



## Full Length Article

# Simultaneous breaking and conversion of petroleum emulsions into synthetic crude oil with low impurities



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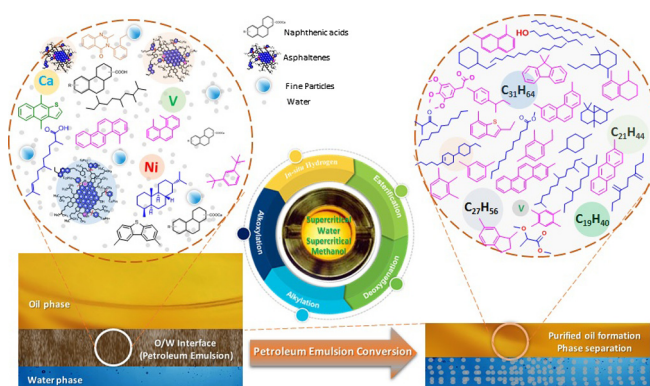
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## HIGHLIGHTS

- Complete demulsification of recalcitrant petroleum emulsions by supercritical fluid.
- 98.5% asphaltene reduction with supercritical methanol at 400 °C.
- Non-distillate fraction in petroleum emulsion was reduced by 94.0%.
- Toxic naphthenic acids and metallic components were sufficiently reduced.

## GRAPHICAL ABSTRACT



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## ABSTRACT

An environmentally-benign supercritical fluid route is developed to demulsify and treat highly intractable petroleum emulsions containing hazardous acidic compounds, heavy fractions, heteroatoms, and metallic impurities without using external catalysts and molecular hydrogen. The produced synthetic crude oil exhibits asphaltene-free fractions with low amounts of impurities, which could be suitable for use in current petroleum refineries. The degree of reductions of asphaltenes and non-distillate fraction are 98.5% and 94.0%, respectively. The deacidification tendency of supercritical methanol results in 90.2% reduction of total acid number. Ni, Ca, and N are removed below detection limits (0.1 ppm for Ni/Ca and 0.01 wt% for N). V and S are reduced with efficiency of 85.0% and 33.6%, respectively.

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## 1. Introduction

Unconventional crude oils are a practical option to meet the increasing global demand for energy and fuel and to find more cost-effective resources. The use of unconventional crude oils (e.g. high acid crudes, heavy and extra-heavy crudes, bitumen), which represent almost two-thirds of the total oil reserves in the

world [1], is considered to be a promising option because of the accelerated depletion of conventional oil reserves. One of the pre-eminent challenges for the recovery, transportation, and treatment of unconventional crude oils in existing refineries is the facile formation of a multiphase complex layer at the interface between the oil and water phases, which are known as oily sludge, petroleum emulsion or rag layer [2,3]. The presence of a large amount of impurities in the unconventional crudes, such as solid particles (e.g. salts and clays), high molecular weight fractions (e.g. asphaltenes and resins connected with heteroatoms and heavy metals), and naphthenic acids, which exhibit high interfacially active properties, leads to the formation of a thick layer of highly stable and intractable multiphase emulsions at the oil-water interface [4–7]. Inappropriate handling and management of the petroleum emulsions can cause serious detrimental effects on public health and environment due to its high toxicity and high production quantity worldwide [8,9]; naphthenic acids and heavy metals are the major toxic components in the petroleum emulsions, which are highly lethal for microorganisms, aquatic algae and aquatic organisms [10–12]. In addition, the increased tendency to form a rag layer by increasing the unconventional oil content in a desalting unit installed in oil refineries often causes significant losses of valuable light fractions trapped in the emulsion phase. The incomplete pre-treatment of the unconventional crude oils at the upstream of oil refineries will generate a huge amount of petroleum emulsions, which will cause serious environmental problems as well as operational problems in the downstream operations, such as pipeline erosion, equipment corrosion and catalyst deactivation.

Current options for treating the emulsions are complete incineration [13,14] or stabilization-/solidification [15–17], which make it extremely difficult to recover the crude oils trapped in the petroleum emulsion. Conventional upgrading techniques, such as carbon rejection (e.g. thermal cracking, delayed coking) and hydrogen addition (e.g. hydrocracking, hydrotreating) would not be suitable for treating the rag layer. A huge amount of energy is required to evaporate the large amount of water in the rag layer (typically 30–85 wt%) to reach typical operation temperatures of the carbon rejection process (450–550 °C) [18]. Furthermore, the presence of a large amount of metal/sulphur species and coke formation would facilitate the deactivation of catalysts employed for the hydrogen addition process [19,20]. In addition, a high amount of hydrogen is required for the hydrogen addition process, which makes it less economically viable [21]. Therefore, it is crucial to develop an effective emulsion breaking and conversion technique to recover the oil trapped in the rag layer and to remove the impurities (e.g. asphaltene, naphthenic acids, heteroatoms, heavy metals) to an affordable level for the reduction of the environmental burden and for the ultimate utilization of the unconventional crude oil in existing refineries.

Supercritical water (scH<sub>2</sub>O) has been extensively studied as an effective extraction and upgrading medium for natural organic deposits, asphalt, and heavy oils [22–24]. Nevertheless, the simultaneous emulsion breaking and conversion of the rag layer into a less hazardous synthetic crude oil has not been investigated. Herein, we developed novel scH<sub>2</sub>O and supercritical methanol (scMeOH) routes for the production of synthetic crude oil from petroleum emulsions in the absence of external hydrogen and catalysts.

## 2. Materials and methods

### 2.1. Materials

The high acid crude and heavy crude oils were obtained from three different sources: Laguna (Venezuela), Rubiales (Colombia),

and Bachquero-13 (Venezuela). HPLC grade of methyl alcohol, dichloromethane (DCM), toluene, isopropanol, heptane, n-hexane, deionized water, and 0.1 N KOH in 2-propyl alcohol for the total acid number (TAN) were purchased from Sigma-Aldrich (USA).

### 2.2. Formation of the petroleum emulsion

Rubiales, Laguna and Bachquero-13 were mixed in a weight ratio of 40:30:30. For the preparation of the rag layer, the crude oil mixture (80 g), heptol (80% heptane and 20% toluene by volume, 160 g), and saline water (which was prepared according to ASTM D-1141, 160 g) were mixed in a weight ratio of 20:40:40 in a shaking incubator (Lab Companion Model # IST-3075R) at 400 rpm for 12 h at 25 °C to ensure the homogeneity of the oil and water phase. Subsequently, the homogenized mixture was further mixed at 3200 rpm for 5 min in a WiseMix mixer (DAIHAN WiseMix VM-10) and then sonicated for 60 min at 45–50 °C in an ultra sonicator (Lab Companion model UC-20). After the sonication, the mixture was centrifuged at 1150 rpm for 1 min at 4 °C. After the centrifugation process, the three phases (oil phase, rag layer, and water phase) were separated in a centrifuge tube. The oil phase and water phase were pipetted out to recover the rag layer. To avoid mixing the three phases, the centrifuge tube was tilted and pipetted out of each phase one by one from the side of the tube without contacting the lower phase [25]. The amount of rag layer formed was 190g and the yield of rag layer was 47.5 wt%. The formation of the rag layer was observed using a Nikon microscope (model # ECLIPSE Ti) with a 60X magnification. To determine the water content in the rag layer, dichloromethane was added to the rag layer and mixed in the WiseMix mixer at 3200 rpm for 5 min. Emulsified water was separated from the emulsion to some extent. The mixture was then centrifuged at 4000 rpm for 30 min. The water in the top layer was pipetted out. During centrifugation, a secondary emulsion formed. Therefore, the above procedure was repeated at least three times to completely remove the water in the rag layer.

### 2.3. Reaction protocol

The emulsion breaking and the conversion of the rag layer were conducted in supercritical water (scH<sub>2</sub>O) and supercritical methanol (scMeOH). The batch reaction system used in this study was a custom-built stainless steel-316 reactor (inner reactor volume of 140 mL) equipped with a magnetic stirrer for agitation with a maximum rate of 1500 rpm. Detailed description on the reactor system is given elsewhere [26]. The amount of water or methanol required to attain the desired pressures at a specific temperature was calculated using the Peng-Robinson-Gasem equation at specific reactor volume. After the reactor was sealed, ambient air inside the reactor was replaced by N<sub>2</sub> to provide inert media and pressurized to 1 MPa before heating. Temperature was increased at a rate of 15 °C min<sup>-1</sup> to the desired temperature of 350–400 °C. Once the predefined temperature and pressure were achieved for 30–90 min reaction, heating was stopped and the reactor was cooled down by quenching using ambient temperature water.

After the reaction was completed, volume of gaseous products was measured using a W-NK-2 wet gas meter (Shinagawa Corporation, Japan) and stored in a Tedlar sampling bag for further analysis. As shown in Fig. 1, in case of the scH<sub>2</sub>O reaction, the liquid product was simply filtered by using a Whatman filter paper #2 to separate the solid residue from the synthetic crude oil. Whereas, after the reaction with scMeOH, the liquid products in the reactor were collected by rinsing with DCM, and the solid residue was separated by filtering the liquid using the filter paper. The DCM and water phases were then separated using a separatory funnel. Separation of DCM and methanol from the synthetic crude oil was car-

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