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In-situ upgrading of Omani heavy oil with catalyst and hydrogen donor

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ABSTRACT

Catalytic aquathermolysis of Omani heavy oil was carried out with NiMo-oleate as an oil soluble viscosity reducing catalyst and glycerol as a hydrogen donor for the first time. The synthesized catalyst was characterized with Fourier Transform Infrared Spectroscopy(FTIR) and X-ray diffraction (XRD).The experiments were carried out in a Parr reactor under nitrogen atmosphere with varying reaction time (24–72 h), glycerol concentration (0–10 wt%), catalyst loading(0–1 wt%), amount of water (0–42 wt%) and the reaction temperature (200–304 °C). Maximum viscosity reduction of 69% (1490–490 cP at 70 °C) occurred at 277 °C reaction temperature and 30 h of reaction. Fourier transform infrared spectra (FT-IR) before and after catalytic aquathermolysis show an increase in the saturate bonds of alkyl groups and a decrease in unsaturated bonds of transalkene groups of the hydrocarbons indicative of hydrogenation activities of the catalyst and glycerol. In addition, gas chromatography (GC) analysis confirmed an increase in lower boiling point components after catalytic aquathermolysis, while asphaltene precipitation showed a decrease in asphaltene content.

1. Introduction

The decline in conventional light crude oil reserves along with the growing global demand has ushered in an era of exploration of unconventional resources such as heavy oil and bitumen. The heavy oil, once an unattractive resource, is now seen as an important source to supplement conventional sources towards meeting demands and hence makes their exploitation more viable. It is estimated that the world's heavy oil and bitumen technically recoverable reserves sit currently at about 1084 Billion barrels of oil, such vast quantities can serve as a complement to dwindling supplies of light crude, which stand at 952 billion barrels [1]. Various methods exist for the recovery of the heavy oil, and are categorized broadly into non thermal and thermal methods. A number of considerations including environmental impact are taken into account to determine the most suitable method for recovery [2–7].

Steam assisted thermal recovery of heavy oil is the most common thermal method currently being employed whereby heat in the form of steam is used to reduce the viscosity of the heavy oil. A lot of work exists in the literature, since it was first demonstrated that the transition metal salts could catalyze reactions responsible for reduction of viscosity during steam injection processes [8]. Further works by others showed that the transition metal salts aided in cleavage of the hetero atom bonds of S, N and O leading to the viscosity reduction of the heavy oil [9–18]. There are also undesired associated polymerization reactions, some of which occur as a result of free radical formation following steam injection reactions, which lead to a regression in the viscosity reduction due to growth of the asphaltene and resin components [20,21]. In several reports, it has been demonstrated that hydrogenolysis and subsequent hydrogenation of the heavy oil prevent regression in heavy oil viscosity. Combination of tetralin and transition metal catalysts has shown a synergistic effect for greater oil upgrading than either tetralin or the catalysts on their own, as well as a prevention of viscosity regression [20–24].

For the reduction of unsaturated bonds which lead to higher value hydrocarbons, others in the literature have employed the use of glycerol as a green solvent owing to its transfer hydrogenation capabilities. Styrene was hydrogenated with glycerol and catalyst with a 100% conversion [25]. In other works Cyclohexene was hydrogenated with glycerol resulting in an 89% conversion to cyclohexane [26]. Both studies observed that the longer the reaction time and higher the temperature, the greater the conversion to the saturated compound. While the typical catalysts used in the literature for transfer hydrogenation of olefins using glycerol are Pt and Pd catalysts, reviews in the oil and gas literature have shown

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that for upgrading, the physical nature of the catalyst plays a more important role in upgrading extent than the active metal itself. In terms of activity, water soluble catalysts are least active, followed by oil soluble, with the most active catalysts being the dispersed catalysts [27].

Prior work focused on using monometallic oil soluble molybdenum oleate in lab and field trials with a 91% viscosity reduction observed [12]. The authors attribute the high reduction in viscosity on the phase similarity between the heavy oil and the catalyst, allowing for higher miscibility and activity. Other work [28] showed the effect of nickel oleate catalyst on upgrading of heavy oil with a reduction in viscosity of 63% achieved. Comparison of bimetallic and monometallic oil-soluble catalysts [29] showed the advantages of synergy in chemically bound catalysts as opposed to their monometallic peers - the NiMo-oleate catalyst used in that study had greater hydrogenation capabilities than the oil soluble nickel and molybdenum catalysts.

This study focuses on the use of dispersed NiMo oleate as an oil soluble catalyst and glycerol as a green hydrogen donor for upgrading of Omani heavy oil using aquathermolysis. Viscosity measurement, sulfur content and GC analysis were used to determine the effect of different parameters (water content, hydrogen donor content, catalyst concentration and temperature) on upgrading of the heavy oil following aquathermolysis. Due to high number of relevant parameters, a design of experiments was used to optimize the upgrading experiments and arrive at optimum reaction conditions necessary for viscosity reduction.

2. Experimental setup

2.1. Synthesis and characterization of catalyst

NiMo oleate was synthesized using the method outlined in the literature [29]. Ammonium heptamolybdate($(NH_4)_6Mo_7O_{24}{\cdot}4H_20$) and nickel nitrate ($Ni(No_3)_2{\cdot}6H_20$) were added to distilled water to create an equimolar solution of Ni:Mo. Excess ammonium hydroxide(25%) was added to the solution and a green precipitate resulted, continuous addition of ammonium hydroxide dissolved this precipitate. Following heating and stirring for 4 h at 80 °C, the excess ammonia was removed, the precipitate was filtered and washed with distilled water to remove any residual ammonia, following which the precipitate was dried in a vacuum oven at 80 °C for 4 h. The resulting ammonium nickel molybdate($(NH_4)HNi_2(MoO_4)_2(OH)_2$) was then mixed with excess oleic acid in a beaker and heated to 220 °C while stirring for 2 h, following which the products was precipitated, filtered and washed with acetone for removal of residual oleic acid. The NiMo oleate filtrate was dried in a vacuum oven at 70 °C for 8 h. Characterization of the catalyst was by FT-IR (Perkin Elmer 100) with samples prepared with KBr and equipment settings of 20 scans per minute. XRD characterization was on a RIGAKU MiniFlex with equipment settings for the x-ray tube at 30 kV and 30 mA, with a scanning frequency setting of 4°/min.

2.2. Heavy oil upgrading

Heavy oil from Oman with a viscosity of 1490 cP at 70 °C was used to determine the effects of experimental parameters on upgrading. The experimental setup consisted of a 500 ml Parr high temperature high pressure batch reactor (model 4575). The start of each experiment involved loading the reactor with 50 g of oil and varying amounts of catalyst, water and hydrogen donor. The reactor was then initially pressurized to 30 bar of nitrogen prior to starting the reaction, with the pressure rising much higher following heating and aquathermolysis reactions. Following reaction, water and any residual gycerol are decanted off, leaving the heavy oil for post reaction analysis.

Parameter effects on the above reactions were determined by One-Factor-at-a-Time experiments, with the experimental set up shown in Table 1. Analysis of these experiments involved comparison with the blank case to evaluate parameter effects.

A Design of Experiment (DOE) was used to determine the optimum conditions for upgrading with parameters and levels shown below in Table 2. A space filling design was used to reduce the number of runs and explore the design space efficiently.

A Brookefield DV-II+ viscometer was used to measure the viscosity of the heavy oil sample following aquathermolysis at 70 °C with the average of 3 runs recorded as the final viscosity and a measured precision of the repeated runs of ±5%. A Rigaku NEX QC+ XRF device was used to measure the sulfur content of the oil samples before and after aquathermolysis. XRF analysis sample preparation involved filling the sample cup equipped with a 4 μm Prolene film with 3grams of heavy crude oil sample. The average of 3 runs was used to report the final sulfur content with a precision of ±1%. To measure the relative amounts of light to heavy components, an Agilent 7680GC with a non-polarpolysiloxane polymer column of 60 m length x 0.25 mm diameter and a maximum temperature limit of 325 °C. The device's precision for retention time was measured to be 2%. GC sample preparation involved removing insolubles by dissolving 1 part heavy oil sample in 40 parts hexane. Starting at a GC oven temperature of 75 °C, a temperature program of 5 °C/min up to 300 °C, and holding at 300 °C for 10 min was used. Eq. (1) is used for the determination of boiling points for all time under 45 min (up to 300 °C):

$$BP = T_i + 5\,t \tag{1}$$

Where BP is the boiling point at retention time t and T_i is the initial temperature (75 °C). The area% under the peaks is normalized and used for comparison of the relative composition in each boiling point band. Tentative identification of the components via gas chromatography analysis was based on an approach reported earlier [30]. The boiling point range of 75–200 °C was designated as gasoline and naphtha(6–11 carbon atoms), 200 °C–250 °C was designated as kerosene(11–18 carbon atoms) with the 250 °C–300 °C designated as the heating/light gasoil(18+ carbon atoms) range. Asphaltene content was measured using precipitation by adding hexane to the oil (in a ratio of 40:1 for hexane:oil) sample before and after upgrading at optimized conditions.

3. Results and discussion

3.1. Characterization of bimetallic catalysts

The XRD spectrum for the synthesized catalyst is shown in Fig. 1, with Peaks at 23°, 26.5°, 29.5° and 34.2° which are characteristic of the crystalline structure from of $(NH_4)HNi_2(MoO_4)_2(OH)_2$ [29].

FT-IR analysis of the oil soluble catalyst was performed following synthesis, with plots shown in Fig. 2. The peaks observed in the synthesized catalyst spectrum, match those observed in the database [31], with the characteristic —CH_2-stretch observed at 2930 cm^{-1} and 2854 cm^{-1} in image (Fig. 2b) - these peaks are absent in the precursor confirming the organometallic nature of catalyst. The peak at 1608 $cm^{-1}$and 3300 cm^{-1} for both curves is indicative of the O—H bridge stretching, the intensity of which is reduced in the catalyst. The band at 2250 cm^{-1} is representative of the N—H stretching vibration in the catalyst precursor (Fig. 2a), a confirmation of the presence of the NH_3^+ group. The peak at 1556 $cm^{-1}$is indicative of the CO_2— stretching vibration of the carboxylic group for the NiMo oleate.