



Vacuum residue upgrading through hydroprocessing with subcritical water



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ARTICLE INFO

Article history:

Received 1 July 2015

Received in revised form 30 August 2015

Accepted 21 September 2015

Available online 14 November 2015

Keywords:

Vacuum residue

Subcritical water

Upgrading

Liquid product

Conversion

Hydroprocessing

ABSTRACT

Vacuum residue upgrading reactions were carried out with subcritical water and catalyst. Experiments were performed in the autoclave batch reactor at the various reaction conditions (i.e. temperature change, catalyst amount, reaction time, and water amount). The maximum liquid product conversion was 55.5 wt.% at 400 °C, 50 g of VR, 0.5 g of MoNaph catalyst, 6 h of reaction time, and 20 g of water amount. For evaluation of liquid products, C/H atomic ratio, aromaticity, aromaticity condensation, and boiling point distribution was measured by elemental analysis (EA), ¹H nuclear magnetic resonance (¹H NMR) and gas chromatography simulated distillation (GC-SIMDIS). Results showed that water converts the vacuum residue to the liquid product, and its conversion yield is comparable to that of the hydrogen gas process. Moreover, synthesized MoS₂ nanosheet catalyst was used to compare the liquid product conversion.

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1. Introduction

Today, 30–40% of total energy is generated from the petroleum crude oil resources [1]. About 50% of this crude oil becomes primarily useful energy products like gasoline and diesel through refinery processes; however, the rest remains residue which is difficult to handle. The firstly gathered residual components have very high viscosity, so they cannot be used directly in its natural state. Vacuum residue (VR), which is distilled at 80 mmHg pressure and over 500 °C temperature, is the most viscous material among residual components. Residue upgrading, especially vacuum residue, has become very important study thanks to the large amount of residual portion. There are many techniques for heavy oil upgrading such as solvent deasphalting [2], delayed coking [3], visbreaking [4], FCC [5] and catalytic hydroprocessing [6]. Catalytic hydroprocessing is widely investigated because of its relatively high productivity and selectivity within the processes [7].

Many studies for treating VR focus on catalytic hydrocracking reactions that produce lighter products [8–13]. Generally hydrogen gas is used for hydrocracking reactions, and experimental conditions are within 400–450 °C and 5–15 MPa [14–17]. High temperature and pressure are essential to break the VR. Hydrogenation

could be the main reaction, and other reactions such as pyrolysis, desulfurization, and ring opening also present.

However, catalytic hydrocracking reactions are very dangerous and even further with the presence of hydrogen. Many safety issues including environmental problems have been intensively researched in hydrocracking area. Therefore, a new approach for vacuum residue upgrading is of great need. In crude oil wells, transporting residual components is an important part for petroleum industry. Reduction of the viscosity is required to ease the transportation of residue. Techniques such as “aquathermolysis” use steamed water as reactant to reduce the viscosity of heavy oil. Many researches revealed that steamed water injection can reduce viscosity of vacuum residue [18]. Catalytic aquathermolysis experiments were performed with various catalysts such as minerals, metal ions, solid acid salts, aromatic sulfonic compounds, surfactants, and metallic chelates [19–24]. These studies showed that water can affect vacuum residue even though their relation is between oil and water.

Aquathermolysis just focuses on viscosity reduction in low temperature and long reaction time. There are few researches for direct production of liquid product from vacuum residue with water. In the condition of high temperature and pressure, water exists in subcritical state. Moreover, it is reported that subcritical state water has solubility for organic compounds [25,26]. This could be adaptable to hydrocracking of vacuum residue. In this study, direct liquid conversions via catalytic upgrading reactions with deionized (DI) water of subcritical state were performed.

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Table 1
Properties of vacuum residue feedstock obtained from SK Innovation Company.

Properties	Value
CCR ^a (wt.%)	22.90
Total nitrogen (wt.%)	0.48
Total sulfur (wt.%)	6.97
Nickel (wppm)	44.50
Vanadium (wppm)	145.10
C5 asphaltene (wt.%)	18.00
C7 asphaltene (wt.%)	10.00
Specific gravity	1.04
C ₇ /H ₇ (atomic ratio)	0.65

^a Conradson carbon residue.

Water was used for safe and cheap alternative material to hydrogen. To observe conversion changes, several variables of reaction temperature, catalyst amount, reaction time and water amount were set as variables. Liquid products were analyzed using elemental analysis (EA), nuclear magnetic resonance (NMR), and gas chromatography simulated distillation (GC-SIMDIS) analysis were carried out for analysis of liquid product components. For comparison, synthesized MoS₂ nanosheet catalyst was used for direct liquid production.

2. Experimental

2.1. Materials

Vacuum residue obtained from SK Innovation Corporation was used. The properties of VR are shown in Table 1. Vacuum residue was kept at 100 °C in an oven for fluidity before reaction. Commercial molybdenum naphthenate (MoNaph, 10 wt.% of Mo, Shepherd Chemical Company) and synthesized MoS₂ nanosheet were used for catalysts. Deionized water (purified by Milli-Q, Millipore) was included as reactant.

2.2. Cracking reactions of the vacuum residue with MoNaph catalyst and water

VR cracking reactions with MoNaph catalyst were carried out in the high pressure autoclave batch reactor (350 ml inner volume, made by Hanwoul Engineering Corporation). Magnetic drive stirring system, temperature and pressure monitoring program via personal computer, and gas vent valve line were included in this system.

Vacuum residue (50 g) was used as feedstock in each experiment. Only one variable was altered within amount of catalyst, amount of water, reaction temperature, and reaction time while the other variables were fixed. VR (50 g), DI water (0, 10 and 20 g) and MoNaph catalyst (0, 0.1 and 0.5 g) were placed in the autoclave reactor. After purging the reactor with He gas for 30 min by 100 ml/min, the autoclave was sealed. Cooling water line was connected to magnetic drive stirring system and the temperature was increased. Temperature was linearly increased from room temperature to purposed reaction temperatures (300, 350, 400 and 450 °C) at a rate of 5 °C/min. When the temperature reached 100 °C, the mixture was stirred at 500 rpm. After reaching designated temperature, the reaction system was maintained for 2, 3, 6 and 8 h of reaction time. During the experiment, temperature and pressure were recorded simultaneously by personal computer program. After the reaction, the autoclave reactor was naturally cooled down to room temperature. From the mixture, the liquid product was separated from the solid residue, and the unreacted water was removed using silica beads.

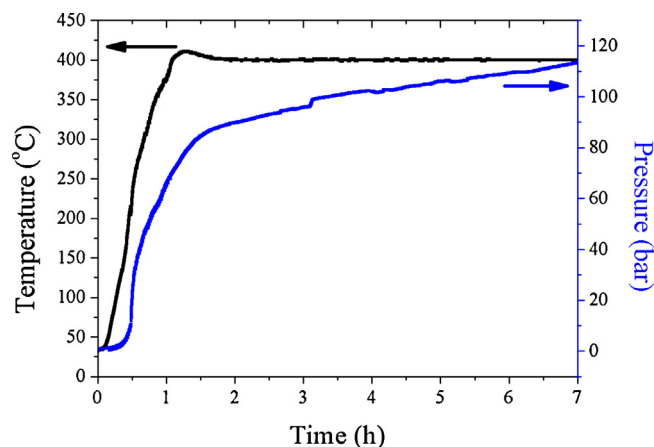


Fig. 1. Pressure profile as a function of reaction time (50 g of VR, 0.5 g of MoNaph catalyst, and 20 g of water).

2.3. Liquid products conversion and analysis

Liquid product conversion was calculated by the following equation.

$$\text{Liquid product conversion (wt.\%)} = \frac{\text{liquid product (g)}}{\text{VR (50 g)}} \times 100 \quad (1)$$

Elemental analysis of liquid products was performed by analyzer 1 (EA1110-FISONS, CE Instruments) for C, H, N, and S and analyzer 2 (Flash EA 1112, Thermo Finnigan) for determination of O in the products. ¹H Nuclear Magnetic Resonance (NMR) spectrometer was operated with the AMX-500 (Bruker Corp.) under the condition with chloroform-d solvent (1 vol.% of dilution), 500.14 MHz of frequency. Gas Chromatography Simulated Distillation (GC-SIMDIS) was performed with the Agilent HT750A-7890M.

2.4. Cracking reactions of the vacuum residue with MoS₂ nanosheet catalyst and water

For comparison, VR cracking reactions with synthesized MoS₂ nanosheet catalyst were carried out in the same batch reactor. MoS₂ nanosheet catalyst was synthesized based on Peng et al. [27].

One variable was altered within amount of catalyst, and reaction temperature while the other variables were fixed. VR (50 g), DI water (5, 10, 20 and 30 g) and MoS₂ catalyst (0.5 g) were placed in the autoclave reactor. After sealing the autoclave, cooling water line was connected to magnetic drive stirring system and the temperature was increased. Temperature was linearly increased from room temperature to purposed reaction temperatures (400, 410, 420 and 430 °C) at a rate of 5 °C/min. When the temperature reached 100 °C, the mixture was stirred at 500 rpm. After reaching designated temperature, the reaction system was maintained for 6 h of reaction time. After the reaction, the autoclave reactor was naturally cooled down to room temperature. From the mixture, the liquid product was separated from the solid residue, and the unreacted water was removed using silica beads.

3. Results and discussion

3.1. Reaction pressure profile as a function of reaction time

Fig. 1 shows the autoclave pressure profile as a function of reaction time at 50 g of VR, 0.5 g of MoNaph catalyst, and 20 g of water at 400 °C. The maximum pressure was 113.2 bar at the end of the

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