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Efficient oil recovery from highly stable toxic oily sludge using supercritical water

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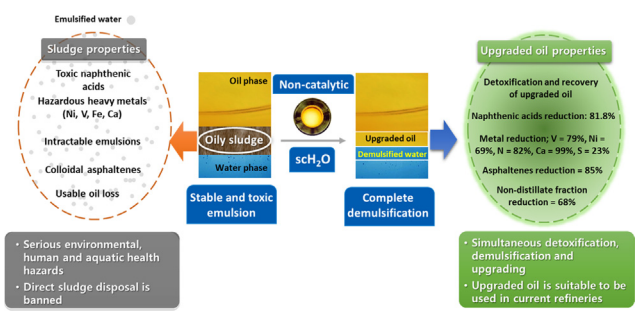
GRAPHICAL ABSTRACT



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ABSTRACT

One of the main challenges in crude oil extraction and refining is the formation of highly toxic intractable petroleum emulsions (oily sludge). Herein, the simultaneous demulsification and recovery of oil with low impurity content, trapped in petroleum emulsions, was investigated using supercritical water (scH_2O). Various parameters, including temperature (350–400 °C), pressure (25–35 MPa), emulsion concentration (10–100 wt%), and reaction time (30–120 min) were explored to establish the optimized conditions. At 400 °C, the asphaltene content (23.7–3.4 wt%) and total acid number (15.4–2.8 mg-KOH/g-oil) decreased significantly, while the naphtha-to-diesel fraction increased from 9 to 21 wt%. These results indicated effective cracking of the toxic interfacially active species to form their non-toxic, non-interfacially active counterparts. By removing the interfacially active compounds that stabilize the petroleum emulsion, clear oil-water separation was achieved after conversion in scH_2O, thereby facilitating the recovery of the upgraded oil. Additionally, heteroatoms and metallic impurities in the upgraded oil were significantly reduced [reduction efficiencies: 79% (V), 69% (Ni), 99% (Ca), 23% (S), 82% (N)]. Finally, plausible reaction mechanisms for the removal of interfacially active compounds were discussed using model compound reactions.

1. Introduction

To meet the rapid growing demand for energy/chemicals and conventional oil depletion, unconventional crude oils (extra heavy oil, high acid crudes, oil/tar sand, tight oil, and bitumen), which make up ~70% of the total global oil reserves [1], are considered to be highly

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promising and practical feedstocks. However, unconventional oils exhibit high viscosity, density, and acidity and comprise large amounts of heteroatoms (nitrogen, oxygen, sulfur) and heavy metals (Ca, V, Fe, Ni) [2,3] that make them unsuitable for processing in existing oil refineries. Additionally, unconventional crude oil contains large amounts of interfacially active compounds (asphaltenes, resins, naphthenic acids, fine particles) [4–9] that facilitate the formation of highly stable petroleum emulsions (oily sludge). These products, which comprise highly complex water-in-oil, oil-in-water, oil-in-water-in-oil, and/or water-in-oil-in-water emulsions, typically form a very thick layer between the oil and water phases. This multiphase complex layer is one of the preeminent problems during crude oil extraction, transportation, and refining and if improperly controlled, causes significant loss of usable oil, catalyst poisoning, and severe corrosion in midstream and downstream oil refinery equipment [10–14]. The formation of petroleum emulsion layers is observed in desalters (rag layer), where sufficient amount of water is used to reduce the natural salinity of the crude oils [15]. Because of its huge production and high stability and toxicity, petroleum emulsions pose a very serious threat to human health, the environment, and aquatic organisms [16,17]. Thus, due to strict environmental regulations, direct sludge disposal has been banned to avoid water and soil contamination.

The generation of oily sludge is inevitable in the petroleum industry and is expected to pose a bigger threat in the near future as increasing amounts of unconventional crude oil are being used. Thus, the development of an efficient treatment technique is crucial. Various methods have been proposed to treat oily sludge, including chemical demulsification [18–20], freezing/thawing [21,22], hydrocyclones [23], membranes [24,25], centrifugal settling [26], ultrasonic irradiation [16], pH control [27,28], and electrostatic coalescence [29,30]. Incineration [31,32], stabilization/solidification [33], and oxidation [34] have also been tested. Although these techniques are effective in treating the oily sludge, each technique has some limitations that are unavoidable at an industrial level. For example, when demulsifier, electrostatic coalescence, and pH control techniques are employed, a secondary rag layer readily forms in the presence of fine secondary droplets and oil-wet clay particles, while pH control is only effective in oil-in-water emulsions. Additionally, the cost and removal of chemicals (demulsifiers and pH controllers) needs to be addressed [28,35]. The use of hydrocyclones and centrifugal settling is not effective for highly stable interfacial films (rag layers), while centrifugation is limited to small-scale operations and is unsuitable for highly stabilized emulsions in which emulsified droplets are very small in size and thus, droplet self-coalescence is limited to the continuous phase [17,29].

Oily sludge typically contains large amounts of alkali/alkaline earth metal impurities such as sodium, calcium, and magnesium in the form of naphthenic acid soaps. Moreover, heavy metal impurities such as vanadium, nickel, and some part of iron embedded in oil-soluble porphyrin organic compounds are preferentially transported into the oily sludge phase to reduce the surface tension [36]. Metal removal from heavy crude oils and oily sludge has attracted much interest because these metals are highly detrimental to catalysts and engender equipment corrosion. Several methods that remove these metallic impurities from petroleum feedstocks have been proposed. Physical methods (distillation, filtration, and solvent extraction) [37,38], chemical methods [39], and hydrodemetallization processes [40] reduce the metal-content in crude oils, however, use of expensive chemicals (hydrofluoric acid, sodium hypochlorite, and n-pentane-containing dimethyl phosphite), complex ultrafiltration equipment, huge loss of crude oil components, and separation issues during solvent extraction processes (solvent recovery, [41] contamination, and regeneration problems) should be considered for practical-scale implementation [36]. It is therefore critical to develop a new treatment that can meet the criteria for ultimate detoxification and utilization of oily sludge. These include recovery of oil trapped in the petroleum emulsions, removal of the metallic contents, environmentally safe and simple operation, a short processing time, and scalability.

Supercritical fluids such as supercritical water (scH_2O), supercritical methanol (scMeOH), and supercritical hydrocarbons (e.g., propane, pentane) have been extensively used for the upgrading of unconventional crude oil and heavy petroleum fractions (oil sand bitumen, heavy crude oils, vacuum residue, coal tar and asphalt) [42–45]. Depending on the nature of supercritical fluids, different upgrading results have been reported. For example, in case of vacuum residue upgrading, when scMeOH was used, the amount of asphaltenes, non-distillable fraction, and metallic impurities were reduced significantly in the upgraded oil, but the formation of coke and gasification were high (coke ~20 wt%, gas yield ~3 wt%) as compared to those in scH_2O (coke ~10 wt%, gas yield ~0.3 wt%) [45]. Supercritical fluids extraction and fractionation based on supercritical hydrocarbons is an effective method to separate valuable light fractions from heavy fractions such as vacuum residue and pitch [46], but extraction of oil that is trapped in the highly stable rag layer would make the whole process be complicated.

Herein, we demonstrate the complete breakage of a petroleum emulsion and the recovery of oil trapped in the emulsion using scH_2O. The unique properties of scH_2O, including high solubility for organic species, extremely low viscosity, high diffusivity, and zero surface tension [47,48], make it an effective medium for the conversion of petroleum emulsions to valuable upgraded oils with significantly lower amounts of interfacially active species, heavy fractions, and impurities. During the reaction in scH_2O, interfacially active asphaltenes and naphthenic acids were converted to non-interfacially active species. Therefore, separation between the oil and water phases is naturally created, thereby facilitating recovery of the upgraded oil by simple liquid-liquid separation. Various emulsion conversion operating parameters, including temperature (350–400 °C), pressure (25–35 MPa), reaction time (30–120 min), and concentration (10–100 wt%), were investigated. At 400 °C, 30 MPa, and 60 min reaction time, the asphaltene content decreased significantly from 23.7 to 3.4 wt% and the total acid number was reduced from 15.4 to 2.8 mg-KOH/g-oil. Additionally, the non-distillable residue fraction was reduced from 50 to 16 wt%. To gain insight into the TAN reduction mechanisms, two model compounds octadecanoic acid and 2-naphthoic acid (ODA and 2-NTA) were treated with scH_2O and the major reaction pathway was determined using DFT calculations.

2. Experimental

2.1. Materials

High acid crudes and heavy crudes were acquired from three different sources of Laguna (Venezuela), Rubiales (Colombia), and Bachaquero-13 (Venezuela). HPLC grade methanol, dichloromethane, toluene, isopropanol, heptane, and n-hexane were purchased from Sigma-Aldrich (USA). Distilled and deionized water were prepared using the AQUAMax™-Basic 363 water purification system (Young Lin Instrument Co., Ltd., South Korea). High-purity hydrogen (99.99%), nitrogen (99.99%), helium (99.99%), and air (99.99%) were purchased from JC Gas Company (South Korea). Sodium chloride (99.0%), sodium bicarbonate (≥99.5%), sodium sulfate (≥99.5%), calcium chloride (≥96.0%), and magnesium chloride (≥98%), used to prepare saline water, were purchased from Sigma-Aldrich and Alfa Aesar® (USA).

2.2. Petroleum emulsion formation

Oily sludge or rag layer formation, its reaction in scH_2O, and the product separation protocol are presented in Scheme 1. Laguna, Rubiales, and Bachaquero-13 were mixed in a 4:3:3 wt ratio to normalize the oil properties (asphaltene content, total acid number, viscosity, flowing temperature) of the unconventional crudes. The crude oil mixture was then mixed with heptol (80 vol% heptane, 20 vol% toluene; 1:2 wt ratio) to prepare the oil phase. Saline water was prepared

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