



Full Length Article

Conversion of petroleum emulsion into light fraction-rich upgraded oil in supercritical methanol

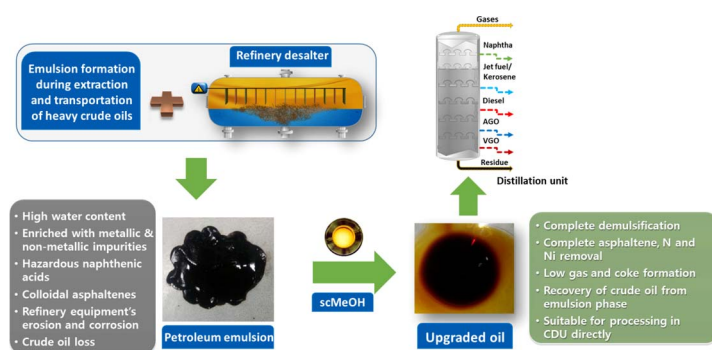


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GRAPHICAL ABSTRACT



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ABSTRACT

Unconventional crude oil extraction, transportation, and downstream refining have encountered a huge formation of petroleum emulsion (or rag layer), which causes serious problems such as equipment corrosion, loss of crude oil, and catalyst poisoning. In addition, if not treated properly, the rag layer engenders toxic and hazardous effects on the environment and living organisms. In this study, we developed a supercritical methanol (scMeOH) route to convert the petroleum emulsions into light fraction-rich upgraded oil with low impurities. Several process variables were investigated, including temperature (350–400 °C), rag layer concentration (16.7–100 wt%), and reaction time (30–90 min). At 400 °C, 35 MPa, 16.7 wt%, and 90 min, a high recoverable oil yield (76.7 wt%) was achieved. In addition, the naphtha-to-diesel fractions increased significantly from 6.0 (rag layer) to 42.0 wt% (upgraded oil), the acidity in terms of total acid number (TAN) was reduced by up to 91.5% from 58.7 (rag layer) to 5.0 mg-KOH/g-oil (upgraded oil), and the heteroatoms (O, N, S) and metallic impurities (Ca, Ni, V, Fe) were reduced significantly in the upgraded oil. A model compound study revealed that esterification is the major deacidification pathway for TAN reduction. The rag layer conversion in scMeOH was compared with those in subcritical water (without adding additional methanol or water) and in supercritical water (scH₂O). Asphaltenes, Ni, and N were completely removed from the toxic rag layer in the presence of scMeOH as compared to scH₂O treatment, which makes it more suitable for upgrading.

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1. Introduction

The exponential population growth and technological advancements have resulted in increased attention paid to the effective utilization of unconventional crude oils (high-acid crudes, heavy crudes, bitumen, oil sands) because conventional crudes are depleting rapidly at the rate of *ca.* 4.5% annually [1]. However, because of their high viscosity, high acidity, high asphaltene contents, large amounts of metallic and nonmetallic impurities, low API gravity, and low H/C ratio, a large amount of the unconventional crudes are not suitable to be processed in existing refineries, which have been optimized to treat conventional crude oils [2]. The complexity of unconventional crudes is attributed to the compositional alteration caused by the different degrees of bacterial degradation in petroleum reservoirs over a long period of time [3]. During extraction, transportation, and desalting of the unconventional crudes, the formation of a highly dense, multiphase emulsion layer between the water and oil phase typically occurs, which is normally referred to as petroleum emulsion or a rag layer [4–7]. Particle-stabilized Pickering emulsions and surfactant-stabilized emulsions are the two dominant mechanisms of the petroleum emulsion formation, which are responsible for the huge loss of crude oil that is trapped in the emulsion phase [8–11]. For example, Pickering emulsions are remarkably stable because of the high detachment energy ($10^7 K_B T$) of the particles from the oil–water interface. The presence of particles at the interface generates high steric hindrance to restrain the droplet coalescence [12]. Indigenous surfactant-based petroleum emulsions are formed by the accumulation and irreversible adsorption of asphaltenes, naphthenic acids (NAs), and external surfactants, and ultimately create highly rigid interfacial films [13–16]. NAs are highly toxic and hazardous components of the wastewater emitted from petroleum refineries, and extracting/processing the unconventional oils and their removal from unconventional crude oil plays a crucial role in pollution control [17,18]. Aquatic organisms are likely exposed to NAs, which is considered to be a serious threat because of the sublethal effects in fish gill tissues [19].

Several methods have been proposed for the demulsification of petroleum emulsions, including electrostatic coalescence [20,21], chemical demulsifiers [22,23], membranes [24], freeze/thaw processes [25,26], centrifugal separators [27], pH control [28], complete combustion [29], stabilization/solidification [30], and fuel in boilers [31]. However, it is still a great challenge to demulsify and utilize the oil trapped in the emulsion phase. Recently, we proposed a new supercritical water (scH₂O)-based route for simultaneous demulsification of the petroleum emulsion and reduction of the asphaltenes and impurities in the recovered oil [32]. The upgraded oil yields were in the range of 75–80 wt% with moderate coke formation (7.1–8.6 wt%) at 400 °C, 30 MPa for 30–90 min. The total acid number (TAN) was reduced by more than 80% and the nondistillable residue fraction (carbon # > C₄₄, boiling point > 535 °C) in the rag layer was reduced by more than 90% in the upgraded oil. However, there is still some amount of residual asphaltenes remained in the upgraded oil (3.6 wt%), which is higher than the upper limit (less than *ca.* 1.6 wt%) of crude distillation unit (CDU) requirements. In addition, when scH₂O was used, the amounts of metallic (Ni, 22.8 ppmw; V, 96.7 ppmw) and heteroatom impurities (S, 1.82 wt%) were not reduced to acceptable limits (Ni + V ≤ 90 ppmw, S ≤ 1.5 wt%) for direct use of the upgraded oil in existing CDUs. The abundance of asphaltenes and impurities in the upgraded oil is detrimental to the environment and the life of catalysts, and engenders severe corrosion to refinery equipment by ash deposition [33]. Therefore, it is crucial to perform an in-depth investigation to address the above-mentioned limitations in reducing naphthenic acids, asphaltene, and impurities to an acceptable extent.

In this work, we demonstrate that the conversion of petroleum emulsion in supercritical methanol (scMeOH) can result in nearly complete removal of asphaltenes and effective reduction in the metallic and heteroatom impurities. Supercritical methanol (scMeOH,

T_c = 239 °C, P_c = 8.08 MPa) has been utilized for the effective conversion of de-oiled asphaltenes into light fractions and for TAN reduction of neat NA mixtures [34,35]. The unique properties of scMeOH, such as *in-situ* hydrogen donation [36], suitable dielectric constants, and relatively weak hydrogen bonding [37] make it a highly promising solvent and reactant for the conversion of the rag layer components into the upgraded crude oil with few impurities. The use of other types of supercritical alcohols (e.g., ethanol, isopropanol) in the rag layer conversion could be another option. Previously, effective conversion of various types of biomass into high-calorific value bio-oil in supercritical ethanol or in supercritical isopropanol have been investigated [38–43]. Some fraction of alcohol was consumed by self-decomposition and participation into the reaction during the reaction. For example, during the macroalgae conversion in supercritical ethanol at 400 °C and 42 MPa, approximately 18 wt% of ethanol was consumed [41]. When considering the much higher price of ethanol and isopropanol than methanol, the use of scMeOH in the rag layer conversion could lead to develop more economically viable process as compared to ethanol and isopropanol. Various process parameters, including temperature (350–400 °C), rag layer concentration (16.7–25 wt%), and reaction time (30–90 min) were explored to optimize the rag layer conversion in scMeOH. In addition, rag layer conversion in subcritical water (subH₂O) and in scH₂O were performed to compare the rag layer conversion behaviors. Finally, to understand the TAN reduction mechanism in scMeOH, two model compounds of NAs (*n*-hexadecanoic acid and 2-naphthoic acid) were treated with scMeOH and an in-depth production distribution was discussed.

2. Experimental section

2.1. Materials

Three unconventional crude oils, Laguna (Venezuela), Rubiales (Colombia) and Bachquero-13 (Venezuela) were provided by SK innovation (South Korea). HPLC grade methanol, dichloromethane (DCM), toluene, isopropanol (IPA), heptane, *n*-hexane, and deionized water, and 0.1 N KOH in IPA for TAN measurement were purchased from Sigma-Aldrich (USA). High-purity H₂ (99.999%), N₂ (99.999%), He (99.999%), and air (99.999%) were purchased from JC Gas Company (South Korea). Sodium bicarbonate (≥99.5%), sodium chloride (99.0%), sodium sulfate (≥99.5%), magnesium chloride (98.0%) and calcium chloride (≥96.0%) for preparing saline water were purchased from Alfa Aesar and Sigma Aldrich (USA). Distilled–deionized (DDI) water was prepared by using an AQUAMax™-Basic 363 water purification system (Younglin Instrument Co., Ltd., South Korea).

2.2. Formation of rag layer

Fig. S1 illustrates the procedures for preparing the rag layer, reaction, and product separation methods used in this study. Laguna, Rubiales, and Bachquero-13 were mixed in a weight ratio of 4:3:3 for preparing a representative unconventional crude oil in terms of acidity, asphaltene content, and metallic/heteroatom impurities. The oil phase used to prepare the rag layer was prepared by mixing heptol (80 vol% heptane and 20 vol% toluene) with the crude oil mixture at a 1:2 weight ratio. The saline water was prepared according to ASTM D-1141. Heptol, saline water, and heavy crude mixture altogether were mixed at a weight ratio of 37:37:18. Commercial grade NA mixtures (Sigma Aldrich; product number: 70340; lot number: BCBP2363) and calcium naphthenate (Wako pure chemical industrials, Ltd., Manufacturer code: 037-08656) were also added (4 wt% each) to the mixture of oil phase and saline water to increase the rag layer formation. The whole mixture was then treated in a shaking incubator (Lab Companion Model # IST-3075R, South Korea) at 400 rpm for 12 h at 25 °C to form a homogeneous phase. Subsequently, the homogenized mixture was treated in a WiseMix vortex mixer (DAIHAN WiseMix® VM-10, South Korea) at

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