Comparative reactivity between thermal and catalytic hydrocracking of vacuum residue: Effect of asphaltenes

Ngoc Thuy Nguyen[a,b,1], Sunyoung Park[a], Jinhwan Jung[a], Jungmo Cho[a,b], Chul Wee Lee[a,b,*], Yong-Ki Park[a,b,*]

[a] Center for Convergent Chemical Process, Korea Research Institute of Chemical Technology (KRICT), Daejeon 305-600, Republic of Korea
[b] School of KRICT, University of Science and Technology (UST), Daejeon 305-333, Republic of Korea

A B S T R A C T

The comparative effect of reaction severity at variation of the temperature (410–440 °C) and time (0.5–4 h) in the presence and absence of Mo-octoate on VR hydrocracking was studied. In the presence of 250 ppm Mo improved selectivity of naphtha and middle distillate fractions. The SARA and H_2 consumption results showed the different tendency of asphaltene conversion during thermal and catalytic hydrocracking. Asphaltenes seemed to be the main fraction converted to coke during hydrocracking reaction. For understanding the tendency of coke formation during hydrocracking of various asphaltene content feedstocks, the effect of asphaltene content on MCR, H/C ratio, M_n, and Ni, V, N, S content of feedstocks was investigated.

Introduction

Vacuum residue (VR) is the heaviest fraction from the bottom of a vacuum distillation column. VR includes a high content of metal (Ni, V), N, S, and asphaltenes. To meet the rising demands for light fuel oils, means of upgrading VR into lighter products have attracted much attention. A slurry-phase hydrocracking process is the best method for upgrading this material to obtain valuable product, while minimizing gas and coke formation [1–3].

Ortiz-Moreno et al. [4–6] studied the effect of reaction conditions, catalyst amount, and catalyst precursors on Maya VR hydrocracking. They concluded that thermal hydrocracking was limited by the production of large amounts of gas and coke. In the presence of a catalyst, the benefits in comparison to thermal cracking were decreased coke and gas formation and increased liquid yield; however, the reaction conversion decreased. Rezaei et al. [7] claimed that there were two sources of hydrogen consumption. The first consumption was used to prevent coke

formation by prohibiting polymerization reaction of heavy molecules into coke. And the other source is hydrogenation of compounds with unsaturated bonds (such as olefins) and aromatic rings of polyaromatic rings present in heavy oil. As an evidence, H/C ratio of liquid products was linearly increased as a function of catalyst amount. In this work, we observed another evidence for the role of H_2 during catalytic hydrocracking of VR by SARA analysis.

Asphaltenes are known as coke precursors because they are prone to form coke during hydrocracking reaction [8–11]. In previous studies, asphaltenes were precipitated from heavy oil by a solvent, such as *n*-pentane or *n*-heptane [12,13]. The influence of asphaltenes on coke formation during the thermal hydrocracking of Brazilian distillation residues was investigated by Goncalves et al. [11]. Based on thermo-gravimetric data, they concluded that asphaltenes are the main contributors to coke formation during the thermal cracking of atmospheric distillation residues [11]. On the other hand, MCR can be used as an indicator for coke formation in the thermal cracking process. The effect of H/C ratio and molecular weight (M_n) on MCR was studied by Ternan and Kriz [14]. They confirmed that increasing the H/C ratio will decrease the coke formation (MCR), while molecules with smaller M_n values will produce less coke than those with larger M_n values. Therefore, in order to understand the effect of asphaltenes on coke formation during hydrocracking reaction, the effect of asphaltene content on

* Corresponding authors at: Center for Convergent Chemical Process, Korea Research Institute of Chemical Technology (KRICT), Daejeon 305-600, Republic of Korea.
E-mail addresses: chulwee@krict.re.kr (C.W. Lee), ykpark@krict.re.kr (Y.-K. Park).
.
[1] On a study leave from Key Laboratory for Petrochemical and Refining Technology, Vietnam Institute of Industrial Chemistry (VIIC), No. 2 Pham Ngu Lao, Hoan Kiem, Ha Noi, Viet Nam.

the properties of feedstock in term of MCR, M_n, and H/C atomic ratio needs to be investigated.

The objective of this study is to compare the effect of reaction conditions (410–440 °C, 0.5–4 h) in the presence and absence of catalyst on the product distribution. H_2 consumption was estimated to show the role of catalyst in reducing the coke formation. Moreover, we studied the effect of asphaltenes on hydrocracking reaction in presence and absence of catalyst by using heavy feedstocks with five different asphaltene contents. The effect of asphaltene content on MCR, H/C ratio, M_n, and content of Ni, V, N, and S in hetero-organic compounds of feedstocks was investigated to understand the trend of coke formation during thermal and catalytic hydrocracking of heavy oils which have various asphaltene contents.

Experimental

Thermal and catalytic hydrocracking experiments

Asphaltene fraction was separated from VR (properties shown in Table 1) by mixing for 4 h with n-pentane in a mass ratio of n-pentane (n-C_5) per VR of 40. The insoluble part was separated by filtering. To get a high asphaltene content in the insoluble part, the filtered insoluble material was mixed again with n-pentane. After the materials were mixed three times, the asphaltene content in the pitch was 79 wt%. Feedstocks with various asphaltene contents were prepared from VR according to Table 2.

Thermal and catalytic hydrocracking experiments were performed in a 100 ml Parr slurry-phase batch reactor in the closed system. The catalyst precursors used in this study were Mo-octoate purchased from Shepherd with 15.4 wt% of Mo. For catalytic hydrocracking reaction, the batch reactor was loaded with 20 g of feedstocks and catalyst with a metal concentration of 250 ppm. The mixture was degassed by purging with H_2 to remove all gas impurities. At the beginning of reaction, the mixture was stirred at 100 rpm and kept stable at 80 °C and 80 bar of H_2 for about 30 minutes, from which mass ratio of H_2/VR is calculated as about 0.02 (wt%) assuming that H_2 is ideal gas [15]. The temperature was increased from 80 °C to the reaction temperature. At 200 °C, the stirring speed was increased to 1500 rpm. For comparison, thermal hydrocracking was performed with the same procedure of catalytic hydrocracking in the absence of catalyst.

After hydrocracking reaction, the gas product was collected in a gas bag to determine the gas composition by GC. The liquid and precipitate were separated by syringe, and they were analyzed by simulated distillation (SIMDIS) so that the liquid product distribution could be quantified. Coke was determined as a toluene insoluble from precipitate. The coke, liquid, and gas yield were calculated based on Ref. [6].

Characterization

Thermo Scientific Flash EA — 2000 Organic Elemental Analyzer (EA) and Thermo Scientific iCAP 7400 duo Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) were used to determine the weight percentage of C, H, N, and S as well as Ni and V metals in the samples. SIMDIS gas chromatography using an Agilent GC 7890 according to ASTM 7169 was carried out to determine the distillation curves of the liquid products. The gas composition, H_2 remaining, and H_2S formation after hydrocracking reaction were determined by GC gas 6500 with FID and a TCD detector. The micro carbon residue (MCR) was tested by a micro carbon residue tester, MCRT-160, following ASTM D 4530-03. The saturate, aromatic, resin and asphaltene contents of the liquid products and feedstocks were also determined by a SARA instrument, IATROSCAN MK-6s, with a Chromarod-S5 column. The average molecular weight (M_n) of feedstocks were determined in Waters e2695 Gel Permeation Chromatograph (GPC) with RI detector, waters fraction collector III, styragel HR — 0.5, 0.5, 4E, 4 column and using 1000 ppm of asphaltenes in THF solvent. X-ray photoelectron spectroscopy (XPS) was performed using an AXIS NOVA spectrometer with Al-Kα radiation. The XPS spectra of Mo 3d were recorded, and their binding energy (BE) referred to the energy of the C 1s peak (BE = 284.8 eV). The morphology of Mo active catalyst phase on the coke were detected by using a Talos F200S transmission electron microscope (TEM).

Results and discussion

Detection of active phase catalyst

Lott and Lee [16] investigated the effective of Mo-octoate oil soluble precursor on reducing coke formation during hydrocracking of various heavy oil feedstocks. The reason for using Mo-octoate precursor is to disperse Mo into the heavy oil. The active phase catalyst was formed in-situ during the hydrocracking process by the decomposition of Mo-octoate precursor to Mo metal at high temperature and the formation of Mo-S active species with excess of S in heavy oil. The evidence for exist of Mo-S active catalyst in the coke product were shown by XRD, XPS [17] and HR-TEM [18].

Fig. 1(A) and (B) demonstrates the XPS of MoS_2 bulk and Mo-species observed in coke after hydrocracking reaction. In Fig. 1(B), there was only one chemical environment for Mo in the dispersed catalyst in the coke phase; the peaks at 227 and 232 eV are ascribed to $Mo_{3d5/2}$ and $Mo_{3d3/2}$, respectively [17]. A comparison with the XPS of MoS_2 bulk showed that it was quite similar with dispersed catalyst phase in the coke. And also, Fig. 1(C) shows an HR-TEM image of crystalline layered MoS_2 in coke after hydrocracking reaction, which is similar to the observation of a previous study [18]. From XPS and HR-TEM analysis suggest that the dispersed active catalyst exists mainly in the form of MoS_2.

Effect of reaction time and temperature on total gas, coke and liquid products

In general, during hydrocracking reaction, three types of products are obtained such as coke, gas and liquid. Fig. 2(A) and (B) shows the total gas, coke and liquid yield depending on thermal and catalytic hydrocracking when reaction time and temperature were controlled. An increasing in the reaction time and temperature promote the decreasing of liquid product yield due to the cracking of liquid into gas [4–6] and polymerization to form the coke [7,19]. In the presence of catalyst, the formation rate of gas and coke was lowered than that of thermal hydrocracking, while higher

Table 1
Properties of VR feedstock.

Properties		Distribution	
API	4.3	SARA analysis (wt%)	
C (wt%)	83.4	Saturate	5.0
H (wt%)	10.1	Aromatic	51.8
N (wt%)	0.54	Resin	18.4
S (wt%)	5.88	Asphaltene	24.8
Ni (wt.ppm)	72.3	SIMDIS (wt%)	
V (wt.ppm)	309.1	Gas oil (343–524 °C)	21.5
CCR (%)	23.3	Residue (524 °C-FBP)	78.5