



Supercritical methanol as an effective medium for producing asphaltene-free light fraction oil from vacuum residue

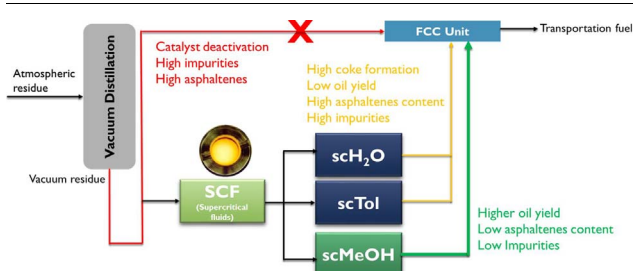


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GRAPHICAL ABSTRACT



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ABSTRACT

The upgrading of vacuum residue (VR) in supercritical methanol (scMeOH) was investigated without using catalysts. Various process parameters, including temperature (350–425 °C), reaction time (30–90 min), and additives (toluene and hydrogen) were explored to optimize the yield of light fraction oil (LFO) with few impurities. At a 400 °C, 16.7 wt% of VR in methanol for 60 min, the LFO produced in scMeOH contained very low asphaltene content (0.74 wt%) and a very low amount of heteroatom/metallic impurities (S, 3.58 wt%; N, non-detectable; Ni, 10.4 ppm; V, 36.9 ppm, Fe, 7.3 ppm). In addition, the naptha-to-diesel fraction increased from 1 wt% (VR feed) to 15 wt% and the saturate + aromatic content increased from 43.7 area% (VR feed) to 59.6 area% in the LFO. When the reaction time was extended to 90 min at 400 °C, a complete removal of asphaltenes could be achieved.

1. Introduction

The upgrading of petroleum residue in supercritical fluids is a promising alternative to conventional carbon-rejection and hydrogen-addition techniques because of its unique fast-transport properties and homogeneous reaction conditions. These characteristics may allow for mass and heat transfer limitations to be overcome [1–3]. When compared to the conventional pyrolysis approaches, a greater amount of light fractions with lower coke yields can be obtained using supercritical fluids as a reaction media. In particular, the upgrading of

vacuum residue (VR) in sub- and supercritical water (subH₂O or scH₂O, T_c = 374 °C and P_c = 22.1 MPa) has been extensively studied because of its unique physicochemical properties, including high hydrocarbon and gas solubility, high diffusivity, and zero surface tension [2–5]. In addition, the dispersion effect of scH₂O could suppress the recombination of neighboring reaction intermediates, suppressing the formation of coke by the so-called “cage effect” [3,6,7].

Although these factors make scH₂O a highly promising medium for VR upgrading, there are some drawbacks. Firstly, the degree of asphaltene removal in the upgraded oil is not satisfactory. For example,

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even though VR upgrading in scH_2O at 380–420 °C and 25 MPa for 1 h resulted in high liquid yield (88.5–94.9 wt%), a large amount of asphaltenes (6.5–18 wt%) persisted in the upgraded oil in scH_2O [8]. Cheng et al. reported that VR upgrading in scH_2O at 25 MPa, 410 °C for 1 h resulted in 5.1 wt% asphaltenes in the upgraded oil [7]. The upgrading of de-oiled asphaltenes in scH_2O resulted in low asphaltene removal (maximum 24 wt% removal) at 400 °C and 30 MPa for a 90 min reaction [9]. Secondly, the removal of heteroatoms (e.g., nitrogen and sulfur) during the scH_2O upgrading process has shown limitations; the degree of nitrogen removal was low (16.4 wt% reduction) when VR was treated in scH_2O at 420 °C and 25 MPa for 1 h [7]. In some cases, the sulfur content in the middle distillate unexpectedly increased after the upgrading of bitumen in scH_2O at 450 °C for 2 h (from 4.2 wt% to 6.0 wt%) [6]. Thirdly, the hydrogen-deficient condition in scH_2O medium can result in upgraded oil with high aromatic contents. For example, the H/C molar ratio of the upgraded oil from Canadian bitumen decreased from 1.51 to 1.20 after reaction at 450 °C in scH_2O for a 1 h reaction condition [6]. Finally, after the upgrading reaction in scH_2O , highly stable petroleum emulsion would tend to form, which leads to the loss of light fraction oil in the form of unrecoverable waste [10]. The formation of emulsion was observed after the upgrading of de-oiled asphaltenes in scH_2O at 16.7 wt%, 400 °C for a 1.5 h reaction [9].

As an alternative to scH_2O , supercritical hydrocarbons such as hexane, xylene and dodecane have been tested in the upgrading of bitumen, heavy oil, and the heavy fraction to produce sweet oil [4,11–14]. Activated carbon and high-pressure hydrogen were utilized with the supercritical hydrocarbons to achieve “hydrogen shuttling” a process, in which the hydrogen is transferred between the hydrocarbon solvent and the activated carbon surface to allow hydrocracking in heavy oils [4]. However, as in the case of scH_2O , a significant removal of asphaltenes has not yet been achieved. For example, the hydrocracking of VR in supercritical hexane in the presence of acid-treated activated carbon resulted in a relatively low VR conversion (57.7 wt%). This conversion, conducted with 6.89 MPa partial hydrogen pressure at 399 °C for 0.5 h reaction condition, resulted in high coke formation (23.6 wt%) [12]. When supercritical *m*-xylene was used under identical reaction conditions, the coke yield slightly decreased to 15.6 wt% [12]. The catalytic conversion of VR in supercritical toluene (scTol) in the presence of a NiMo/activated carbon catalyst resulted in a high yield upgraded oil (91.3 wt%) at 10 MPa H_2 , 380 °C for 1 h, but a considerable amount of asphaltenes (5.6 wt%) was present in the upgraded oil (which corresponds to 68% asphaltene removal) [11]. In addition, there has been no report regarding metal removal efficiency when either supercritical hydrocarbon or scH_2O were used for petroleum residue upgrading. Therefore, it is highly desirable to develop economically viable and efficient upgrading techniques that could achieve high oil yield, low coke formation, and high removal of asphaltenes and heteroatom/metallic impurities in the upgraded oil.

5 In this study, we explore the use of supercritical methanol (scMeOH , $T_c = 239$ °C and $P_c = 8.1$ MPa) as an effective medium for VR upgrading. scMeOH exhibited a lower dielectric constant than high-temperature water, which could lead to a desirable solubility of oil fractions [15,16], and retard the coke formation when compared to non-solvent upgrading in case of using de-oiled asphaltenes as the feedstock [9]. In addition, with its hydrogen donation ability, scMeOH can serve as the hydrogenolysis agent to depolymerize high-molecular-weight species into small fractions. In addition, scMeOH can act as a radical quenching agent through the initial donation of α -hydrogen in hydride form, followed by the formation of an electron-deficient hydroxyalkylation mechanism [17,18]. The other proposed hydrogen donation mechanism of alcohol in its supercritical state is Meerwein–Ponndorf reduction. In this process, alcohol reduction initially occurs, which leads to alkoxide ion and proton transfer, followed by α -hydrogen donation and ketone formation [19]. In its supercritical state, methanol could undergo dehydrogenation to produce methanal, and

through a further addition reaction, it can produce methyl formate. In this scMeOH decomposition pathway, more than 35% of hydrogen could be produced [20]. Other alcohols (e.g., ethanol and isopropanol) at their supercritical state could generate hydrogen, but methanol is much cheaper than ethanol and isopropanol, which make it more promising to develop a practical-scale upgrading unit. Previously scMeOH was used for upgrading of fast pyrolysis bio-oil [21–24]. In this study, witnessing those mentioned advantages, scMeOH was utilized for the first time for petroleum residue upgrading. VR upgrading in scMeOH was compared with conventional visbreaking, hydrovisbreaking, scH_2O - and supercritical toluene-based upgrading to understand the unique upgrading behavior of scMeOH .

2. Experimental

2.1. Materials

The VR feed, which was the bottom product of the vacuum distillation unit, was supplied by an oil refinery in South Korea. Because VR did not flow at room temperature, preheating at 120 °C for 60 min was required prior to each reaction for sampling. High-performance liquid chromatography (HPLC)-grade methanol (MeOH , $\geq 99.9\%$), toluene (Tol , $\geq 99.9\%$), and dichloromethane (DCM , CH_2Cl_2 , $\geq 99.9\%$) were purchased from Daejung Chemical & Metals Co. (South Korea), and anhydrous carbon disulfide (CS_2) was purchased from Sigma-Aldrich (USA). Distilled and de-ionized (DDI) water was prepared using the AQUAMax™-Basic 363 water purification system (Younglin Instrument Co., Ltd., South Korea). The specific resistance of DDI water was in the range of 1–15 $\text{M}\Omega$ cm. High-purity nitrogen (99.99%) and hydrogen (99.99%) was purchased from the JC Gas Company (South Korea).

2.2. Experimental apparatus

The VR upgrading was carried out in a custom-built, batch reactor with an inner volume of 140 mL. Detailed information on the reactor was described elsewhere [23]. Only a short description will be given here. This reactor was equipped with a magnetically-driven mechanical stirrer. The temperature of the reactor was controlled using two electrical heating elements: a heating furnace, and cartridge heaters inserted inside the reactor wall, which were connected to a programmable proportional–integral–derivative (PID) temperature controller.

2.3. Experimental methods

The reaction parameters examined in this study are listed in Table 2. In case of a reaction without supercritical fluids and hydrogen, 10 g of VR was introduced into the reactor, and then the reactor was purged with nitrogen several times and pressurized with N_2 at 1 MPa (case 1, Table 2). The reactor was heated to 400 °C with 500-rpm stirrer motion. In case a hydrovisbreaking reaction occurred, N_2 purging was substituted with 1 MPa of H_2 (case 2). When the supercritical solvent was used for VR upgrading, 45 g of solvent and an experimentally desired amount of VR were introduced into the reactor, and then purged with nitrogen several times and pressurized with N_2 at 1 MPa. The reactor was heated to experimentally desired temperatures with a 500 rpm stirring motion. The reaction pressure was maintained in the range of 30–35 MPa. After the reaction completed, the heating system was turned off and the reactor was quenched rapidly using ambient-temperature water. When the temperature fell below 80 °C, the reactor was air cooled to room temperature using an electric fan. The time required for temperature ramping (~ 23 min), water-quenching cooling (8–10 min), and air cooling (~ 40 min) was not included in the reaction times. Fig. S1 shows the representative temperature and pressure profiles of the reaction. Two or three replicates were conducted for each set of conditions, and the average values are reported.

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