions were produced gradually from the heavy fractions according to a continuous reaction path, resulting in low yields. The residue conversion rate increased with increasing the reaction temperature. When operating at 410 °C, naphtha and middle distillate yields increased significantly, leading to a decrease in VGO yields after 4 h reaction. Operating at 430 °C gave the highest naphtha yield with a sharp decrease in residue. However, the thermal cracking behavior tends to produce lighter products, so when the reaction conditions become harsh, even the naphtha fraction starts to be cracked after 2 h reaction. Obviously, the temperature including both catalytic and thermal effects was 410 °C, and this reaction temperature was chosen to perform in the next following study.

Fig. 1 shows the effect of reaction temperature on sulfur and nitrogen removal. Sulfur content of asphaltenes decreased with increasing the residue conversion in all cases. It is interesting that

Table 2. Effect of reaction temperature on product distributions obtained from catalytic hydrocracking at 380, 410, and 430 °C

Temperature (°C)	380				410				430			
Reaction time (h)	0.25	1	2	4	0.25	1	2	4	0.25	1	2	4
Gas (wt%)	0.8	2.8	4.3	5.6	2.9	6.4	6.9	7.5	4.8	8.4	16.1	26.2
Liquid (wt%)	99.2	97.2	95.3	90.9	97.1	93.4	92.7	87.3	94.0	83.3	60.7	32.4
Naphtha (IBP-177 °C) (wt%)	0.8	0.6	0.7	3.6	0.9	2.9	3.3	8.1	3.1	7.9	16.0	10.6
Middle distillate (177-343 °C) (wt%)	2.5	3.4	3.9	7.8	6.0	13.1	17.9	23.1	10.8	19.5	21.3	11.4
Vacuum gas oil (343-524 °C) (wt%)	19.7	21.0	23.3	27.0	24.6	27.9	31.7	29.3	29.4	28.0	14.0	8.0
Residue (524 °C-FBP) (wt%)	76.3	72.2	67.4	52.5	65.7	49.5	39.8	26.8	50.7	27.9	9.4	2.4
Coke (wt%)	0.0	0.0	0.4	3.5	0.0	0.2	0.4	5.2	1.2	8.3	23.2	41.4
Asphaltenes (wt%)	48.4	42.1	37.7	26.1	39.7	29.4	23.0	13.6	31.2	17.3	7.0	0.7
DAO (wt%)	50.8	55.1	57.6	64.9	57.4	64.0	69.7	73.7	62.8	66.0	53.7	31.7

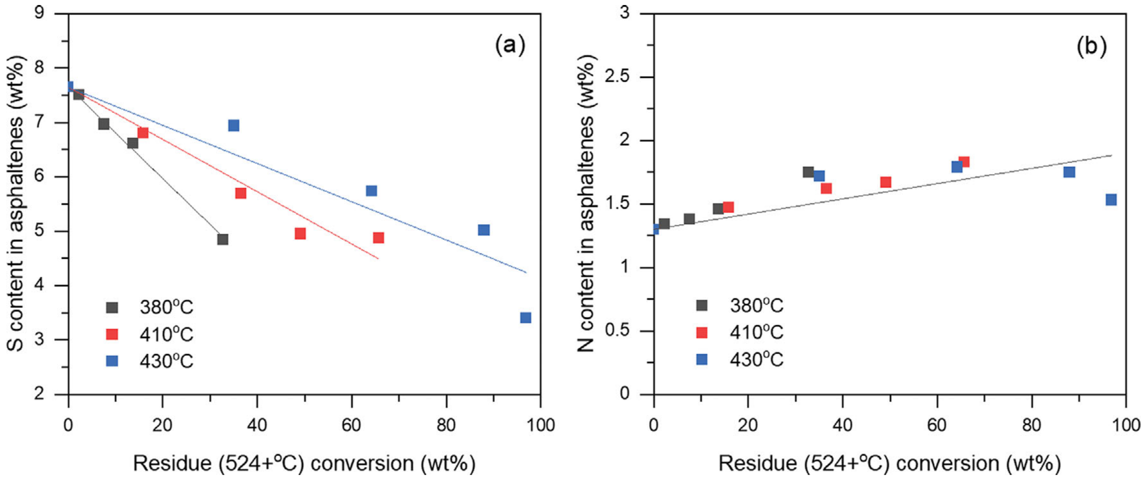

Fig. 1. Effect of temperature on (a) sulfur and (b) nitrogen content in asphaltenes.

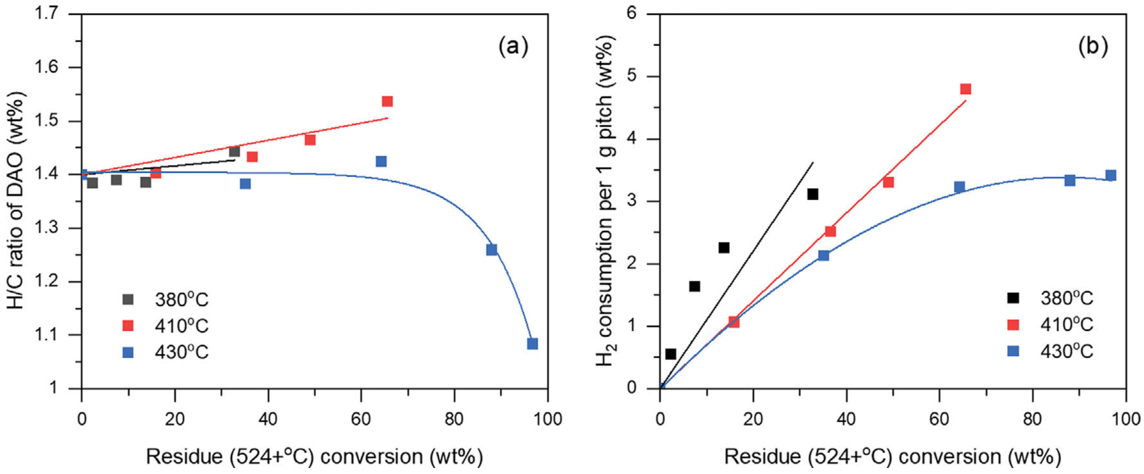

Fig. 2. Effect of temperature on (a) H/C ratio of DAO and (b) H_2 consumption.

the lower the reaction temperature, the lower the sulfur content in asphaltenes at the same residue conversion. This indicates that hydrodesulfurization took place more actively at lower temperature with minimizing the loss of asphaltene weight because the hydrogenation reaction easily occurred even below 400 °C. On the other hand, nitrogen removal hardly happened under these conditions. It has been reported that the C-C and C-S bonds are favored to be cracked, whereas the C-N bond is difficult to crack because it is located inside the asphaltene core [7]. Nitrogen content in asphaltenes decreased at extremely high residue conversion (above 90 wt%) at high reaction temperature, suggesting that the removal of nitrogen in asphaltenes is related to the asphaltene precipitation [18].

Fig. 2(a) shows the effect of reaction temperature on the hydrogen to carbon molar ratio of DAO products. It was observed that the H/C ratio increased with increasing the residue conversion at 380 and 410 °C, indicating that the DAO became more aliphatic. However, at 430 °C the H/C ratio of DAO was kept constant and then decreased sharply at high residue conversion. These results imply that the SDA pitch is refractory to be hydrocracked at high temperatures. The alkyl side chains seemed to be cut down quickly and a hydrogenation reaction was not facilitated. This is also related to the H_2 consumption result as shown in Fig. 2(b). At 430 °C there was no increase in the H_2 consumption at high residue conversion region. This indicates that thermal cracking was dominant at high temperature conditions and consequently increased the gas and coke yields and decreased the DAO yield, as listed in Table 2. As a result, 410 °C was the most suitable temperature for SDA pitch hydrocracking due to the best quality of liquid products and the high H_2 consumption.

2. Effect of Catalyst Concentration

To study the effective catalyst amounts for upgrading asphaltene-rich oil, reactions with various Mo-octoate concentrations were carried out (Fig. 3). Non-catalytic hydrocracking showed a high coke formation rate, which led to a decrease in the amount of liquid product. At the beginning of the non-catalytic hydrocracking reaction, coke formation occurred immediately, reaching 7 wt%. The coke yield increased rapidly from 7.1 to 28.5 wt% as the reaction time increased (Fig. 3(d)). There was no coke induction period in the absence of the catalyst during the reactions. These results are explained based on asphaltene behavior.

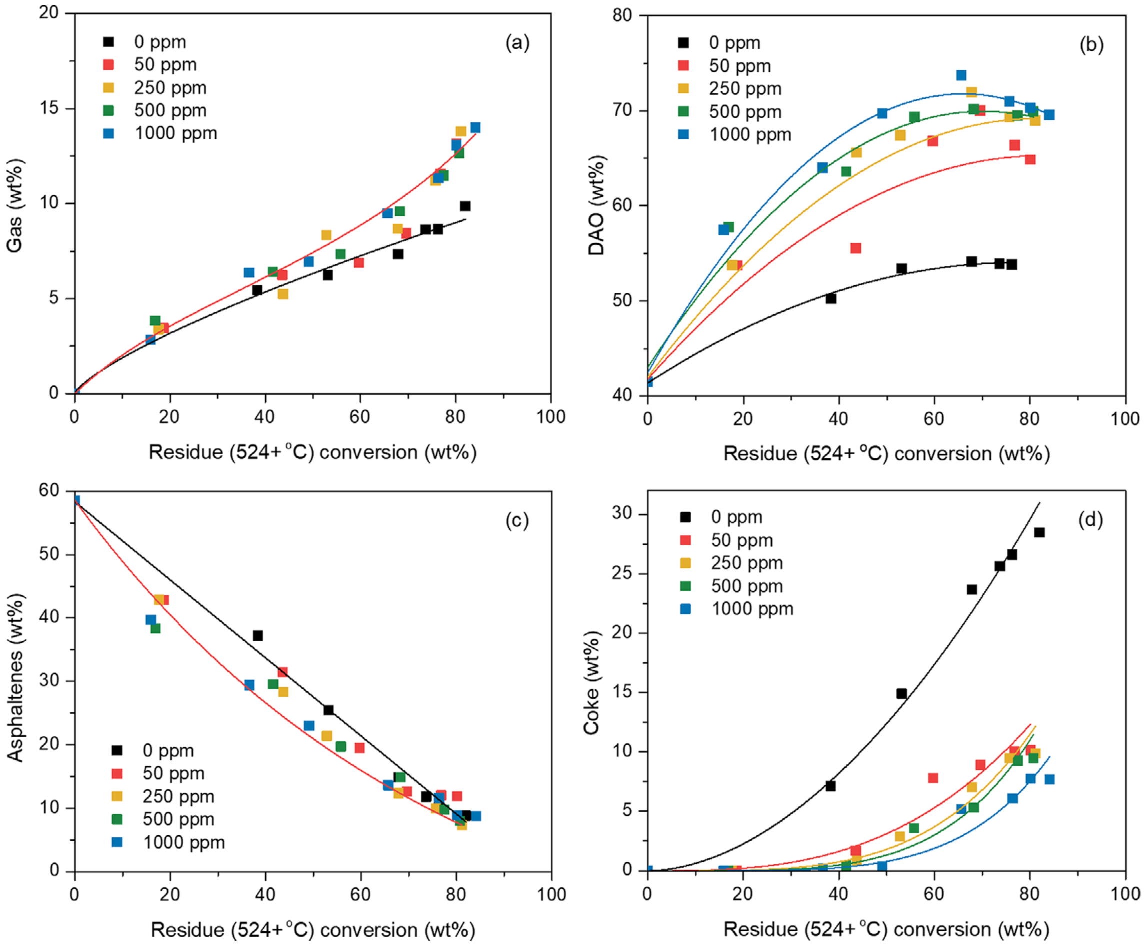

Fig. 3. Effect of catalyst concentration on (a) gas, (b) DAO, (c) asphaltene, and (d) coke yields.

Generally, the molecular weight of asphaltenes decreases during the hydrotreating process. It has been reported that size exclusion chromatography (SEC) was used to characterize the molecular weight distribution of asphaltenes and that the asphaltene masses decreased due to the dealkylation of alkyl side chains [32]. NMR analysis was also applied to determine the change in the asphaltene structure during the reaction, and it was found that the severity of the hydrocracking process influenced the alkyl side chains and naphthenic rings [30]. This agrees well with the results of this study. At the beginning of the reaction, the weight of asphaltenes in the feed decreased sharply from 58.53 wt% to nearly 48 wt%, which implies that the alkyl branches tend to be cleaved at high reaction temperatures. The polyaromatic rings mainly remained since these core aromatic rings are hardly cracked. Instead, the aromatic sheets undergo stacking and form nanoaggregate structures. The number of aromatic sheets increased as the reaction time increased, leading to the formation of asphaltene nanoaggregates [8,30,33]. Phase separation occurs as soon as the cluster concentration exceeds the solubility limit of the mixture, and polymerization makes the coke irreversible [7].

In the presence of the catalyst, the coke induction period was strongly controlled compared to the thermal cracking (Fig. 3(d)). The coke yield in the presence of the catalyst was lower than that in its absence. The greater the amount of catalyst applied, the less coke was formed. With only 50 ppm of catalyst, the coke induction period was shown at 20 wt% of residue conversion. 250 and 500 ppm of catalyst extended the coke induction period to nearly 40 wt% of conversion, reaching 50 wt% of residue conversion when 1,000 ppm Mo-octoate was applied. Moreover, the catalyst improved the DAO yield (Fig. 3(b)). These results were also found in previous studies [18,26]. The higher the amount of catalyst used, the higher was the heptane-soluble yield. Therefore, better performance (higher liquid yield and lower coke yield) was obtained when 1,000 ppm of catalyst was used for SDA pitch hydrocracking. It was observed that the DAO yield decreased when the reaction time was extended and the residue conversion was higher than 60 wt%. This indicates that the DAO was also transformed into gaseous products or asphaltenes in the high residue conversion region [34].

Fig. 4 shows the effect of Mo concentration on the liquid product distribution. When hydrocracking of SDA pitch was performed in the presence of the catalyst, a higher yield of liquid products was obtained. In the absence of the catalyst, the VGO yield increased with an increase in conversion up to 40 wt% before decreasing. When the catalyst was used, the maximum VGO yield was obtained at 50 wt% conversion, which was higher than the non-

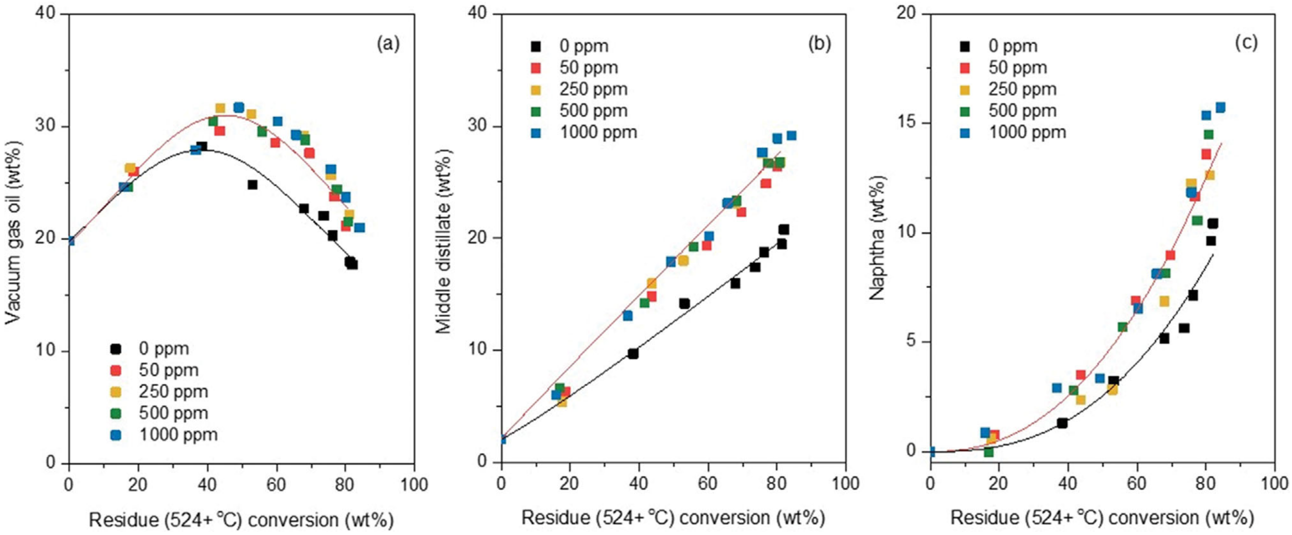

Fig. 4. Effect of catalyst amount on (a) vacuum gas oil, (b) middle distillate, and (c) naphtha with respect to residue conversion.

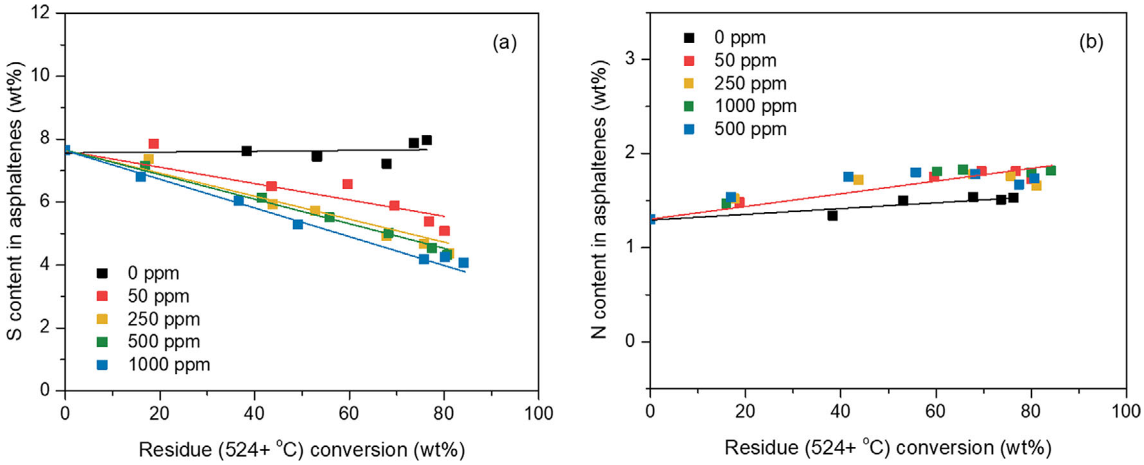

Fig. 5. Effect of catalyst amount on (a) sulfur and (b) nitrogen contents in asphaltenes.

catalytic hydrocracking result. Moreover, the yield of middle distillate and naphtha in the catalytic hydrocracking was higher than the non-catalytic hydrocracking. These results indicate that the yield of the liquid products was improved by inhibiting coke formation. There was little difference in the distribution of the liquid product even when the catalyst concentration was changed. The same trend of liquid product distribution even at various catalyst concentrations indicates that the reactions producing VGO, middle distillate, and naphtha were mainly influenced by thermal cracking. In all cases, the VGO yield increased during the first 50 wt% residue conversion and then decreased, indicating that VGO is an intermediate product of the hydrocracking reaction and is converted to lighter fractions as the reaction proceeds. Meanwhile, the middle distillate and naphtha yields continuously increased. The general trend of the consecutive route can be seen as residue→VGO→middle distillate→naphtha, regardless of the change in catalyst concentration, with or without catalyst [18,19].

Fig. 5 shows the change in sulfur and nitrogen content in asphaltenes after SDA pitch hydrocracking with different catalyst concentrations as a function of residue conversion. The higher the catalyst concentration applied, the more sulfur is removed from the asphaltenes. This result demonstrates that the desulfurization of asphaltene is strongly influenced by the presence of the catalyst. Indeed, C-S bond cleavage is favored by hydrogenolysis on the catalyst surface [35]. However, nitrogen removal from asphaltenes is more complicated. The nitrogen content of asphaltenes after catalytic hydrocracking was slightly higher than that after non-catalytic hydrocracking. This is related to the fact that it is difficult to remove asphaltenic nitrogen during hydrotreating reactions because nitrogen is located inside the aromatic ring of asphaltene molecules [6].

Fig. 6(a) shows the change in the quality of the DAO through the H/C ratio. It was observed that the DAO became more aliphatic during the catalytic hydrocracking reactions, whereas the liquid product without the catalyst had a more aromatic character. The H/C ratio of DAO obtained from catalytic hydrocracking was

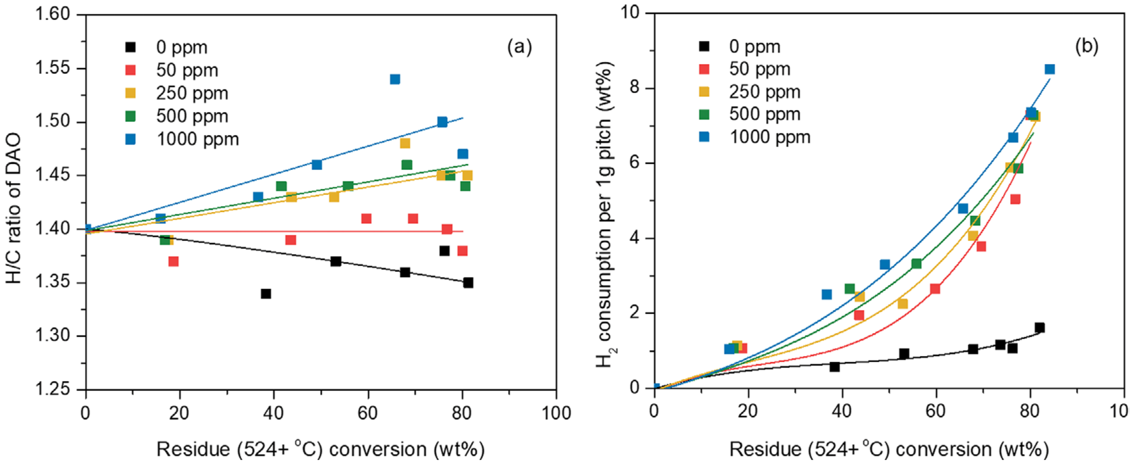

Fig. 6. Effect of catalyst amount on (a) H/C ratio of DAO and (b) H_2 consumption.

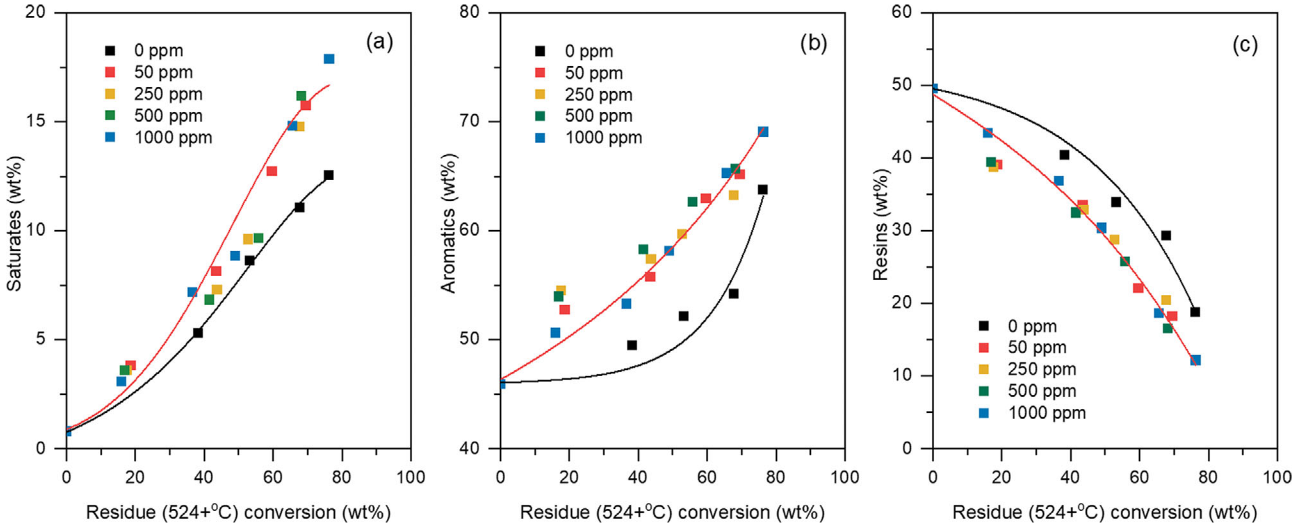

Fig. 7. Effect of catalyst amount on (a) saturates, (b) aromatics, and (c) resins distributions.

higher than that obtained from non-catalytic hydrocracking. The H/C ratio notably increased with increasing catalyst concentration. This also shows that the catalyst concentration influences the hydrogenation reaction. Thermal cracking was prevalent in non-catalytic hydrocracking, and the feedstock was converted to more olefinic and aromatic products. These results agree with previous research on heavy oil hydrocracking [18,26,27,36,37].

In addition, greater hydrogenation occurred at higher catalyst concentration, and H_2 consumption depended on the catalyst concentration, as shown in Fig. 6(b). In the non-catalytic hydrocracking reaction, there was little increase in H_2 consumption despite the increase in residue conversion. This indicates that hydrogenation or radical scavenging reactions hardly occurred in the absence of the catalyst. H_2 consumption increased with increasing catalyst concentration. This implies that the hydrogenation reaction was restricted at low catalyst concentration. Moreover, from the reduced coke formation, it can be inferred that a high catalyst concentration improves the hydrogenation rate and promotes the conversion of polyaromatic hydrocarbons to smaller molecules [18,27, 37]. These results demonstrate that asphaltene-rich feeds, such as SDA pitch, can be effectively converted to lighter oil fractions with high yields in the presence of adequate catalyst amounts.

Fig. 7 shows the effect of catalyst concentration on yields of saturates, aromatics, and resins of DAO products after the hydrocracking reactions. It has been reported that heavy molecules were cracked gradually to produce smaller molecules during catalytic hydrocracking reactions [34]. It was observed that the resins decreased concurrently with increases in saturates and aromatics. Similar to the tendency of the boiling point distribution of the liquid product (Fig. 4), there was no significant difference in SARA distribution even when the catalyst concentration was changed. This implies that thermal cracking mainly affects the transformation of SARA fractions. In catalytic hydrocracking, the yields of saturated hydrogen and aromatics were higher than in non-catalytic hydrocracking, while yields of resin and asphaltenes were lower than in non-catalytic hydrocracking. These results indicate that the quality of the liquid product is improved in the catalytic hydrocracking by inhibiting coke formation.

Table 3. Comparison of catalytic performances between fresh and recycled catalysts in hydrocracking of SDA pitch

Product distribution	Fresh catalyst	Recycled catalyst
Gas (wt%)	6.9	8.9
Liquid yield (wt%)	92.7	88.2
Naphtha (IBP-177 °C) (wt%)	3.3	3.6
Middle distillate (177-343 °C) (wt%)	17.9	15.5
Vacuum gas oil (343-524 °C) (wt%)	31.7	30.5
Residue (524 °C-FBP) (wt%)	39.8	38.6
Coke (wt%)	0.4	2.9
Asphaltenes (wt%)	23.0	23.4
Sulfur in asphaltenes (wt%)	5.0	5.5
H/C ratio of DAO	1.5	1.4

It has been reported that the Mo catalyst precursor is converted to MoS_2 by the excessive sulfur content of heavy oil [26]. It is also known that the MoS_2 catalyst acts as an active site to prevent the coke formation and promote hydrogenation olefin or poly-aromatic rings [27]. To investigate the reusability of the dispersed Mo catalyst in the SDA pitch hydrocracking, a recycled catalyst was prepared and applied to the hydrocracking test at 410 °C, 110 bar H_2, for 2 h. For the preparation of the recycled catalyst, the catalytic hydrocracking of SDA pitch was conducted at 410 °C, 110 bar H_2, for 2 h, and then the coke (toluene insoluble) was collected. The result is summarized in Table 3. Compared to the fresh catalyst results, the gas and coke yields were higher and the liquid yield was lower when the used catalyst was applied to the second run. This means that the reactivity of the reused Mo catalyst was limited in the catalytic hydrocracking of SDA pitch because some coke was formed and deposited on the catalyst particle through the first reaction [38].

Fig. 8 shows the TEM images of MoS_2 slabs in the coke obtained from the catalytic hydrocracking of SDA pitch using (a) fresh catalyst and (c) recycled catalyst. It was confirmed that the Mo-octoate precursor was converted into MoS_2 active species during the reaction [30,39]. MoS_2 average slab length of the fresh catalyst was 6.9 nm and that of the used catalyst was 6.7 nm, and there was little difference in the MoS_2 length. However, the MoS_2 of the fresh catalyst was finely dispersed in the form of single slabs, while the used catalyst maintained the highly stacked MoS_2 in the heavily agglomerated coke [40]. This result suggests that the low reactivity of the reused catalyst was related to the MoS_2 slab stacking and the agglomerated coke [41]. It has been reported that the reuse of MoS_2 catalyst formed from Mo octoate is possible for hydrocracking of medium asphaltene content feeds such as VR [36]. However, it was confirmed that the MoS_2 catalyst cannot be reused in the hydrocracking of SDA pitch unless it is maintained in a highly dispersed form due to the strong coking tendency of the asphaltene-rich feeds.

3. Effect of Pressure

To investigate the effect of hydrogen pressure on the SDA pitch hydrocracking, reaction experiments were conducted using a 1,000 ppm Mo-dispersed catalyst in a semi-batch reactor to maintain a constant pressure during the reaction. Fig. 9 shows the product distributions influenced by variation in reaction pressure. The pressure was varied from 70 to 130 bar of hydrogen. The DAO product yield increased with increasing hydrogen pressure, whereas the coke yield decreased with increasing pressure. This indicates that the hydrogenation reaction was promoted at high H_2 pressure conditions by preventing the radical reactions in the hydrocracking process, and the coke formation was controlled by the hydrogen atoms [33]. Thus, it is important to control coke formation by H_2 pressure under the same catalyst concentration conditions, especially when the reaction becomes more severe [37]. This is also related to the decreased DAO yield at low pressures (70 and 90 bar) in the region of high residue conversion above 60 wt % while maintaining the DAO yield at high pressure (130 bar). Asphaltene content in the feed decreased continuously during the hydrocracking reaction. Lower asphaltene content was obtained at higher H_2 pressures in the low residue-conversion region. However, the content of the remaining asphaltenes was similar, with no significant difference in the region of high residue conversion over 60 wt%. This implies that the conversion of asphaltenes in the SDA pitch was limited, even at a high H_2 pressure, when the severity of the reac-

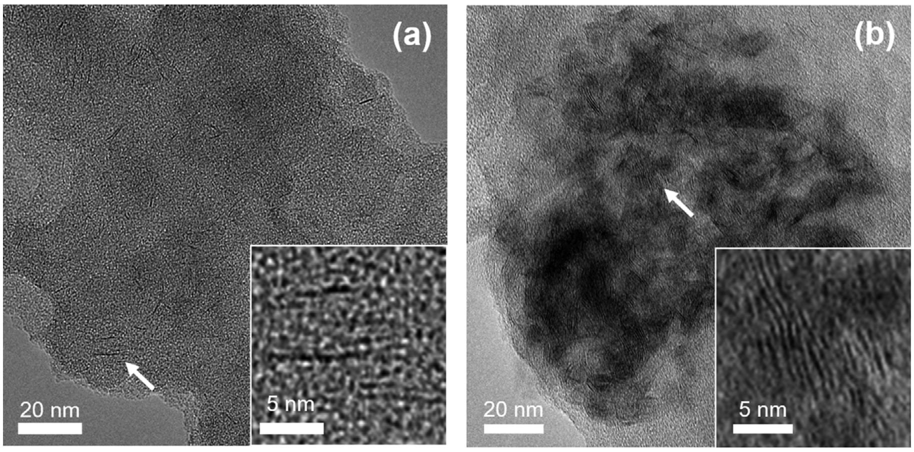

Fig. 8. TEM images of MoS_2 slabs dispersed in the coke obtained from catalytic hydrocracking of SDA pitch using (a) fresh catalyst and (b) recycled catalyst.

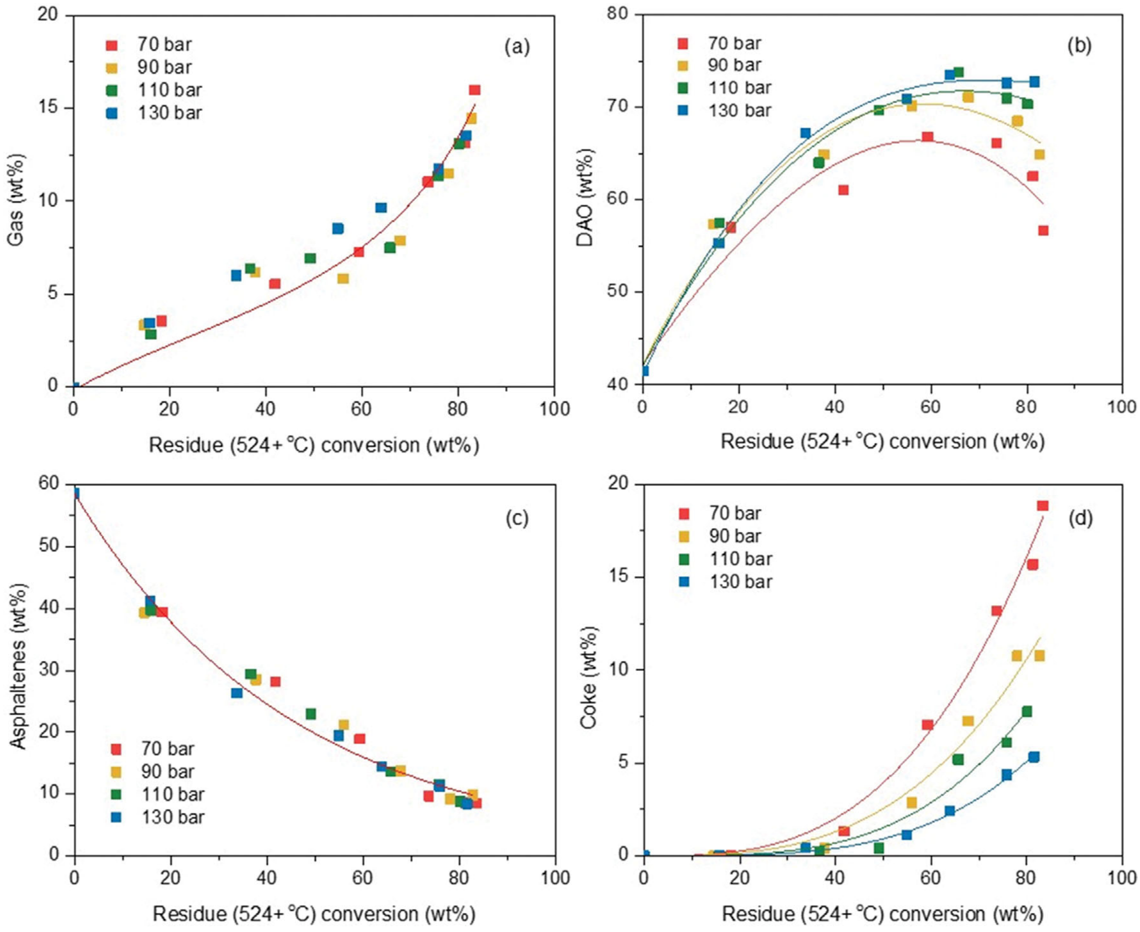

Fig. 9. Effect of H_2 pressure on (a) gas, (b) DAO, (c) asphaltene, and (d) coke yields.

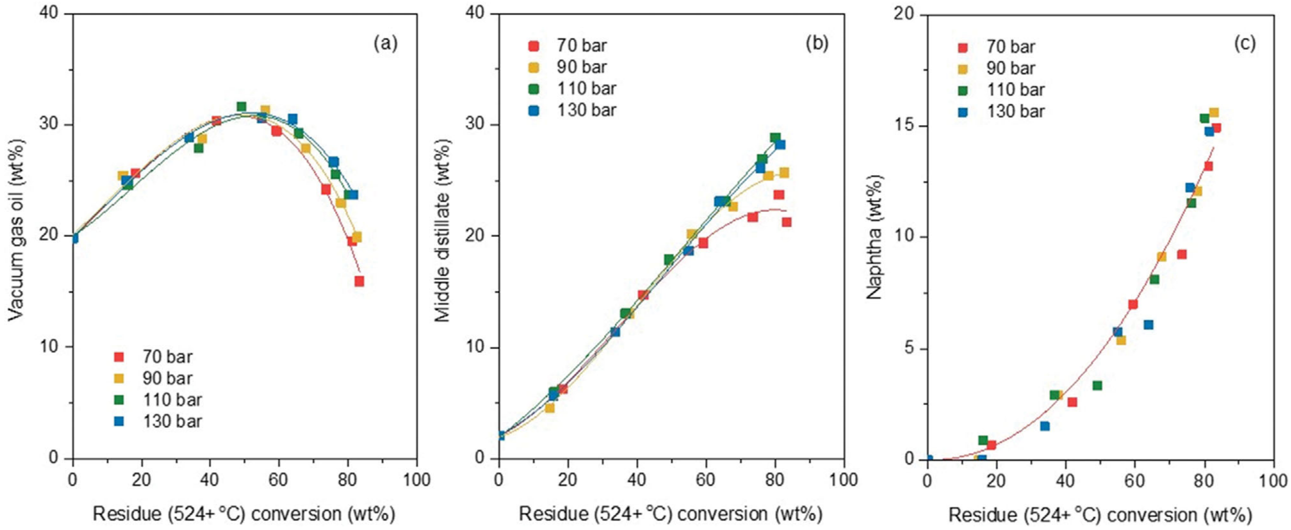

Fig. 10. Effect of H_2 pressure on (a) vacuum gas oil, (b) middle distillate, and (c) naphtha yields.

tion increased.

Fig. 10 shows the liquid product distribution obtained from catalytic hydrocracking reactions under pressure variation at 410 °C with 1,000 ppm Mo-octoate. The VGO yield increased with an increase in the VR conversion up to 50 wt% and then decreased, whereas the middle distillate and naphtha yields continuously increased with increasing residue conversion. Although the H_2 pressure was changed, the behavior of each fraction yield followed

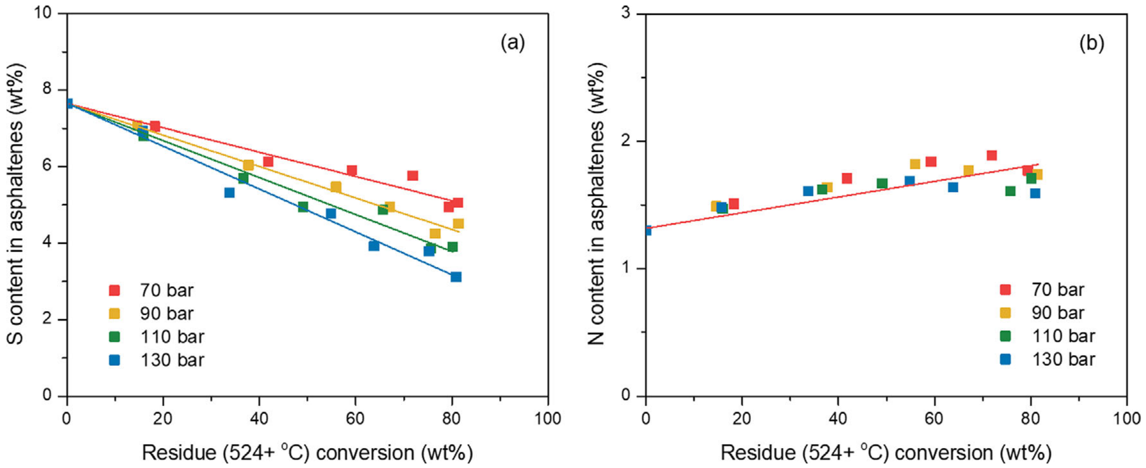

Fig. 11. Effect of H_2 pressure on (a) sulfur and (b) nitrogen contents in asphaltenes.

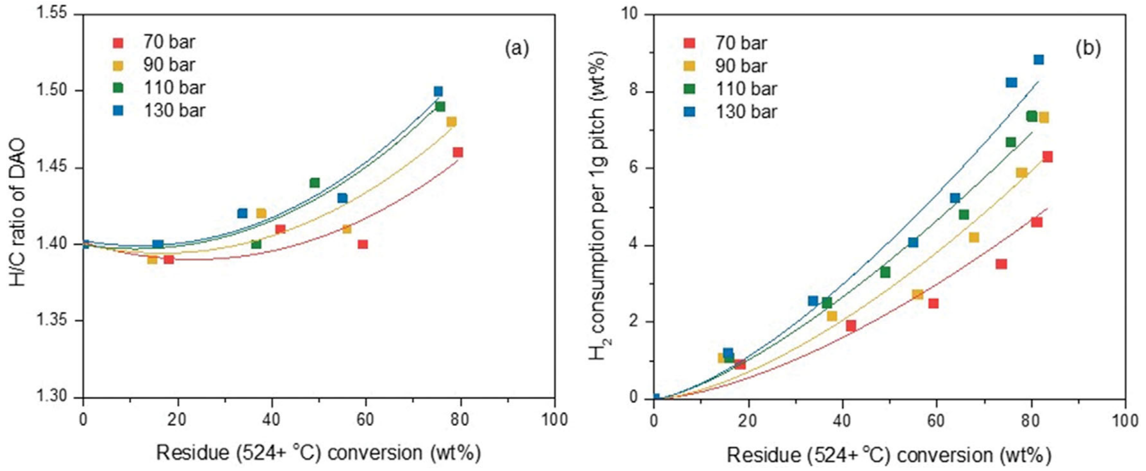

Fig. 12. Effects of H_2 pressure on (a) H/C ratio of DAO and (b) H_2 consumption.

similar features at a low residue conversion (below 50 wt%). In this region, the residue and VGO fractions were gradually hydrocracked to generate light products. This phenomenon continuously increased the amounts of middle distillate and naphtha. However, at high residue conversion (above 50 wt%), the yields for VGO and middle distillate at low pressure were lower than those under high-pressure conditions. It has been reported that the heavy residue molecules are gradually cracked into smaller hydrocarbons as residue→VGO→middle distillate→naphtha, and the catalyst contributes to maximizing the liquid product yield [18,19]. However, these results indicate that radical reactions and coke formation are difficult to control under low-pressure and high-residue-conversion conditions. An H_2 pressure of 110 bar or higher was required to obtain stable liquid yields in the hydrocracking of SDA pitch.

To investigate the effect of pressure on the quality of the catalytic hydrocracking products, elemental analysis was performed with the remaining asphaltene and DAO. Fig. 11 shows the sulfur and nitrogen content of the asphaltenes separated from the liquid products. A linear trend of sulfur reduction was observed during the hydrocracking of the SDA pitch. Sulfur removal was enhanced with increasing H_2 pressure at the same catalyst concentration, implying that asphaltene-rich feeds could be hydrotreated effectively under hydrogen-rich conditions. This is because nitrogen is bound to aromatic rings, and this form is very stable, which is in good agreement with previous results [42,43].

Fig. 12 shows the H/C atomic ratio of DAO and H_2 consumption as a function of the H_2 pressure change. The H/C ratio of DAO increased with increasing residue conversion and further improved with higher H_2 pressure. The H_2 consumption increased steadily as the residue conversion increased because the reaction was in a semi-batch system. As a higher H_2 pressure was applied, higher H_2 consumption was noted. H_2 was used for hydrodesulfurization, hydrogenation, ring opening, and stabilization of free radicals in the catalytic hydrocracking of the SDA pitch. Therefore, higher liquid yields, sulfur removal, and H/C ratio of DAO were obtained while minimizing coke formation under high H_2 pressure. These results are also consistent with previous reports that higher H_2 pressure enhances the conversion of asphaltenes to small molecules instead of coke formation [37,44]. In particular, H_2 pressure plays an important role in the catalytic hydrocracking of asphaltene-rich

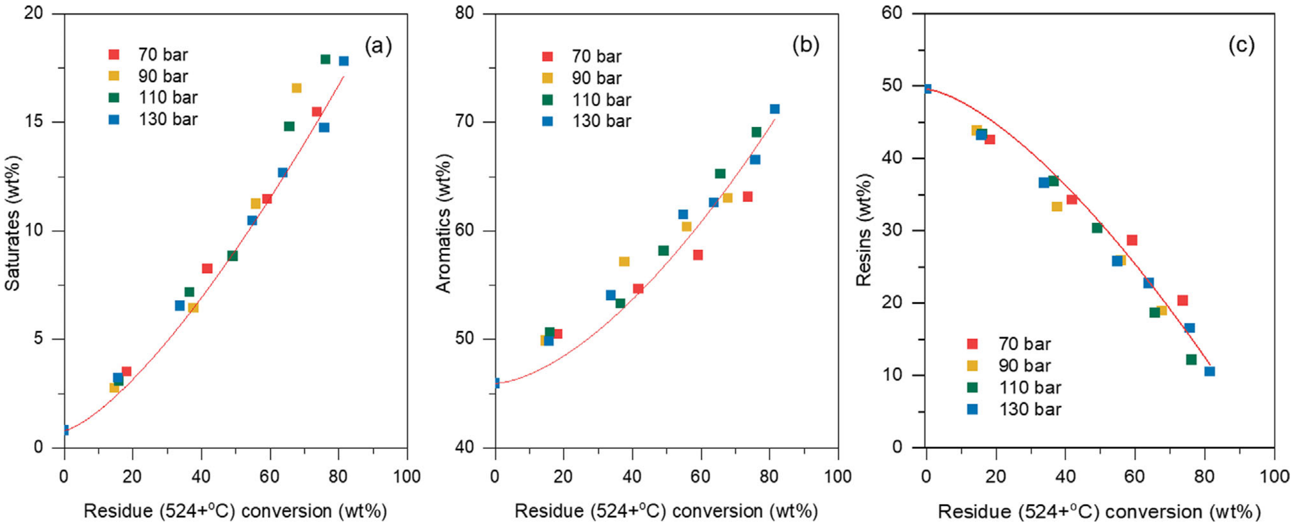

Fig. 13. Effect of H_2 pressure on (a) saturate, (b) aromatic, and (c) resin distributions.

feedstocks such as SDA pitch. Apparently, a high pressure of more than 110 bar inhibits coke formation and improves the product quality. However, owing to the high asphaltene content of the SDA pitch, a large amount of hydrogen is consumed in the hydrocracking reaction when operating at high pressure [22]. Note that the H_2 consumption was influenced by the asphaltene content of the feedstock, and the precipitation of solid particles was diminished by sufficient H_2 supplementation. Therefore, it is necessary to consider the economic feasibility and target products by managing the optimal conditions when handling high asphaltene content feeds.

The effect of reaction pressures in the catalytic hydrocracking of SDA pitch on yields of saturates, aromatics, and resins of DAO products is presented in Fig. 13. The resins decreased while saturates and aromatics increased with increasing the residue conversion. It was also observed that there was no significant difference in the SARA distribution even when the H_2 pressure was varied. This indicates that the thermal cracking mainly affected the transformation of SARA fractions, similar to that already observed in Fig. 7.

CONCLUSIONS

This study highlights the performance of a slurry-phase reactor in the catalytic hydrocracking of SDA pitch under different operating conditions. The hydrogenation reaction of SDA pitch was favored at low temperature and asphaltenes could be progressively converted into lighter fractions. On the other hand, at high temperature the thermal cracking reaction was promoted, which resulted in excessive generation of gas and coke, reducing the liquid yield. 410 °C was seen as a temperature that could expose both catalytic and thermal effects in the hydrocracking of SDA pitch. Coke formation was found to be unavoidable in the treatment processes with high asphaltene content feedstocks, such as SDA pitch. Coke appeared immediately when the reaction was conducted in the absence of the catalyst. However, the coke induction period was prolonged by control of the radical reactions when a small amount of catalyst was introduced. The catalyst also enhanced the hydrogenation and hydrodesulfurization reactions. Higher Mo catalyst concentrations resulted in improved product quality, including higher liquid yield, lower coke yield, and higher sulfur removal. At least 500 ppm of Mo catalyst was required for the hydrocracking of SDA pitch with controllable coke generation in the semi-batch system. The catalytic hydrocracking of SDA pitch under high H_2 pressure was also beneficial in inhibiting coke formation, promoting desulfurization, and increasing the H/C ratio of the liquid products. In fact, when operated at high H_2 pressures above 110 bar the reaction had a great impact on the asphaltene conversion and coke suppression by enhancing the hydrogenation reaction and controlling the free radicals. However, low-pressure conditions did not effectively inhibit coke formation and decreased the liquid yield, even in the presence of high catalyst concentrations. Abundant hydrogen supply and moderate catalyst concentrations were essential for the slurry-phase hydrocracking of asphaltene-rich feedstocks to enhance the product quality and control coke formation.

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REFERENCES

1. J. Ancheyta and J. G. Speight, *Hydroprocessing of heavy oils and residua*, CRC Press (2007).
2. J. Ancheyta, *Modeling of processes and reactors for upgrading of heavy petroleum*, CRC Press (2013).
3. M. J. Angeles, C. Leyva, J. Ancheyta and S. Ramírez, *Catal. Today*, **220-222**, 274 (2014).

4. M. Absi-Halabi, A. Stanislaus and D. L. Trimm, *Appl. Catal.*, **72**, 193 (1991).
5. H. M. S. Lababidi, H. M. Sabti and F. S. AlHumaidan, *Fuel*, **117**, 59 (2014).
6. J. Ancheyta, G. Centeno, F. Trejo and G. Marroquín, *Energy Fuels*, **17**, 1233 (2003).
7. J. Ancheyta, F. Trejo and M. S. Rana, *Asphaltenes: Chemical transformation during hydroprocessing of heavy oils*, CRC Press, Taylor & Francis Group, Boca Raton (2010).
8. O. C. Mullins, *Energy Fuels*, **24**, 2179 (2010).
9. T. M. Nguyen, J. Jung, C. W. Lee and J. Cho, *Fuel*, **214**, 174 (2018).
10. J. G. Speight, *The chemistry and technology of petroleum*, Fifth Edition. Taylor & Francis (2014).
11. I. A. Wiehe, *Energy Fuels*, **26**, 4004 (2012).
12. I. Gawel, D. Bociarska and P. Biskupski, *Appl. Catal. A Gen.*, **295**, 89 (2005).
13. V. Sámano, F. Guerrero, J. Ancheyta, F. Trejo and J. A. I. Díaz, *Catal. Today*, **150**, 264 (2010).
14. G. Díaz-Boffelli, J. Ancheyta, J. A. D. Muñoz and G. Centeno, *Energy Fuels*, **32**, 55 (2018).
15. H. R. Olar, M. Halafawi and L. Avram, *Pet. Coal.*, **63**, 278 (2021).
16. R. Sahu, B. J. Song, J. S. Im, Y. P. Jeon and C. W. Lee, *J. Ind. Eng. Chem.*, **27**, 12 (2015).
17. H. Martinez-Grimaldo, H. Ortiz-Moreno, F. Sanchez-Minero, J. Ramírez, R. Cuevas-Garcia and J. Ancheyta-Juarez, *Catal. Today*, **220-222**, 295 (2014).
18. H. Ortiz-Moreno, J. Ramírez, F. Sanchez-Minero, R. Cuevas and J. Ancheyta, *Fuel*, **130**, 263 (2014).
19. K. S. Go, S. H. Lim, Y. K. Kim, E. H. Kwon and N. S. Nho, *Catal. Today*, **305**, 92 (2018).
20. A. Quitian and J. Ancheyta, *Energy Fuels*, **30**, 10117 (2016).
21. H. B. Park, K. D. Kim and Y. K. Lee, *Fuel*, **222**, 105 (2018).
22. N. T. Nguyen, K. H. Kang, P. W. Seo, N. Kang, D. Van Pham, C. Ahn, G. T. Kim and S. Park, *Energies*, **13**, 4444 (2020).
23. N. T. Nguyen, K. H. Kang, H. H. Pham, K. S. Go, D. Van Pham, P. W. Seo, N. S. Nho, C. W. Lee and S. Park, *J. Ind. Eng. Chem.*, **102**, 112 (2021).
24. K. H. Kang, N. T. Nguyen, P. W. Seo, H. Seo, G. T. Kim, N. Kang, C. W. Lee, S. J. Han, M.-C. Chung and S. Park, *J. Catal.*, **384**, 106 (2020).
25. R. Prajapati, K. Kohli and S. K. Maity, *Fuel*, **288**, 119686 (2020).
26. N. T. Nguyen, S. Park, J. Jung, J. Cho, C. W. Lee and Y. K. Park, *J. Ind. Eng. Chem.*, **61**, 32 (2018).
27. H. Rezaei, S. J. Ardakani and K. J. Smith, *Energy Fuels*, **26**, 2768 (2012).
28. J. R. Kershaw and K. J. T. Black, *Energy Fuels*, **7**, 420 (1993).
29. A. Hassan, L. Carbognani and P. Pereira-Almao, *Fuel*, **87**, 3631 (2008).
30. N. T. Nguyen, K. H. Kang, C. W. Lee, G. T. Kim, S. Park and Y. K. Park, *Fuel*, **235**, 677 (2019).
31. X. Li, S. Hu, L. Jin and H. Hu, *Energy Fuels*, **22**, 1126 (2008).
32. I. Merdrignac, C. Truchy, E. Robert, I. Guibard and S. Kressmann, *Pet. Sci. Technol.*, **22**, 1003 (2004).
33. Q. Sheng, G. Wang, N. Jin, M. M. Husein and J. Gao, *Fuel*, **255**, 115736 (2019).
34. G. Félix and J. Ancheyta, *Fuel*, **241**, 495 (2019).
35. S. Humbert, G. Izzet and P. Raybaud, *J. Catal.*, **333**, 78 (2016).
36. H. Rezaei, S. J. Ardakani and K. J. Smith, *Energy Fuels*, **26**, 6540 (2012).
37. N. Panariti, A. Del Bianco, G. Del Piero, M. Marchionna and P. Carniti, *Appl. Catal. A Gen.*, **204**, 215 (2000).
38. H. Rezaei and K. J. Smith, *Energy Fuels*, **27**, 6087 (2013).
39. G. Bellussi, G. Rispoli, D. Molinari, A. Landoni, P. Pollesel, N. Panariti, R. Millini and E. Montanari, *Catal. Sci. Technol.*, **3**, 176 (2013).
40. B. Liu, K. Zhao, Y. Chai, Y. Li, D. Liu, Y. Liu and C. Liu, *Fuel*, **246**, 133 (2019).
41. H. Rezaei, X. Liu, S. J. Ardakani, K. J. Smith and M. Bricker, *Catal. Today*, **150**, 244 (2010).
42. F. Trejo, J. Ancheyta, G. Centeno and G. Marroquín, *Catal. Today*, **109**, 178 (2005).
43. S. Mitra-Kirtley, O. C. Mullins, J. Van Elp, S. J. George, J. Chen and S. P. Cramer, *J. Am. Chem. Soc.*, **115**, 252 (1993).
44. S. H. Kim, K. D. Kim and Y. K. Lee, *J. Catal.*, **347**, 127 (2017).