energy&fuels

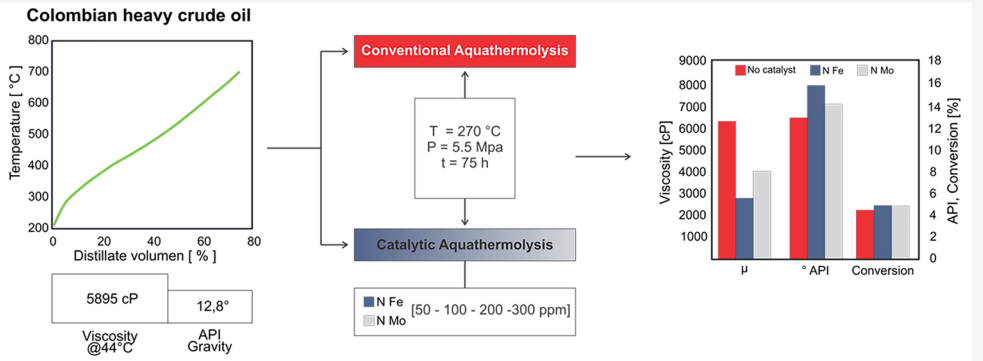
pubs.acs.org/EF Article

Effect of the Catalytic Aquathermolysis Process on the Physicochemical Properties of a Colombian Crude Oil

Keyner S. Núñez-Méndez, Luis M. Salas-Chia, Daniel Molina V,* Samuel F. Muñoz, Paola A. León, and Adan Y. León

Cite This: https://dx.doi.org/10.1021/acs.energyfuels.0c04142 Read Online

ACCESS | Metrics & More | Article Recommendations



ABSTRACT: In this work, the catalytic aquathermolysis process of a Colombian heavy crude oil was studied. Reactivity tests were conducted in a microbatch reactor at 270 °C and saturation pressure of 5.5 MPa, during 66 h, using iron and molybdenum naphthenates in concentrations of 50−300 ppm as catalysts. The use of these catalysts reduced the gas yield from 1% to 4.2% w/w, the viscosity from 10% to 52.3% with iron naphthenate, and from 11.6% to 31.4% with molybdenum naphthenate. Crudes subjected to catalytic aquathermolysis increased their API gravity from 1.1 to 2.5 and 0.5 to 1.8 units, showing a significant decrease in complex fractions with boiling points above 340 °C and conversions in the order of 7% and 8% with respect to the precursors of molybdenum and iron naphthenates. Unlike other studies, the changes in the physical properties were correlated with changes in the chemical structure by ATR-FTIR spectroscopy. The average molecular parameters showed that the greatest differences with respect to the base crude oil were the length of the alkyl chains, the aromaticity, and the sulfurization. Results indicate different characteristics from the catalysts being studied, with iron naphthenate yielding better favorable effects in the change of the physicochemical properties of the improved crude oils. The experimental methodology proposed in this work indicates that the catalytic aquathermolysis process is a recovery method that allows for improving the properties of the crude oils, under reservoir conditions, due to the formation of products of smaller size and molecular weight.

1. INTRODUCTION

Heavy and extra-heavy crude oil reserves represent around 70% of the recoverable crude oil worldwide and have become the focus of attention to supply the world energy demand,[1] but due to the low API gravity, high viscosity, and high content of heteroatoms such as sulfur, nitrogen, and oxygen in this type of oil,[2−4] primary and secondary recovery methods have low efficiency in the production. For this reason, different enhanced oil recovery (EOR) methods have been implemented with numerous ongoing heavy and extra-heavy oil projects, reaching an associated production of approximately 2 million barrels per day.[5] Thermal EOR methods (THEOR) play an important role in enhanced oil recovery,[6−9] because of representing around 47.7% of the enhanced recovery methods,[10] and are focused on reducing the viscosity of the crude oil in the reservoir to increase its mobility and facilitate its production through the addition of a hot fluid.

THEOR methods include hot water injection (HWF), continuous steam injection (SD), cyclic steam injection (CSS), steam-assisted gravitational drainage (SAGD), and in situ combustion (ISC), among others, but steam injection methods are widely used since they have proven to be very successful worldwide for decades.[10−12] However, these methods have

Received: December 8, 2020
Revised: February 17, 2021

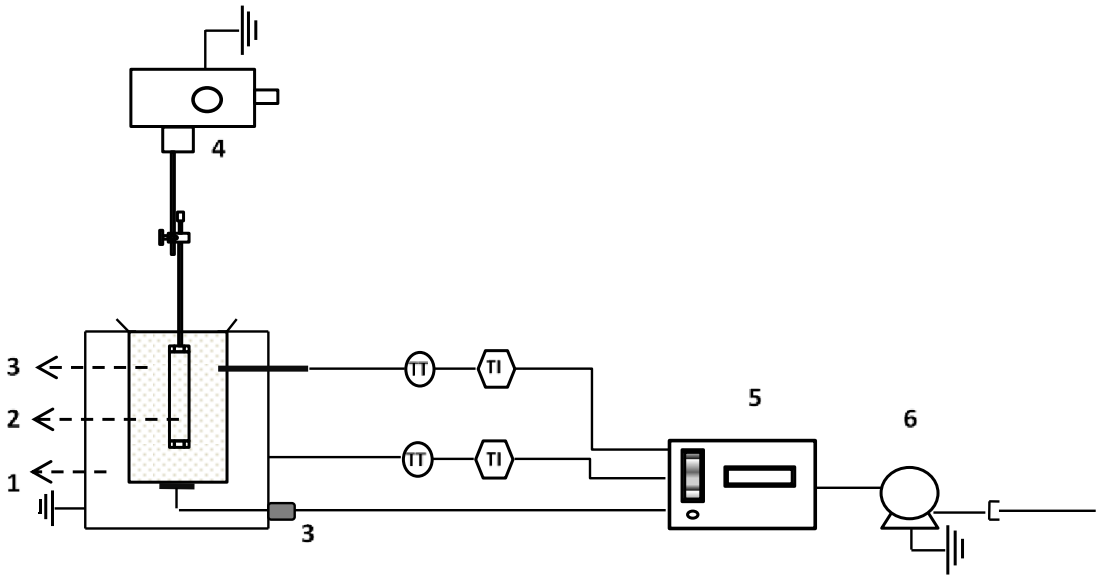


Figure 1. Schematic of the thermal bath and reactor used for the catalytic aquathermolysis tests: (1) fluidized sand bath, (2) batch reactor, (3) sand (Al_2O_3), (4) mechanical stirrer, (5) temperature control, and (6) compressor.

some operational problems that reduce the recovery factor between 15% and 20%.[1] The first problem is the loss of approximately 25% of the injected energy, depending on the conditions of each reservoir,[13] and second problem is the high production of acid gases, such as H_2S and CO_2, that causes corrosion and possible unfavorable effects on the environment.[14−16]

From this in situ gas generation, it has been possible to show that the presence of steam on the petroleum produces chemical changes, called aquathermolysis reactions, as proposed by Hyne,[17] who determined that there are intermediate reactions such as hydrolysis, water−gas shift (WGS), and hydrodesulfurization, which are generated due to the oil−steam chemical interaction and the reservoir minerals. Generally, aquathermolysis reactions occur in the temperature range between 200 and 325 °C, in which hydrocarbons with a wide distribution of molecular weights are produced. Although preliminary studies showed that the production of gases negatively affects the crude oil quality, subsequent studies showed that the changes generated in the crude oil correspond to an in situ upgrading.[18−20] Thus, the conditions in the process, the nature of the crude oil, the substrate, and the steam quality, play important roles in the physicochemical properties of the improved crude oil.

Considering the reactions and compounds generated during the aquathermolysis, the addition of catalysts was proposed as an optimized alternative to the conventional steam injection method.[21−23] The usage of catalysts with transition metal precursors (iron, nickel, molybdenum, tungsten, cobalt, zinc), in the presence of hydrogen and sulfur, decreases the activation energy required for reactions in lower temperatures and reaction times to take place. Different chemical compounds have been developed and studied to act as a catalytic system in the reactions of aquathermolysis. In general, catalysts have been classified into heterogeneous and homogeneous. Homogeneous catalysts are divided into soluble in water, such as the salts of molybdenum, tungsten, iron, nickel, cobalt, and soluble in oil, such as molybdenum naphthenate, iron pentacarbonyl, and chromium *tert*-butyl alcohol, among others.[24−31]

To implement this process in the oil field, so as to consolidate it as a hybrid technology, different fundamental operational parameters must be analyzed, like some research works that have evaluated different parameters and their influence on the results: kind of reactor, temperature, residence time, and type of catalyst.[32−38] These works use a base crude oil, with known characteristics, and carry out an experimental design capable of evaluating the sensitivity of the variables under study. As an example, for a heavy crude oil treated at 260 °C during 72 h, the viscosity reduced 46.2%, and the API gravity increased 3 units.[22] Several authors have determined that the aquathermolysis on heavy crude oils, under a temperature of 320 °C and reaction times around 72 h, allows viscosity reductions of 33% with an increase in API gravity of approximately 4 units. Regarding the recovery of liquids or improved crude oils in the presence of catalysts in the laboratory, an increase of around 15% was demonstrated with respect to tests in the absence of a catalyst.[37,39−42]

To evaluate the physicochemical changes of the upgraded crude oil, different characterization techniques have been used, among which the measurements of density, viscosity, simulated distillation, thermogravimetry, elemental analysis, and SARA compositional analysis (saturated, aromatic, resins, and asphaltenes) stand out.[31,34,40] To determine the average chemical structure of crude oils and their products, analytical techniques have been used, including nuclear magnetic resonance (NMR), infrared (FTIR) and ultraviolet (UV−vis) spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray energy dispersive spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS), among others.[35,36,38,43−45] Due to the variability of the physicochemical properties of the heavy crude oils and their fractions, there is a significant difference in their nature, and in consequence, their characterization becomes complex.

The role of catalytic agents in aquathermolysis does not occur directly. The mixtures that are used in the experimental tests and are injected in the reservoir are precursors. At a certain temperature and in the presence of organosulfuric compounds, precursors are converted into metallic sulfides.

https://dx.doi.org/10.1021/acs.energyfuels.0c04142
Energy Fuels XXXX, XXX, XXX−XXX

The formation of metallic sulfides and their presence in produced crude oil would make it possible to recycle these catalytic compounds and their use in upstream and downstream processes. On the other hand, pilot tests of the technology have been carried out, reporting favorable results for production increasing and upgrading oil. However, the massification to a commercial scale has not yet been done.[46−50]

Catalytic aquathermolysis technology is fundamentally dependent on the catalyst used and the concentration supplied. Therefore, there is a need to evaluate the appropriate concentration of the catalyst to be applied in the recovery of typical Colombian heavy crude oils. Consequently, this research aims to study the effect of the variation in the metal ion concentration of iron naphthenate and molybdenum naphthenate on physicochemical properties of upgraded crude oils, such as density, viscosity, and percentage of light hydrocarbons conversion. Furthermore, the compositional variation of the crude oil is analyzed using average molecular parameters from ATR-FTIR and UV−vis spectroscopy techniques.

2. EXPERIMENTS

2.1. Materials. For the aquathermolysis tests, a Colombian heavy crude oil with an API gravity of 12.8 and a viscosity of 5895 cP (at 44 °C) was used. The catalysts used for this research were organic salts according to the efficiency recorded by this type of catalyst in previous studies. From a commercial point of view and taking into account the rock−fluid interaction, it is necessary to mix the catalyst in an additional solvent or organic compound.[27] Along with salts of iron naphthenate (6% iron, Strem Chemicals) and molybdenum naphthenate (6% of molybdenum). Molybdenum naphthenate was synthesized following the methodology reported by León et al.[51] The catalyst was prepared by reaction between naphthenic acid (technical grade, Sigma-Aldrich, P/N 70340) and bis(acetylacetonate) dioxomolybdenum(VI) (Sigma-Aldrich, P/N 227749) mixed with a mass ratio of 3.74:1.

2.2. Catalytic Aquathermolysis Tests. A 170 cm^3 batch reactor was used. The cylinder is 13.5 cm long and 4 cm in diameter, and it was constructed with Swagelok stainless steel accessories. The reactor works under isothermal and isochoric conditions at defined reaction times. The cylinder or reactor is connected to a variable speed motor that transmits a reciprocating rotational motion, immersed in a fluidized sand bath (Al_2O_3) that allows conducting the system heating. For the tests, a quantity of crude oil with a precursor (iron naphthenate or molybdenum naphthenate) is added at the estimated concentration and distilled water with a 2:1 mass ratio. Then, the reactor is pressurized with nitrogen at room temperature. Figure 1 shows a schematic of the reaction system used for aquathermolysis.[52]

The reactions were carried out at 270 °C, with a pressure of 5.51 MPa. The reaction time was 66 h. The aquathermolysis reactions without catalyst (no catalyst) were carried out under the same temperature, pressure, and reaction time conditions. The tests were carried out under the same temperature conditions, considering the operating window of the aquathermolysis reactions generated in the range from 200 to 300 °C.[17] The pressure of 5.51 MPa at 270 °C guarantees the presence of saturated steam under reservoir conditions. The parameters according to the operating window of the conditions were established. Test conditions such as temperature, pressure, and reaction time were established, according to the process operating window and the applied parameters in other studies.[53−55]

Catalytic aquathermolysis was investigated using oil-soluble catalysts (nickel and iron naphthenate). These catalysts have been applied in catalytic aquathermolysis studies with representative results in upgraded crude oil.[56−58] The effect of the catalyst concentrations on 50, 100, 200 and, 300 ppm of metal ion was evaluated.

Subsequently, the reactor was cooled with an ice−water mixture and slowly depressurized. The treated crude oil was then separated from the mixture by means of a Hettich Universal 320 R centrifuge with a speed of 15,000 rpm.

The mass balance was carried out by gravimetry, using the following equations

$$m_{gas(final)} = m_{R(initial)} - m_{R(final)} \quad (1)$$

$$m_{oil(final)} = m_{oil(initial)} - m_{gas(final)} \quad (2)$$

$$\%gas = \frac{m_{gas} \times 100}{m_{gas(final)} + m_{oil(final)}} \quad (3)$$

$$\%oil = \frac{m_{oil(final)} \times 100}{m_{oil(initial)}} \quad (4)$$

where $m_{gas(final)}$ is the gas mass after reaction, $m_{oil(initial)}$ is the crude oil mass before reaction, $m_{oil(final)}$ is the crude oil mass after reaction, $m_{R(initial)}$ is the reactor mass before reaction, $m_{R(final)}$ is the reactor mass after reaction, %gas is the gas percentage after reaction, and %oil is the crude oil percentage after reaction, all in grams.

2.3. Characterization. *2.3.1. Viscosity.* Viscosity was measured with an Anton Paar rheometer, following the ASTM D7042 standard. A crude oil sample was placed between two parallel plates, and the shear stress of the crude was quantified along a temperature range between 20 and 50 °C. To determine the percentage of viscosity reduction with respect to the initial crude oil, the viscosity results were analyzed at 44 °C. The importance of quantifying the oil upgrading from its viscosity changes refers to the link of this property with the mobility relation and the flow of this phase in the porous medium.

2.3.2. ATR-FTIR Spectroscopy. The infrared spectrum was measured on a Bruker Tensor II FTIR spectrometer with an ATR cell and single-pass diamond reflection glass in the wavelength range between 400 and 4000 cm^{-1}.

2.3.3. UV−vis Spectroscopy. To obtain an adequate spectrum and considering the variability of the physicochemical properties of each crude oil, the appropriate sample concentration was determined in chloroform, in such a way that it was higher than a concentration that generates imperceptible peaks and lower than a concentration that presents too much noise. According to this premise and following the range established in the state-of-the-art method between 10 and 100 ppm,[59] the spectra were evaluated every 10 ppm, where the spectrum with a concentration of 60 ppm yielded the most adequate result. A quartz cell with a crude−solvent mixture was used in a Multiskan GO microplate apectrophotometer. The spectra were measured in the wavelength range between 200 and 600 nm. For each crude oil sample, the spectra were taken in triplicate.

2.3.4. Simulated Distillation. The simulated distillation curve was obtained following the ASTM D7169 standard. For this analysis, 0.2 g of crude oil was added to 10 mL of carbon disulfide (CS_2). Then, an aliquot of 1.5 mL of the previous solution was deposited in a vial, which was placed in a sample holder of an HP 6890 gas chromatograph.

3. RESULTS AND DISCUSSION

3.1. Heavy Crude Oil Characterization. Table 1 shows the characteristics of the Colombian base crude oil used to

Table 1. Properties of Colombian Heavy Crude Oil Used for Aquathermolysis

Property	Unit	Value
Density (°API)	g/cm^3	0.9806/12.8
Viscosity	cP at 44 °C	5895
$T_{5\%,wt}$	°C	278.7
$T_{20\%,wt}$	°C	381
$T_{30\%,wt}$	°C	430.3
$T_{50\%,wt}$	°C	535.5

https://dx.doi.org/10.1021/acs.energyfuels.0c04142
Energy Fuels XXXX, XXX, XXX−XXX

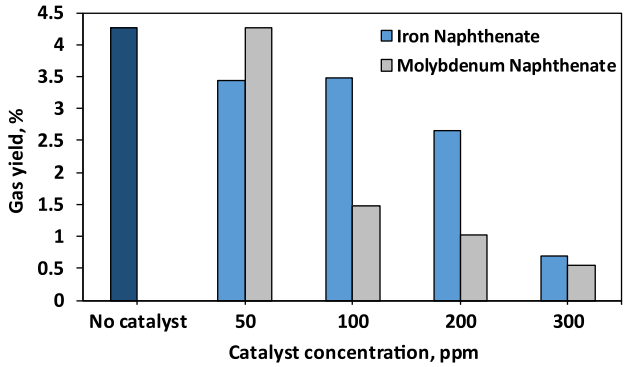


Figure 2. Percentage of gas yield from the catalytic aquathermolysis tests with different concentrations of iron and molybdenum naphthenate.

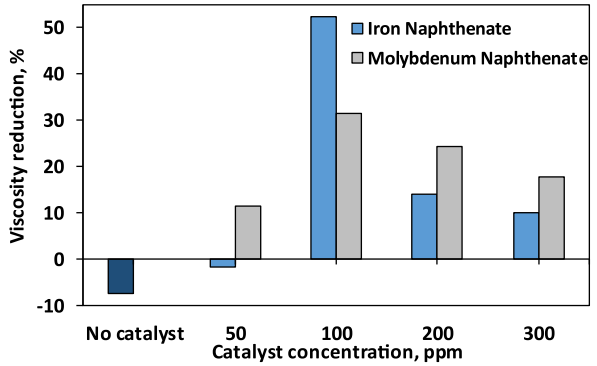


Figure 3. Percentage of viscosity reduction for different concentrations of iron and molybdenum naphthenate.

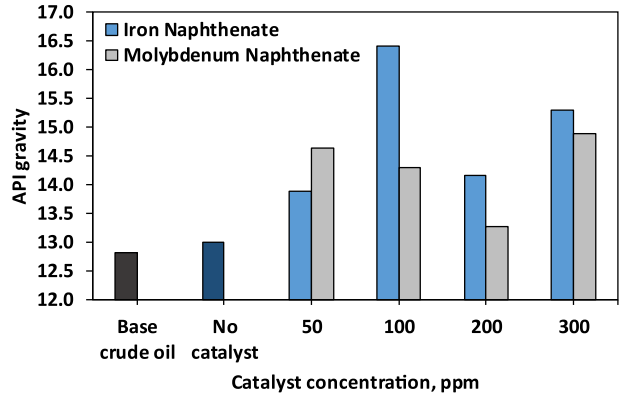


Figure 4. API gravity for upgraded crude oil improved via catalytic aquathermolysis under different concentrations of iron and molybdenum naphthenate.

study the effect of the concentration and nature of the catalyst under steam injection conditions. These characteristics allow us to establish that the selected crude corresponds to a heavy crude oil.

3.2. Colombian Crude Oil Reactivity under Catalytic Aquathermolysis Conditions. The percentage of gas yield is estimated by the difference in the mass balance between the initial crude oil and the liquid products obtained in the reactivity tests. Figure 2 compares the results of the yield, in percentage by weight of the gas, with respect to the base crude oil, without and with catalyst, at different concentrations.

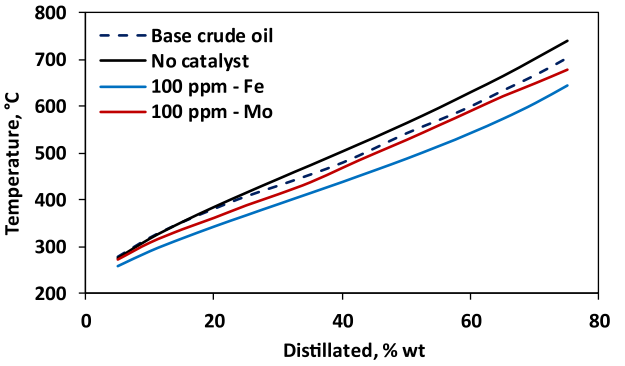


Figure 5. Distillation curves of the base crude oil and the upgraded crude oil under aquathermolysis conditions.

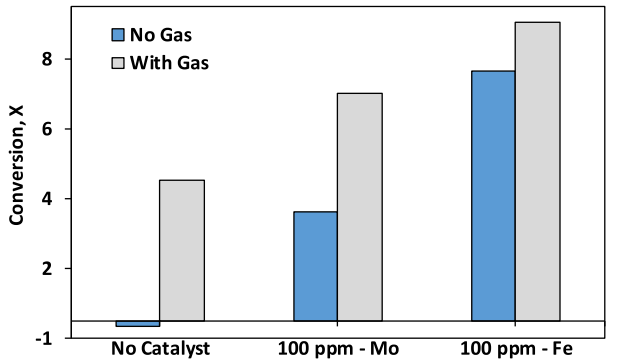


Figure 6. Conversion of the base crude oil and the upgraded crude oils obtained under aquathermolysis conditions.

The results (Figure 2) show that the gas yield decreases proportionally with the increase in the concentration of the catalysts. Metal sulfide catalysts split hydrogen H_2 molecules into hydrogen free radicals, which react with crude oil to obtain the upgraded crude oil. In general, the presence of catalysts favors the combination of hydrogen free radicals and hydrocarbon free radicals to form a stable molecule. In the process, the condensation of hydrocarbon free radicals is suppressed, and at the same time, the gas yield is reduced.[60]

From the results, it can be indicated that the catalytic aquathermolysis conditions applied in this research imply an improvement in the decrease in gas yield with respect to the steam injection process. The sequence of the gas product yield presented the following order: no catalyst < molybdenum naphthenate < iron naphthenate. Thus, the trends of the results can be attributed to the fact that each catalyst has a selectivity according to the nature and reactivity of the crude oil. With the molybdenum naphthenate tests, a greater decrease in gas yield was obtained compared to iron naphthenate when concentrations higher than 50 ppm were used. These results follow the same trend reported in other works, although both have a favorable effect on the properties of the upgraded crude oil.[21,61−63]

3.3. Quality Analysis of Crude Oils Obtained in the Catalytic Aquathermolysis Process. Viscosity reduction is one of the most representative evaluation parameters in an upgraded crude oil since this property is closely related to the physicochemical properties of the crude oil and to the mobility ratio, directly representing a higher recovery factor.[39,40,64] Figure 3 shows the percentage of viscosity reduction of the upgraded crude oils with respect to the base crude oil (at 44

https://dx.doi.org/10.1021/acs.energyfuels.0c04142
Energy Fuels XXXX, XXX, XXX−XXX

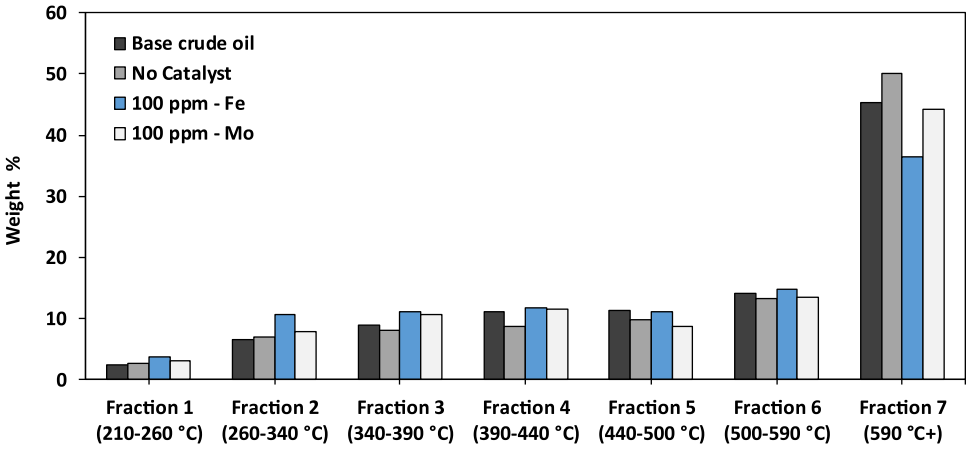


Figure 7. Representative fractions of the distillation curves of the base crude oil and the upgraded crude oils under aquathermolysis conditions.

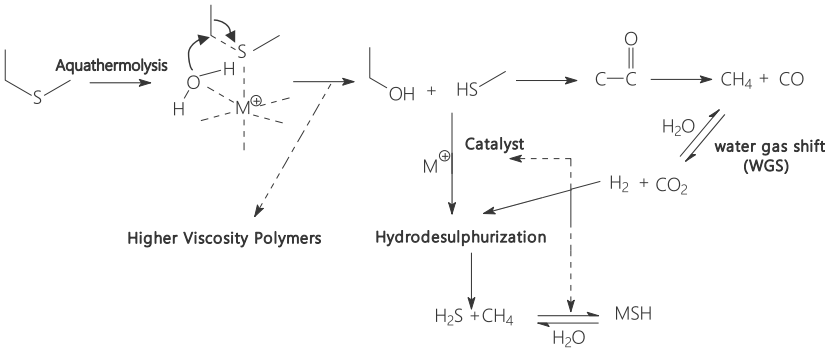


Figure 8. Reaction mechanism in catalytic aquathermolysis.

Table 2. Functional Groups Assignment in Infrared Spectroscopy

Intensity	Wavelength (cm^{-1})	Characteristic structure
1	747	Deformation of aromatic CH bonds out-of-plane =C−H (4H)
2	812	Deformation of aromatic CH bonds out-of-plane =C−H (2H or 3H)
3	870	Deformation of aromatic CH bonds out-of-plane =C−H (1H)
4	1033	Sulfoxides groups
5	1375	CH_3 methyl group
6	1455	CH_2 methylene group
7	1607	Aromatic C=C stretch
8	1707	Carboxylic group C=O stretch
9	2921	CH_2 asymmetric stretch
10	2960	CH_3 asymmetric stretch

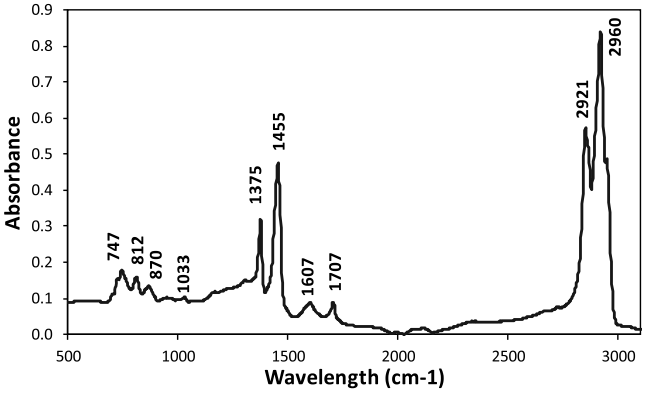


Figure 9. ATR-FTIR spectrum of the base crude oil.

°C). The test in the absence of catalyst showed an increase in viscosity of 7.46%, possibly due to polymerization. This effect occurs because of the instability and combination of the hydrocarbon free radicals formed, which tend to create more complex and branched molecules due to condensation reactions.[18,65]

The highest percentage of viscosity reduction was achieved at 100 ppm of either iron or molybdenum naphthenate, with a reduction of 52.3% and 31.4%, respectively. For the 200 and 300 ppm tests on the iron naphthenate precursor, a lower reduction in viscosity is observed than that obtained at 100 ppm. According to the crude oil−water ratio, it is important to consider that the sulfur content remains constant. Therefore, the amount of catalyst formed depends on the sulfur content available for the reaction (Figure 8). Another reason is that at higher concentrations of the naphthenate salt, the organic phase tends to participate in hydrogenation reactions, justified by the additional hydrogen consumption. Further, the decrease in the hydrogen content favors the combination of species, which in the same way tends to form compounds of higher molecular weight.[32,61,63] This effect on the molybdenum catalyst precursor is less pronounced because each catalyst develops reactions of a different nature and intensity. The results show that catalyst concentration plays an important role in upgraded crude. The results presented trend with the works reported by several authors. For example, the reduction of the viscosity of heavy crude with a Citric-Fe(III) complex does not change significantly above 2000 ppm.[66]

https://dx.doi.org/10.1021/acs.energyfuels.0c04142
Energy Fuels XXXX, XXX, XXX−XXX

Table 3. Hydrocarbon Chemical Characterization Parameters from Infrared Spectroscopy[a]

Parameter	Relationship
Aromaticity	$C1 = \frac{I_{1600}}{I_{747}}$
Oxidation	$C2 = \frac{I_{1710}}{I_{1455}}$
Branching	$C3 = \frac{I_{1375}}{I_{1455}}$
Paraffinicity	$C4 = \frac{(I_{747} + I_{1735})}{I_{1600}}$
Sulfurization	$C5 = \frac{I_{1030}}{I_{1465}}$
Degree of condensation	$C6 = \frac{I_{870}}{(I_{747} + I_{812})}$
Alkyl chain length	$C7 = \frac{I_{2927}}{I_{2957}}$

[a]Represented is the intensity of the absorbance band shown by the ATR-FT-IR spectrum at a wavelength specified *n*.

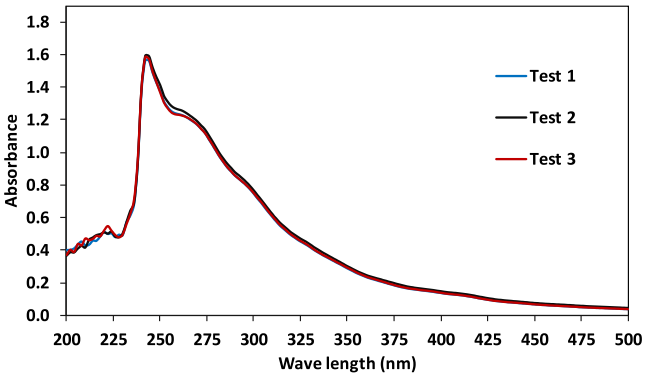


Figure 11. Calibration of UV−vis spectra for a representative base crude oil.

Figure 4 shows the API gravity of the upgraded crude oil obtained in this work. The results show that the aquathermolysis in the absence of catalyst shows a slight increase in API gravity, around 0.5 units with respect to the base crude oil, and this occurs due to the reactions of polycondensation and polymerization. The addition of metallic

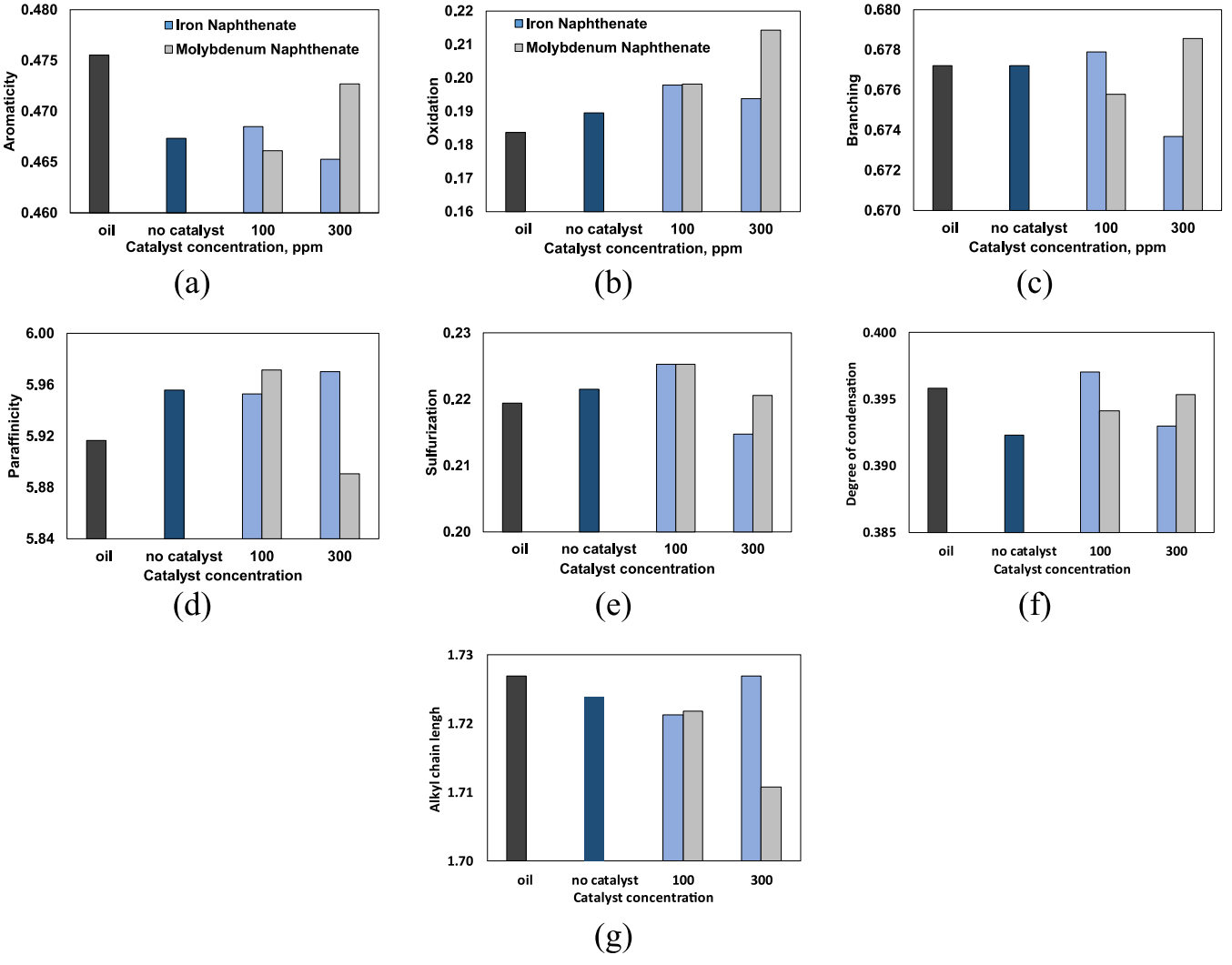


Figure 10. Characterization parameters, obtained by FTIR spectroscopy, of the upgraded crude oils under aquathermolysis conditions in the presence of iron naphthenate and molybdenum naphthenate: (a) aromaticity, (b) oxidation, (c) branching, (d) paraffinicity, (e) sulfurization, (f) degree of condensation, and (g) alkyl chain length.

https://dx.doi.org/10.1021/acs.energyfuels.0c04142
Energy Fuels XXXX, XXX, XXX−XXX

Table 4. Absorbance, at Different Wavelengths, of the Upgraded Crude Oil via Aquathermolysis with Iron and Molybdenum Naphthenates

	Benzene compounds (242 nm)		Naphthenic compounds (262 nm)		Porphyrin compounds (412 nm)	
Catalyst concentration (ppm)	Fe	Mo	Fe	Mo	Fe	Mo
Base crude oil	1.589	1.589	1.252	1.252	0.129	0.129
Without catalyst	1.699	1.699	1.373	1.373	0.151	0.151
50	1.771	1.702	1.465	1.429	0.154	0.147
100	1.844	1.780	1.542	1.479	0.156	0.151
200	1.643	1.676	1.358	1.407	0.141	0.139
300	1.822	1.726	1.475	1.400	0.151	0.145

salt (precursor) in the reservoir yields metallic sulfides from the rupture of the R−S−R bond in aromatic and/or aliphatic structures. Furthermore, under favorable conditions, it is possible to obtain fewer complex structures, which favor the crude oil quality and its improved recovery. Nonetheless, the absence of hydrogen and catalyst leads to polycondensation and polymerization, which in turn, reduce the physicochemical quality of the crude.[17,24,65,67]

Note that the 100 ppm iron naphthenate test attained the largest increase in API gravity, around 3.59 units. Meanwhile, for concentrations of 50, 200, and 300 ppm, the increase in API gravity was 1.6, 1.23, and 2.48 units, respectively. For molybdenum naphthenate, the greatest increase in API gravity, 2.07 units, was observed at a concentration of 300 ppm. However, this increase is smaller than that with iron naphthenate for the same concentration. Likewise, for concentrations of 50, 100, and 200 ppm, the API gravity increased by 1.8, 1.47, and 0.45 units, respectively. In general, the results show that the API gravity of the upgraded crudes are higher with respect to the base crude and upgraded crude without catalyst. The changes can be attributed to the modifications of the chemical structure of the upgraded crude oil in each test due to the breaking of alkyl chains and multiple reactions. These results allow us to conclude that the two catalysts formed in situ have different selectivities, but both have a favorable effect on the properties of the upgraded crude oil.

According to the results obtained in viscosity and API gravity measures (Figures 3 and 4), the samples with the most representative changes in viscosity and density were selected to be analyzed by simulated distillation and ATR-FT-IR spectroscopy characterization. In this investigation, the simulated distillation curves of the base crude and the upgraded crude oils under catalytic aquathermolysis conditions were studied. The purpose of this section was to determine the fractions yield behavior and its conversion with a boiling point above 340 °C (340 °C+). Figure 5 compares the distillation curve of base crude oil and upgraded crude oils under aquathermolysis conditions with 100 ppm of metal ion, according to the highest efficiency in the tests. The trends of the crude oil distillation curves in the presence of a catalyst show significant differences with respect to the base crude oil and the crude obtained without catalyst.

The upgraded crude oils showed an increase in liquid products around 300 °C, being higher in the presence of iron naphthenate. From the distillation results it can be deduced that the presence of iron naphthenate produces a greater quantity of lower weight compounds compared to molybdenum naphthenate. On the other hand, the results show that under aquathermolysis conditions, but in the absence of a catalyst, polycondensation reactions are favored, and therefore, compounds with higher boiling points are generated.

In this work, the fractions with the highest molecular weight in the crude oils and with boiling temperatures above 340 °C were considered. Therefore, it is important to evaluate its conversion, based on the liquid product yield produced with respect to the boiling point below 340 °C (340 °C−) during each of the aquathermolysis tests. To calculate the conversion at 340 °C (340 °C−), the following equation was used

$$X_{340^\circ C+} = \frac{(W_{340^\circ C+,\mathrm{crude}} - W_{340^\circ C+,\mathrm{liquids}}) \times 100}{W_{340^\circ C+,\mathrm{crude}}} \quad (5)$$

where $X_{340\ ^\circ C+}$ is the conversion of the base crude heavy fractions with temperatures above 340 °C (340 °C+), and $W_{340\ ^\circ C+\mathrm{crude}}$ and $W_{340\ ^\circ C+\mathrm{liquids}}$ are the fractions in the crude oil and liquid products, respectively. Figure 6 shows the conversion of the base crude oil and the respective upgraded crude oils.

To calculate the conversion of the 340 °C+ fraction, two scenarios are considered: first, the transformation toward liquids (without gas), and second, the conversion toward liquids and gases (with gas). The results show an increase in the conversion to liquid products when the tests are conducted in the presence of catalysts. However, when the conversion to liquids and gases is considered, the results show a greater increase with molybdenum than with iron naphthenate. On the other hand, the conversion obtained under aquathermolysis conditions, without the presence of acatalyst, yields a negative value. This can be attributed to the conditions that govern the free radical reactions, to the presence of the catalysts formed in situ, and to the hydrogen produced by the water−gas shift reactions.

Figure 7 shows the representative fractions of the distillation curves for this study, which were obtained following the ASTM D-7169 standard. Under aquathermolysis conditions, without a catalyst, an increase of the 590 °C+ fraction is observed. Meanwhile, for the upgraded crude oils in the presence of a catalyst, a significant increase is observed between fractions 1 to 4. Comparing the upgraded crude oil with molybdenum naphthenate and the base crude oil, the light fractions of the former increase in the following order: fraction 4 > fraction 3 > fraction 2 > fraction 1. Also, when the crude oil is enhanced with iron naphthenate, the light fractions increase in the following order: fraction 2 > fraction 3 > fraction 4 > fraction 1. On the other hand, for the two upgraded crude oils in the presence of a catalyst, the content of the complex fractions 590 °C+ (vacuum bottoms) decreases in the reverse order.

The most complex compounds in crude oils, resins, and asphaltenes are mainly concentrated in the 590 °C+ fraction. Thus, from the results, the transformation of fraction 7 can be

https://dx.doi.org/10.1021/acs.energyfuels.0c04142
Energy Fuels XXXX, XXX, XXX−XXX

attributed to the reactivity of resins and asphaltenes under catalytic aquathermolysis conditions, as indicated by other authors.[51,61,68] Figure 8 illustrates the general scheme of the reaction mechanism proposed in the catalytic aquathermolysis process, where it can be observed how the mechanisms are interconnected. Thus, the product of one reaction can become the raw material of another. The process also illustrates the formation of organosulfur compounds, which can polymerize or react with water to produce species that tend to participate in a series of reactions.[17,69] However, the presence of precursors and water leads to polymerization inhibition with the lower molecular weight formation.

3.4. Characterization by ATR-FTIR and UV−Vis Spectroscopy. An infrared spectrum represents the amount of energy absorbed by the functional groups present in the sample molecules. Given the large number of functional groups present in hydrocarbons, several studies have identified specific wavelengths where the absorbance intensity allows representing the functional groups and characteristic structures of crude oils.[42,70,71] Table 2 shows the wave numbers assignment established in this research. Figure 9 was included in order to define the wavelengths for the samples. To determine the structural difference between the base crude oil and the upgraded crude, characterization parameters were used.

From the functional groups identified, the parameters of aromaticity, oxidation, branching, paraffinicity, sulfidation, degree of condensation, and length of alkyl chains reported by several authors were calculated.[44,72] These parameters are described in Table 3 and compared in Figure 10. The parameters show that the aromaticity in the upgraded crude oils decreases compared to the base crude oil. This can be attributed to the reduction of C=C bonds. On the other hand, the results show that concentrations of molybdenum naphthenate higher than 100 ppm yield a decrease in gases, which in turn reduces the breakdown of liquid products (Figure 2). Meanwhile, the likelihood of aromatic hydrocarbon free radical condensation increases.

An increase in the concentration of molybdenum naphthenate favors the formation of aromatic structures with a higher content of branched linear structures. Upgraded crude oils in the presence of the two catalysts, at 100 ppm, showed insignificant differences with respect to the initial crude. Meanwhile, higher concentrations of iron naphthenate favored the formation of substituted aromatic compounds with alkyl chains of greater length compared to molybdenum naphthenate.

The results show that the improved crude oil paraffinicity grew in the presence of 100 ppm of catalyst. However, in reactions with 300 ppm of molybdenum naphthenate, this parameter significantly decreases. The paraffinicity grows proportionally to the length of the alkyl chains located in the aromatic species. Regarding the oxidation parameter, it increases in all the samples relative to the base crude oil, especially at 300 ppm of molybdenum naphthenate. It is well known that catalysts act especially in the weakest bonds with heteroatoms (C−R, R: S, O), causing reactions such as oxygenation, alcoholization, and esterification.[68,73,74] Therefore, greater oxidation is associated with new species formation with functional groups that contain oxygen and sulfur as alcohols, ethers, esters, thioesters, thiols, and sulfoxides, among others. This allows corroborating that oxidation reactions are developed in the catalytic aquathermolysis tests carried out.

The maximum value of the sulfidation parameter in the upgraded crude oils was obtained at 100 ppm of the metal ion in the precursor, and at higher concentrations, it decreased. This indicates that low concentrations of iron and molybdenum naphthenate yield a lower concentration of metal sulfide in the reaction. These results are attributed to the oxidation of sulfides into sulfoxides. On the other hand, with the increase in the concentration of the precursors of iron naphthenate and molybdenum naphthenate, the oxidation of sulfides decreases and the conversion of sulfur toward the formation of metal sulfide improves.

The aromatic condensation parameter is related to polyaromatic structures. As shown in Figure 10, this parameter increases in the presence of precursors at 100 ppm, being moderately higher for iron naphthenate. This indicates that at low concentrations of metallic sulfide, the reactions are governed by reactions between the radicals of the aromatic rings. With the increase in the concentration of iron and molybdenum naphthenate, species with a lower degree of aromatic condensation are generated, possibly due to desulfurization and hydrogenation reactions.

From the results obtained in this work, it is evident that the most relevant parameters for the catalytic aquathermolysis are the length of alkyl chains, the aromaticity, and the sulfurization because these showed great differences between the initial and the upgraded crude oil. Therefore, they agree with the structural effect generated by the aquathermolysis in the presence of catalysts. Thus, the variability of the results depends on the nature and concentration of the catalyst precursor, which produces a molecular change in the upgraded crude oil. From the UV−vis spectra (Figure 11), the wavelengths at 242, 262, and 412 nm, which represent the concentration of benzene, naphthenic and porphyrin species, respectively,[59] presented a standard deviation of 0.8%, 1.1%, and 0.4%, respectively.

Table 4 shows the absorbances for the upgraded crude oils obtained under aquathermolysis conditions in the presence of iron and molybdenum naphthenate. The results show an increase in the concentration of benzene and naphthenic compounds in the tests within 50 and 100 ppm. However, in this concentration range, the content of aromatic and naphthene compounds is higher with iron than with molybdenum, which allows the formation of lower molecular weight species from structures with a higher degree of complexity.

On the basis of the results of viscosity, API gravity, simulated distillation, and the analysis of UV−vis and ATR-FTIR spectroscopy, for the upgraded crude oils, it can be appreciated that the difference in properties is related to the performance and chemical composition of the products. In general, the catalytic aquathermolysis is a recovery process that improves the properties of crude oils in the reservoir and promotes the formation of higher liquid yields due to the multiple reactions to the presence of sulfur and to the participation of hydrogen that yield compounds with a wide variety of size and molecular weights.

4. CONCLUSIONS

During the aquathermolysis of heavy crude oils, molybdenum naphthenate and iron naphthenate have different selectivities and favor the conversion of complex compounds into compounds of smaller molecular size, especially aromatic and naphthenic compounds.

https://dx.doi.org/10.1021/acs.energyfuels.0c04142
Energy Fuels XXXX, XXX, XXX−XXX

The steam injection process in the presence of iron naphthenate, with a concentration of 100 ppm, showed an outstanding 53% reduction in viscosity, greater light components yield, and favorable physicochemical conditions.

Catalyst concentration plays an important role in upgraded crude oil under catalytic aquathermolysis conditions. However, an increase in the catalyst concentration does not always generate a greater reduction in viscosity or improvement in the physicochemical properties of the hydrocarbon. Although the reactivity process due to the thermal effect is governed by free radical reactions, the presence of hydrogen produced in the process participates in the occurrence of multiple reactions that improve the quality of the crude oil. Finally, the results of this work indicate that the catalysts used have great potential in recovery methods.

AUTHOR INFORMATION

Corresponding Author

Daniel Molina V − *Laboratorio de Resonancia Magnética Nuclear, Universidad Industrial de Santander-UIS, A.A. 678 Bucaramanga, Colombia;* orcid.org/0000-0002-7897-2526; Email: dmolina@uis.edu.co

Authors

Keyner S. Núñez-Méndez − *Grupo de Recobro Mejorado, GRM, Universidad Industrial de Santander-UIS, A.A. 678 Bucaramanga, Colombia*

Luis M. Salas-Chia − *Grupo de Recobro Mejorado, GRM, Universidad Industrial de Santander-UIS, A.A. 678 Bucaramanga, Colombia*

Samuel F. Muñoz − *Grupo de Recobro Mejorado, GRM, Universidad Industrial de Santander-UIS, A.A. 678 Bucaramanga, Colombia*

Paola A. León − *Grupo de Recobro Mejorado, GRM, Universidad Industrial de Santander-UIS, A.A. 678 Bucaramanga, Colombia*

Adan Y. León − *Grupo de Recobro Mejorado, GRM and Grupo de investigación en Corrosión, GIC, Universidad Industrial de Santander-UIS, A.A. 678 Bucaramanga, Colombia*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.energyfuels.0c04142

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the financial support provided by the Universidad Industrial de Santander (UIS) and their professionals' staff according to Project No. 2681 (Capital Semilla).

REFERENCES

(1) Lang, L.; Li, H.; Wang, X.; Liu, N. *J. Pet. Sci. Eng.* **2020**, *185*, 106659.

(2) Castañeda, L.; Muñoz, J.; Ancheyta, J. *Fuel* **2012**, *100*, 110−127.

(3) Larter, S.; Head, I. *Elements* **2014**, *10* (4), 277−283.

(4) Wiehe, I.; Liang, K. *Fluid Phase Equilib.* **1996**, *117* (1−2), 201−210.

(5) Babadagli, T. Philosophy of EOR. *J. Pet. Sci. Eng.* **2020**, *188*, 106930.

(6) Butler, R.; McNab, G.; Lo, H. *Can. J. Chem. Eng.* **1981**, *59* (4), 455−460.

(7) Alvarado, V.; Manrique, E. *Energies* **2010**, *3*, 1529−1575.

(8) Sarathi, P. *In-Situ Combustion Handbook - Principles and Practices*; National Petroleum Technology Office, Tulsa, OK, USA, 1999.

(9) Wu, Z.; Wang, L.; Xie, C.; Yang, W. *Fuel* **2019**, *252*, 109−115.

(10) Al Dasani, A.; Bai, B. *J. Pet. Sci. Eng.* **2011**, *79*, 10−24.

(11) Zhao, Y. *J. Pet. Sci. Eng.* **2020**, *189*, 107016.

(12) Wang, Y.; Ren, S.; Zhang, L.; Peng, X.; Pei, S.; Cui, G.; Liu, Y. *Fuel* **2018**, *211*, 471−483.

(13) Mahmoud, M.; Alade, O. S.; Hamdy, M.; Patil, S.; Mokheimer, E. M.A. *Energy Convers. Manage.* **2019**, *202*, 112203.

(14) Wang, K.; Yan, W.; Deng, J.; Tian, H.; Li, W.; Wang, Y.; Wang, L.; Ye, S. *J. Pet. Sci. Eng.* **2018**, *167*, 241−248.

(15) Barroux, C.; Lamourux-Var, V. Using geochemistry to address H_2 production risk due to steam injection in oil sands. *SPE Annual Technical Conference and Exhibition*; Society of Petroleum Engineers, 2013.

(16) Barrios, J. Estimation of the H_2S formation under injection conditions for the Orinoco oil belt. *SPE International Improved Oil Recovery Conference*; Society of Petroleum Engineers, 2010.

(17) Hyne, J. *Aquathermolysis: a Synopsis of Work on the Chemical Reaction between Water (Steam) and Heavy Oil Sands during Simulated Steam Stimulation*; AOSTRA Library and Information Service, 1986.

(18) Liu, X.; Li, Y.; Zhang, Z.; Li, X.; Zhao, M.; Su, C. Synthesis of silica/metatitanic acid nanocomposite and evaluation of its catalytic performance for aquathermolysis reaction of extra-heavy crude oil. *J. Energy Chem.* **2015**, *24* (4), 472−476.

(19) Yi, S.; Babadagli, T.; Li, H. Use of nickel nanoparticles for promoting aquathermolysis reaction during cyclic steam stimulation. *SPE Annual Technical Conference and Exhibition*; Society of Petroleum Engineers, 2018.

(20) Chen, Y.; Yang, C.; Wang, Y. *J. Anal. Appl. Pyrolysis* **2010**, *89* (2), 159−165.

(21) Zhong, L.; Liu, Y.; Fan, H. Liaohe extra-heavy crude oil underground aquathermolytic treatments using catalyst and hydrogen donors under steam injection conditions. *SPE Annual Technical Conference and Exhibition*; Society of Petroleum Engineers, 2003.

(22) Jiang, S.; Liu, X.; Liu, Y.; Zhong, L. In situ upgrading heavy oil by aquathermolytic treatment under steam injection conditions. *SPE Annual Technical Conference and Exhibition*; Society of Petroleum Engineers, 2005.

(23) Nares, H.; Schacht-Hernández, P.; Ramírez-Garnica, M.; Cabrera-Reyes, M. Upgrading heavy and extraheavy crude oil with ionic liquid. *SPE Annual Technical Conference and Exhibition*; Society of Petroleum Engineers, 2007.

(24) Wang, Y.; Chen, Y.; He, J.; Li, P.; Yang, C. *Energy Fuels* **2010**, *24*, 1502−1510.

(25) Chao, K.; Chen, Y.; Li, J.; Zhang, X.; Dong, B. *Fuel Process. Technol.* **2012**, *104*, 174−180.

(26) Zhang, Z.; Barrufet, M.; Lane, R.; Mamora, D. Experimental study of in-situ upgrading for heavy oil using hydrogen donors and catalyst under steam injection condition. *SPE Annual Technical Conference and Exhibition*; Society of Petroleum Engineers, 2012.

(27) Maity, K.; Ancheyta, J.; Marroquín, G. *Energy Fuels* **2010**, *24* (5), 2809−2816.

(28) Betiha, M.; ElMetwally, A.; Al-Sabagh, A.; Mahmoud, T. *Energy Fuels* **2020**, *34* (9), 11353−11364.

(29) Belgrave, J.; Moore, M.; Ursenbach, M. *J. Can. Petrol. Technol.* **1997**, *36*, 38−44.

(30) Chao, K.; Chen, Y.; Liu, H.; Zhang, X.; Li, J. *Energy Fuels* **2012**, *26* (2), 1152−1159.

(31) Wu, C.; Lei, G.; Yao, C.; Jia, X. In situ upgrading extra-heavy oil by catalytic aquathermolysis treatment using a new catalyst based anamphiphilic molybdenum chelate. *SPE Annual Technical Conference and Exhibition*; Society of Petroleum Engineers, 2010.

(32) Foss, L.; Petrukhina, N.; Kayukova, G.; Amerkhanov, M.; Romanov, G.; Ganeeva, Y. *J. Pet. Sci. Eng.* **2018**, *169*, 269−276.

https://dx.doi.org/10.1021/acs.energyfuels.0c04142
Energy Fuels XXXX, XXX, XXX−XXX

(33) Hao, H.; Su, H.; Chen, G.; Zhao, J.; Hong, L. Viscosity reduction of heavy oil by aquathermolysis with coordination complex at low temperature. *Open Fuels Energy Sci. J.* **2015**, *8*, 93−98.
(34) Hassanzadeh, H.; Galarraga, C.; Abedi, J.; Scott, C.; Chen, Z.; Pereira-Almao, P. Modelling of bitumen ultradispersed catalytic upgrading experiments in a batch reactor. *Canadian International Petroleum Conference*; Petroleum Society of Canada, 2009.
(35) Kayukova, G.; Foss, L.; Feoktistov, D.; Vakhin, A.; Petrukhina, N.; Romanov, A. *Pet. Chem.* **2017**, *57* (8), 657−665.
(36) Olvera, J. N. R.; Gutierrez, G. J.; Serrano, J.A. R.; Ovando, A. M.; Febles, V. G.; Arceo, L. D. B. *Catal. Commun.* **2014**, *43*, 131−135.
(37) Shuwa, S.; Al-Hajri, R.; Mohsenzadeh, A.; Al-Waheibi, M.; Jibril, B. Heavy crude oil recovery enhancement and in situ upgrading during steam using Ni-Co-Mo dispersed catalyst. *SPE EOR Conference at Oil and Gas West*; Society of Petroleum Engineers, 2016.
(38) Sitnov, S.; Mukhamatdinov, I.; Vakhin, A.; Ivanova, A.; Voronina, E. *J. Pet. Sci. Eng.* **2018**, *169*, 44−50.
(39) Hashemi, R.; Pereira, P. Experimental study of simultaneous Athabasca bitumen recovery and upgrading using ultra dispersed catalysts injection. *SPE Canadian Unconventional Resources Conference*; Society of Petroleum Engineers, 2011.
(40) Lin, D.; Feng, X.; Wu, Y.; Ding, B.; Lu, T.; Liu, Y.; Chen, X.; Chen, D.; Yang, C. *Appl. Surf. Sci.* **2018**, *456*, 140−146.
(41) Patel, H.; Shah, S.; Ahmed, R.; Ucan, S. Effects of nanoparticles and temperature on heavy oil viscosity. *J. Pet. Sci. Eng.* **2018**, *167*, 819−828.
(42) Rodrigues, R.; Rocha, J.; Oliveira, L.; Dias, J.; Muller, E.; Castro, E.; Filgueiras, P. *Chemom. Intell. Lab. Syst.* **2017**, *166*, 7−13.
(43) Lin, D.; Zhu, H.; Wu, Y.; Lu, T.; Liu, Y.; Chen, X.; Peng, C.; Yang, C.; Feng, X. *Fuel* **2019**, *245*, 420−428.
(44) Vakhin, A.; Sitnov, S.; Mukhamatdinov, I.; Aliev, F.; Kudryashov, S.; Afanasiev, I.; Petrashov, O.; Varfolomeev, M.; Nurgaliev, D. *Pet. Sci. Technol.* **2018**, *36* (22), 1857−1863.
(45) Du, H.; Li, M.; Liu, D.; Ren, Y.; Duan, Y. *Appl. Petrochem. Res.* **2015**, *5* (2), 89−98.
(46) Qin, W.; Xiao, Z. *Adv. Mater. Res.* **2012**, *608-609*, 1428−1432.
(47) Chen, Y.; Wang, Y.; Wu, C.; Xia, F. *Energy Fuels* **2008**, *22* (3), 1502−1508.
(48) Chen, Y.; Wang, Y.; Lu, J.; Wu, C. *Fuel* **2009**, *88* (8), 1426−1434.
(49) Li, G.; Chen, Y.; An, Y.; Chen, Y. *Fuel Process. Technol.* **2016**, *153*, 94−100.
(50) Zhang, J.; Han, F.; Yang, Z.; Zhang, L.; Wang, X.; Zhang, X.; Jiang, Y.; Chen, K.; Pan, H.; Lin, R. *Energy Fuels* **2020**, *34* (5), 5426−5435.
(51) León, A.; Guzmán, A.; Laverde, D.; Chaudhari, R.; Subramaniam, B.; Bravo-Suárez, J. *Energy Fuels* **2017**, *31*, 3868−3877.
(52) Leon, A.-Y.; Guzman M, A.; Picon, H.; Laverde C, D.; Molina V, D. *Energy Fuels* **2020**, *34* (8), 9231−9242.
(53) Chen, G.; Yuan, W.; Bai, Y.; Zhao, W.; Gu, X.; Zhang, J.; Jeje, A. *Pet. Chem.* **2017**, *57* (5), 389−394.
(54) Khalil, M.; Liu, N.; Lee, R. *Ind. Eng. Chem. Res.* **2017**, *56* (15), 4572−4579.
(55) Huang, S.; Cao, M.; Cheng, L. *Energy Fuels* **2018**, *32* (4), 4850−4858.
(56) Yi, Y.; Li, S.; Ding, F.; Yu, H. *Pet. Sci.* **2009**, *6* (2), 194−200.
(57) Li, C.; Huang, W.; Zhou, C.; Chen, Y. *Fuel* **2019**, *257*, 115779.
(58) Banda-Cruz, E.; Padrón-Ortega, S.; Gallardo-Rivas, N.; Páramo-García, U.; Díaz-Zavala, N.; Melo-Banda, A. *J. Eng. Technol.* **2017**, *6* (1), 49−58.
(59) Muraza, O.; Galadima, A. *Fuel* **2015**, *157*, 219−231.
(60) Lee, H.; Park, S. *Kongop Hwahak* **2016**, *27* (4), 343−352.
(61) Suwaid, M.; Varfolomeev, M.; Al-Muntaser, A.; Yuan, C.; Starshinova, V.; Zinnatullin, A.; Vagizov, F.; Rakhmatullin, I.; Emelianov, D.; Chemodanov, A. *Fuel* **2020**, *281*, 118753.
(62) Kudryashov, S.I.; Afanasiev, I.S.; Petrashov, O.V.; Vakhin, A.V.; Sitnov, S.A.; Akhmadiayrov, A.A.; Varfolomeev, M.A.; Nurgaliev, D.K. *Neft. Khoz.* **2017**, *2017* (8), 30−34.
(63) Xu, Y.; Ayala-Orozco, C.; Wong, M. Heavy oil viscosity reduction using iron III para-toluenesulfonate hexahydrate. *SPE Annual Technical Conference and Exhibition*; Society of Petroleum Engineers, 2018.
(64) Wu, C.; Lei, G.-L.; Yao, C.-j.; Sun, K.-j.; Gai, P.-y.; Cao, Y.-b. *J. Fuel Chem. Technol.* **2010**, *38* (6), 684−690.
(65) Gu, X.; Zhang, F.; Chen, G.; Zhang, J.; Meng, M.; Li, B.; Zhang, Z. *Russ. J. Appl. Chem.* **2016**, *89* (12), 2061−2065.
(66) Xu, H.; Pu, C. *J. Fuel Chem. Technol.* **2011**, *39* (8), 606−610.
(67) Wang, Y.; Chen, Y.; He, J.; Li, P.; Yang, C. *Energy Fuels* **2010**, *24*, 1502−1510.
(68) Avbenake, O.; Al-Hajri, R.; Jibril, B. *Pet. Sci. Technol.* **2020**, *38* (14), 800−807.
(69) Meléndez, L.; Lache, A.; Orrego-Ruiz, J.; Pachón, Z.; Mejía-Ospino, E. *J. Pet. Sci. Eng.* **2012**, *90*, 56−60.
(70) Mohammadi, M.; Khorrami, M.; Vatani, A.; Ghasemzadeh, H.; Vatanparast, H.; Bahramian, A.; Fallah, A. *Spectrochim. Acta, Part A* **2020**, *232*, 118157.
(71) Douda, J.; Alvarez, R.; Bolaños, N. *Energy Fuels* **2008**, *22*, 2619−2628.
(72) Chen, M.; Li, C.; Li, G.; Chen, Y.; Zhou, C. *Pet. Sci.* **2019**, *16* (2), 439−446.
(73) Tverdov, I.; Khafizov, N.; Madzhidov, T.; Varfolomeev, M.; Yuan, C.; Kadkin, O. *ACS Omega* **2020**, *5* (31), 19589−19597.

https://dx.doi.org/10.1021/acs.energyfuels.0c04142
Energy Fuels XXXX, XXX, XXX−XXX