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## Catalytic upgrading evaluation under steam injection conditions with spectroscopy 1H-NMR

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### ABSTRACT

Steam injection has mainly been applied due to its physical recovery mechanisms. However, a chemical process could arise and is called aquathermolysis. These reactions could be favored by the addition of a catalyst, which acts on cracking reactions of some heavy compounds. Therefore, an experimental evaluation of catalytic aquathermolysis of heavy oil was carried out in a microreactor batch. The experiments were performed at three different reaction times (24 h–62 h) and temperatures between 240 °C–300 °C. Iron naphthenate, molybdenum naphthenate, and nickel naphthenate were the catalysts used. Oil upgrading was measured by changes in the physical property, and the identification of reactive molecules by nuclear magnetic resonance 1H-NMR technique to obtain average molecular parameters. The average number of carbons in alkyl chains was determined to simplify the samples' compositional analysis, as well as the number of substituted rings and the aromaticity factor. The experimental results showed an increase in the viscosity reduction efficiency as Mo < Ni < Fe. In addition, the catalysts increased the API° gravity and decreased the viscosity by 10° and 79%, respectively. Furthermore, naphtha and kerosene production increased the conversion of the 300 °C+ fraction up to 8%. Finally, upgraded oils showed a smaller difference in alkyl chains length.

### KEYWORDS

aquathermolysis; enhanced oil recovery; heavy oil; steam; upgrading

### 1. Introduction

Worldwide statistics indicates the existence of oil reserves of more than 1.65 trillion barrels, of which only 30% corresponds to conventional oil fields (Bjornseth 2013; Lang et al. 2020). Therefore, the remaining 70% constituted by heavy oil, extra-heavy oil, and oil sands, represents both a focus and a challenge for the current oil industry (Bjornseth 2013; Larter

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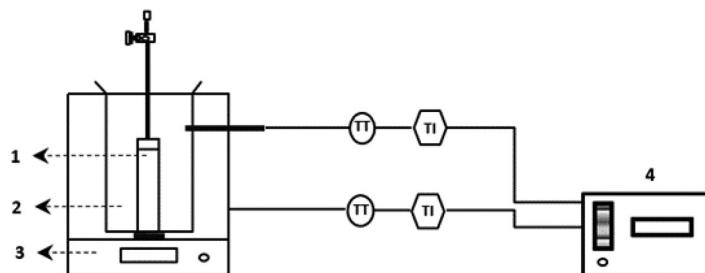
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and Head 2014). Considering the viscosity and mobility in the reservoir of this kind of oil, their production by primary and secondary methods is limited and inefficient. Thus, the application of enhanced oil recovery techniques is required, among which thermal processes are more suitable (Santos et al. 2014; Li et al. 2021). The main purpose of thermal methods is to increase the reservoir temperature in order to generate different recovery mechanisms, such as oil viscosity reduction (Blevins, Duerksen, and Ault 1984). Within the thermal recovery techniques, cyclic steam injection, steam flooding, steam-assisted gravity drainage (SAGD), and in-situ combustion stand out (Bennion et al. 2007; Thomas 2008; Alvarado and Manrique 2010; León et al. 2015). These processes have been studied and applied conventionally and in a hybrid configuration with solvents, gas, and catalysts (Pérez et al. 2018; Dong et al. 2019; Babadagli, 2020).

During steam injection, the steam reacts with some hydrocarbons and minerals in the reservoir. The reactions resulting from the contact between heavy oil or oil sands and water at high temperature was defined as aquathermolysis (Hyne et al. 1982; Hyne 1986). In the temperature range between 200 and 325 °C, these reactions produce carbon dioxide, carbon monoxide, lower molecular weight hydrocarbons, and hydrogen sulfide (Hoffmann et al. 1995; Lamoureux-Var et al. 2005;

Wang et al. 2018; Butron et al. 2015; Mokheimer et al. 2018). The intermediate reactions involved in the aquathermolysis are pyrolysis, hydrolysis, Water Gas Shift, and hydrodesulfurization (Belgrave, Moore, and Ursenbach 1994; Belgrave, Moore, and Ursenbach 1997; Barroux et al. 2013; Muraza and Galadima 2015; Kapadia, Kallos, and Gates 2015; Zhao et al. 2016). The result of heavy oils' aquathermolysis under catalysts shows an increase of saturated and aromatic components, which decreases oil apparent molecular weight and its viscosity (Zhong et al. 2003; Jiang et al. 2005; Nares et al. 2007). This process is called catalytic aquathermolysis and it could generate oil in situ upgrading (Chen et al. 2008; Chen, Yang, and Wang 2010; Qin and Xiao 2013; Li et al. 2016; Leon et al.; Zhang et al. 2020; Vakhin et al. 2020).

Different studies have been carried out to assess the feasibility of in situ upgrading under steam injection using commercial and experimental catalysts (Hassanzadeh et al. 2009; Galarraga and Pereira-Almao 2010; Rivera Olvera et al. 2014; Hao et al. 2015; Shuwa et al. 2015; Chavez and Pereira-Almao 2016; Kudryashov et al. 2017; Foss et al. 2018). Displacements and static tests in batch reactors have focused on changes in oil properties such as API° gravity, hydrogen-carbon ratio, SARA, and viscosity (Lin et al. 2018). Various chemical compounds have been developed and studied to act as a catalytic system in aquathermolysis reactions. Homogeneous catalysts are divided into water-soluble: molybdenum, tungsten, iron, nickel,



**Figure 1.** Schematic of the microreactor used for catalytic aquathermolysis: (1) Microreactor; (2) Sand bath ( $\text{Al}_2\text{O}_3$ ); (3) Magnetic stirrer; (4) Temperature control.

and cobalt salts and oil-soluble: molybdenum naphthenate, iron pentacarbonyl, chromium tert-butyl alcohol, among others (Mohammad and Mamora 2008a; Wang et al. 2010; Maity, Ancheyta, and Marroquín 2010; Zhang et al. 2012; Betiha et al. 2020). One of the main challenges is the identification of the compounds' families that are implicated in aquathermolysis reactions.

This article puts forward an experimental evaluation of catalytic aquathermolysis in Colombian heavy oil. Tests were carried out in a batch microreactor, with the presence of a catalyst, oil, and water at typical steam injection conditions. Iron naphthenate, molybdenum naphthenate, and nickel naphthenate were the catalysts studied. The initial oil and the upgraded oils were subjected to density, simulated distillation, and thermogravimetric analysis TGA, as well as  $^1\text{H}$  NMR to determine changes in the chemical structure. These results are paramount for future work in the selection of catalyst, screening base on oil composition, operation ranges, and numerical reservoir simulations of the technology in development.

## 2. Experimental section

### 2.1. Materials

Conventional steam injections pilots are being implemented in a Colombian oil field with an API gravity of  $12.8^\circ$  and viscosity of 5584 cP (@  $45^\circ\text{C}$ ). For that reason, this oil was selected in this study (Perez et al. 2020). Additionally, iron naphthenate (6 wt% iron, Strem Chemicals), nickel naphthenate (6% wt% nickel, Strem Chemicals), and molybdenum naphthenate were used as catalysts for the aquathermolysis tests. Molybdenum naphthenate was synthesized using the methodology reported by León et al. (2017). To sum up, the catalyst was prepared by a reaction between naphthenic acid (technical grade, Sigma-Aldrich, P/N 70340) and bis (acetyletonate) dioxomolybdenum (VI) (Sigma-Aldrich, P/N 227749), mixed with a mass ratio of 3.74:1.

## 2.2. Catalytic aquathermolysis tests

The experiments were carried out in a batch microreactor with a capacity of 16 cm<sup>3</sup>. During the tests, the microreactor was submerged in a sand bath (Al<sub>2</sub>O<sub>3</sub>) at high temperatures. The temperature was monitored through a K-9810 Taylor-type digital thermometer, as well as temperature control. Figure 1 shows a schematic representation of the equipment (León et al. 2017; León et al. 2020).

For the aquathermolysis tests in presence of catalysts, 4 g of oil were added to the reactor with catalyst, with a concentration of 1670 ppm. Additionally, 2 g of distilled water were added to keep a mass ratio of 2:1 between oil and water (Mohammad and Mamora 2008b; Zhang et al. 2012). The phases were separated using a Hettich Universal 320 R centrifuge with a speed of 3000 rpm for 40 min. The experimental evaluation was distributed in two stages. Firstly, the catalyst was the only variable, and the tests were performed at the same temperature and pressure conditions (270 °C and 800 psi). Secondly, the time and temperature effects of the test were evaluated. These factors varied in three levels, where the set temperatures were 240 °C, 270 °C and 300 °C, and the test times were 24 h, 48 h, and 62 h the ranges of the variables were established based on the technology's operational screening (Hama et al. 2014). In addition, the catalyst with the best performance during the first phase was used in the second phase of the study as well. The separation of the selected catalysts in later stages is not a problem due to the low concentrations and the retention of part of these in the reservoir.

## 2.3. Characterization

### 2.3.1. Density and viscosity measurements

The density of the initial oil and the obtained products were carried out through the application of the ASTM D70-09 standard for bituminous materials. On the other hand, dynamic viscosity was evaluated using an Anton Parr rheometer and the results were obtained using the RheoPlus software V3.62. The importance of quantifying the oil upgrading from its viscosity changes refers to the link between this property and the mobility ratio, as well as the flow in the porous medium.

### 2.3.2. Thermogravimetry analysis TGA

Thermal decomposition kinetics or reactivity of heavy oils was performed on a thermogravimetric analyzer (Athlon thermogravimetric analyzer). Thermal decomposition was performed in the temperature range between

**Table 1.** Properties of the Colombian heavy crude oil.

Property	Unit	Value
Density / °API	g/cm <sup>3</sup>	0.9841 / 12.29
Viscosity	cP @44 °C	5895
T <sub>5</sub> %, wt	°C	278.7
T <sub>20</sub> %, wt	°C	381
T <sub>30</sub> %, wt	°C	430.3
T <sub>50</sub> %, wt	°C	535.5

25 and 800 °C, at a heating rate of 15 °C/min with a nitrogen flow of 50 mL/min.

### 2.3.3. Simulated distillation by gas chromatography

This method was applied according to the ASTM D7169 standard for samples with a boiling point up to 720 °C. This standard allows obtaining the distribution of the true boiling points of heavy and extra heavy oils, atmospheric and vacuum residues, among many others.

### 2.3.4. <sup>1</sup>H-NMR Analysis

Hydrocarbons are formed by complex structures, which change based on technologies such as catalytic aquathermolysis (Wiehe and Liang 1996). Therefore, this study analyzed the average molecular parameters of the original oil compared to the upgraded oils. The parameters were estimated by the analysis of <sup>1</sup>H-NMR spectroscopy and the application of correlation available in the literature. <sup>1</sup>H-NMR spectra were measured and analyzed on a Bruker Avance III spectrometer at a resonance frequency of 400.16 Hz with a magnetic field of 9.4 T. The obtained spectra were normalized using the MestReNova software V3.0 and the average molecular parameters were calculated using the methodology proposed by several authors (Silva et al. 2004; Poveda and Molina 2012; Mondal et al. 2015).

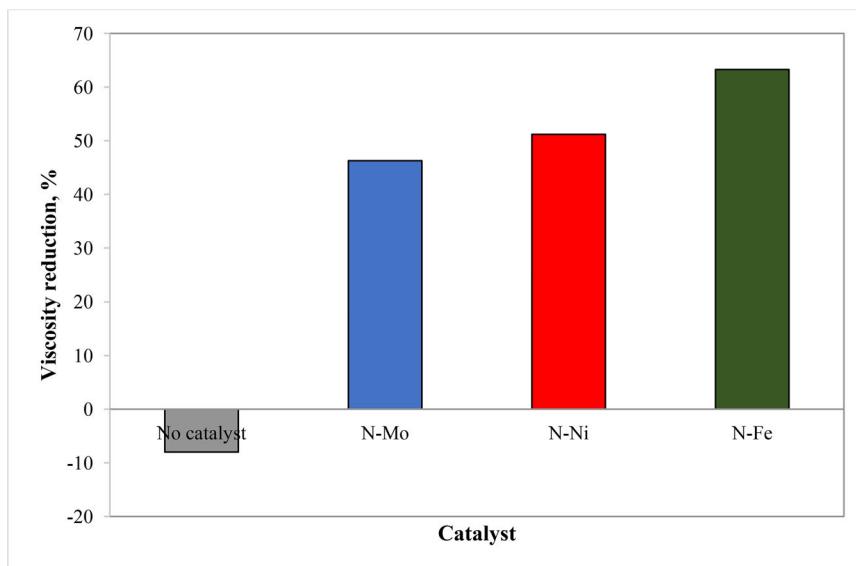
## 3. Results and discussion

### 3.1. Properties of Colombian base crude oil

Some properties of the selected oil for this study are shown in Table 1. The viscosity and density of the fluid indicate that this is a heavy crude oil composed of a representative number of heavy molecules.

### 3.2. Changes in the oil physical properties of crude oil

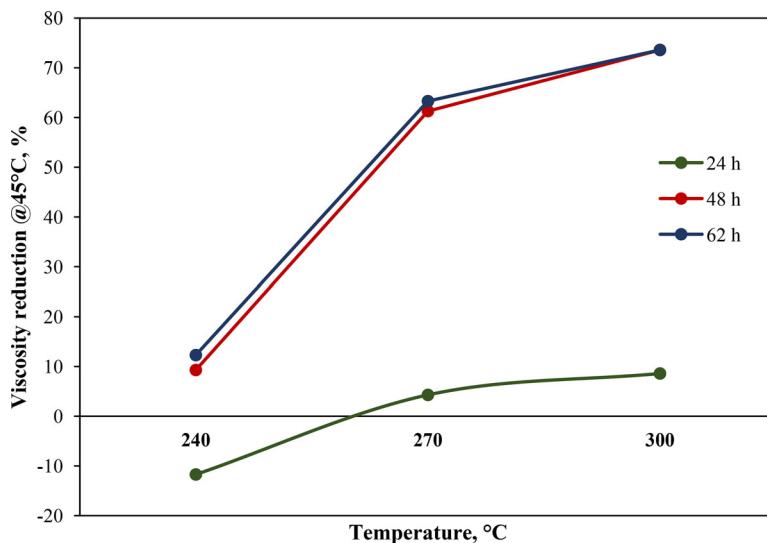
Figure 2 shows the viscosity reduction for each catalyst. The catalysts had a considerable effect on the oil upgrading with an increasing order efficiency of Mo < Ni < Fe. In the absence of catalyst, crude oil presented a slight



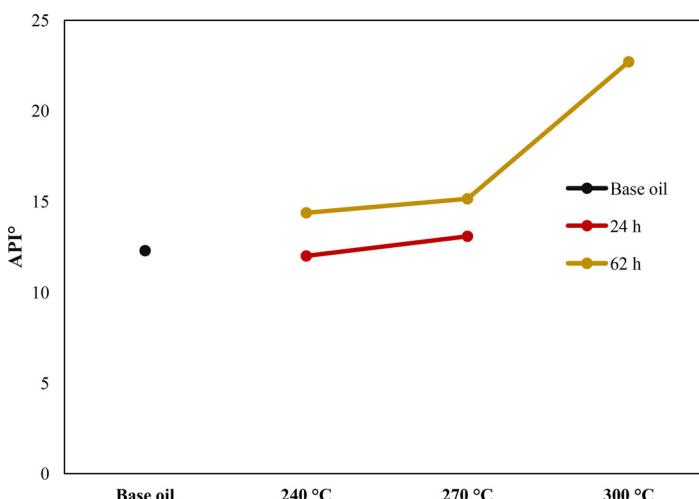
**Figure 2.** Viscosity reduction for the upgraded oils as a function of the used catalyst.

increase in its viscosity attributed to polymerization reactions (Hyne 1986; Rivas, Campos, and Borges 1988; Wu et al. 2010). On the other hand, the presence of iron naphthenate in the crude oil generated an average viscosity reduction of 63%, followed by nickel and molybdenum naphthenate, with reductions of 51 and 46%, respectively. At typical steam injection temperatures, iron catalysts are more efficient. However, as the temperature increases, the activation of other metal ions such as molybdenum and nickel is higher.

Figures 3 and 4 show the API° gravity and viscosity reduction for both the original and the upgraded oils after the reaction at different times and temperatures. The obtained results indicated that the most significant effect was due to temperature since at low process temperatures such as 240 °C, no representative changes in the oil properties were evident, while at 270 °C and 300 °C the viscosity reduction reached values up to 79% and the °API gravity increased in 10°. Experimental tests carried out at 240 °C showed that at low reaction times and temperatures the acid polymerization effect ensued and low hydrogen production generated larger molecules (Hyne 1986; Mohammad and Mamora 2008b). This caused a slight increase in the oil viscosity and oil density in the 24 h test. On the other hand, at 48 and 62 h, the positive effect of the catalyst began to be evident, achieving a maximum reduction of up to 20%, which is associated with an increase in °API gravity of 2°. These results agree with those obtained by other authors in which the catalytic efficiency of iron and the representative effect of temperature on oil upgrading are highlighted (Fan, Liu, and Zhong 2001; Zhong et al. 2003; Jiang et al. 2005; Mohammad and Mamora



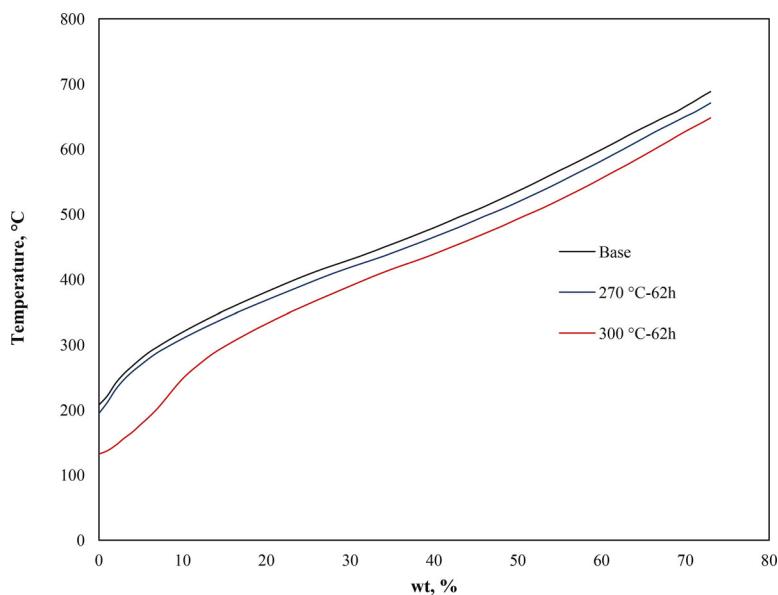
**Figure 3.** Viscosity reduction for the upgraded oils with iron naphthenate as a temperature and reaction time function.



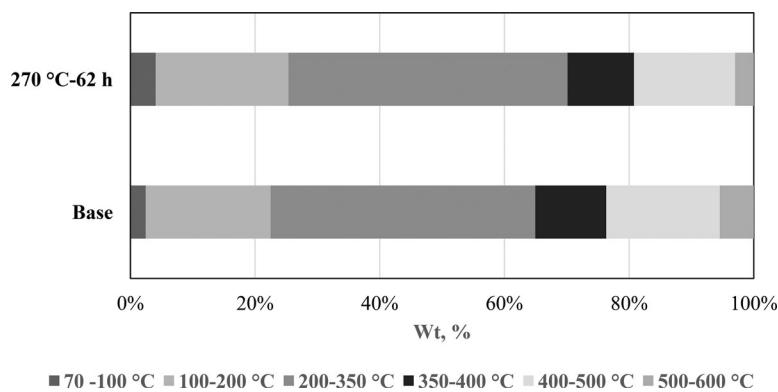
**Figure 4.** API<sup>°</sup> Gravity for the original oil and the upgraded oils with iron naphthenate as a test time and temperature function.

2008a; Wang et al. 2010; Zhang et al. 2012; Wang et al. 2014). According to the results described, iron naphthenate was evaluated during the second phase.

Figure 5 shows the results of simulated distillation for the original oil and two upgraded oils. There was a slight change in the initial boiling point in the sample at 270 °C and 62 h. At 300 °C, the simulated distillation curve showed a change in the initial boiling point of approximately 50 °C, which is associated with a 300 °C + conversion fraction of 8.6%. This was also evidenced through thermogravimetric analysis. The results of Figure 6



**Figure 5.** Simulated distillation curve for the original oil and the upgraded oils with iron naphthenate.



**Figure 6.** Percentage loss in mass of distilled volatile components in the original oil and an upgraded oil with iron naphthenate using TGA analysis.

show the increase of distilled components percentage between 100 and 350 °C; consequently, the proportion of the distilled components between 400 and 600 °C decreased in the upgraded oils. These results support the transformation of heavy species into light and medium components

### 3.3. Changes in the chemical structure of crude oil

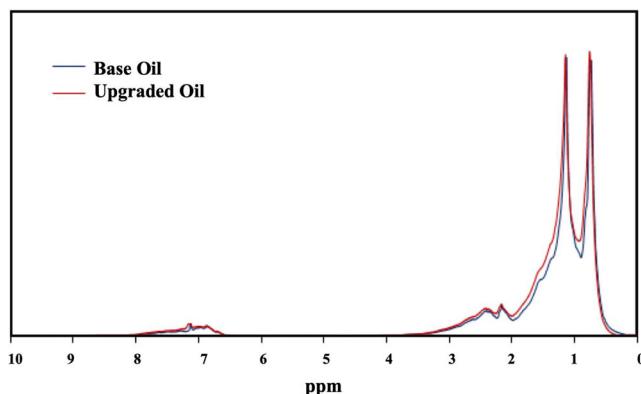
Table 2 shows the functional groups and the average molecular parameters identified according to the specific regions of the  $^1\text{H-NMR}$  spectra. Table 3 shows the changes of chemical structures as well as the maximums and minimums of the obtained spectra from all analyzed samples.

**Table 2.** Structural assignments in the  $^1\text{H}$ -NMR Spectra.

Chemical shift, ppm	Structural assignment	Average molecular parameter
H <sub>1</sub> 1.0-0.5	H $\gamma$ to aromatic ring/terminal CH <sub>3</sub>	H $\gamma$ = H <sub>1</sub> H/100
H <sub>2</sub> 1.9-1.0	H $\beta$ to aromatic/in paraffinic CH and CH <sub>2</sub>	H $\beta$ = H <sub>2</sub> H/100
H <sub>3</sub> 1.9-4.5	H $\alpha$ to aromatic ring	H $\alpha$ = H <sub>3</sub> H/100
H <sub>4</sub> 9.0-6.0	Aromatic proton	Har = H <sub>4</sub> H/100
H <sub>5</sub> 7.2-6.0	Mono-aromatic proton	Hm = H <sub>5</sub> H/100
H <sub>6</sub> 7.2 – 9.0	Di-aromatics and some tri-tetra-aromatics	H <sub>D-T</sub> = H <sub>6</sub> H/100
H <sub>7</sub> 3.5 – 4.5	Hydrogen atoms in CH <sub>2</sub> carbons (CH <sub>2</sub> bridges between aromatic rings)	R <sub>CH<sub>2</sub></sub> = H <sub>7</sub> H/100
	Aromaticity factor	Fa = Har / (H $\alpha$ + H $\beta$ + H $\gamma$ + Har)
	Average length of paraffinic chain	n = (H $\alpha$ + H $\beta$ + H $\gamma$ ) / H $\alpha$
	Substituted rings	r = [0.25(4.12 + H $\gamma$ / H $\beta$ ) - 1] [(n-1) / 2]

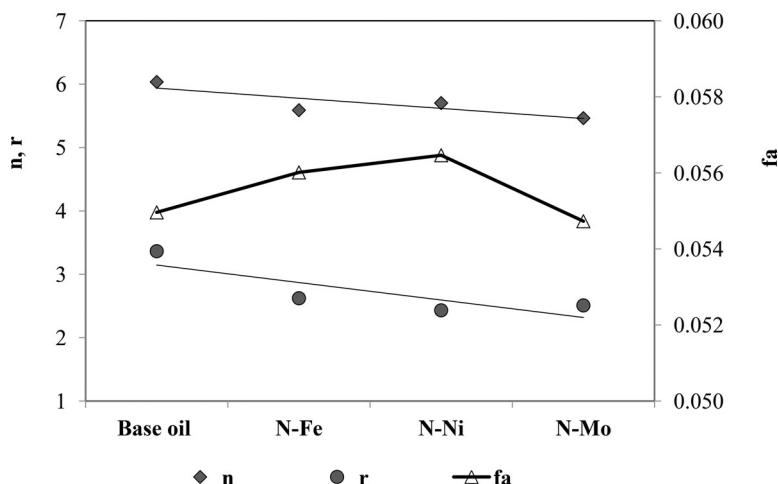
**Table 3.** Variation coefficient of molecular parameters obtained by NMR.

Average molecular parameter	Min.	Max.	Variation coefficient
H $\alpha$	15.64	18.46	0.86
H $\beta$	50.26	52.08	0.14
H $\gamma$	25.15	28.50	0.89
Har	5.23	5.65	0.09
Hm	1.70	2.10	0.11
H <sub>D-T</sub>	3.39	3.71	0.02
R <sub>CH<sub>2</sub></sub>	0.49	0.91	0.51

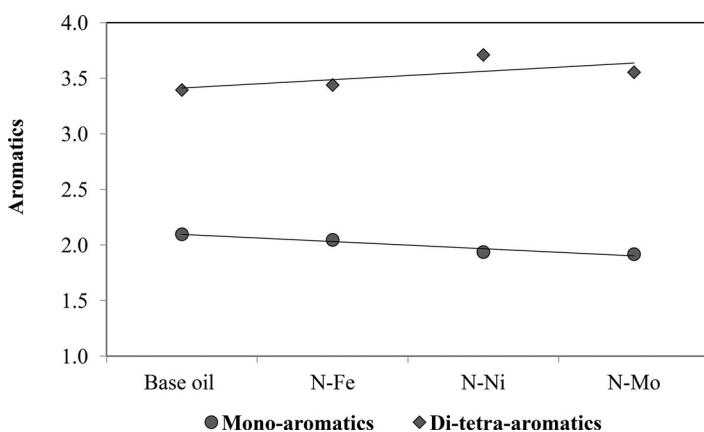
**Figure 7.**  $^1\text{H}$  NMR spectrum for base oil and upgraded oil at 300 °C and 62 h.

The average molecular parameters presented a grade of dispersion. Also, there was a greater dispersion in aliphatic hydrogens indicating that during the aquathermolysis, the alkyl chains had greater reactivity. In addition, Figure 7 shows the  $^1\text{H}$  NMR spectrum for the base crude oil and for the upgraded oil at 300 °C and 62 h.

Regarding the catalysts sensibility, the molecular parameters obtained by NMR indicated that the aromaticity factor (fa) of the upgraded oils increased in the order of Mo > Fe > Ni (Figure 8). Figure 9 shows that oil obtained by nickel naphthenate had a higher content of polyaromatic species. Instead, oil obtained by iron naphthenate tended to form a higher



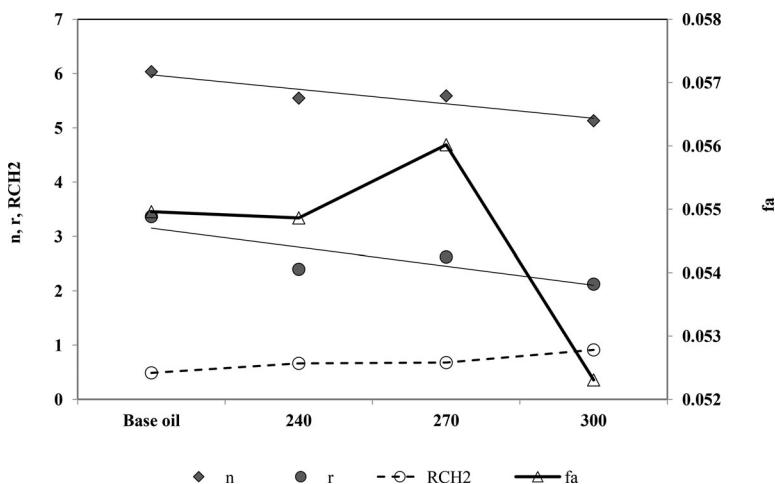
**Figure 8.** Average molecular parameters for the original oil and the upgraded oils obtained for each catalyst.



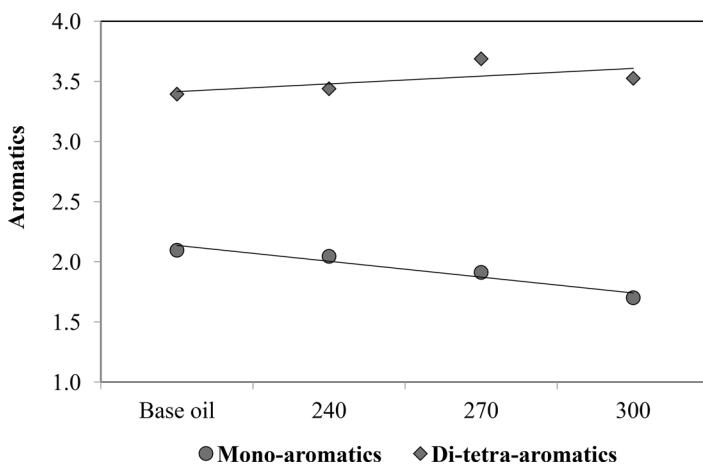
**Figure 9.** Distribution of aromatic hydrogen for the original oil and the upgraded oils obtained for each catalyst.

content of mono-aromatic compounds. Also, it is observed that there was a slight significant change in the length of the alkyl chains. Therefore, the results show that the hydrogenation reactions in the presence of the nickel naphthenate salt obtained less efficiency than the other catalysts, at the established reactivity conditions. These observations suggest that the formation of condensed polycyclic aromatic species is to be expected and under aquathermolysis conditions, the nature of the organic salts greatly influences both the shape and the distribution of the aromatic and aliphatic hydrogen content on the upgraded oils.

The behavior of the molecular parameters indicated a smaller difference in the length of the alkyl chains in the range of 240–270 °C. However, this parameter had lower values at 300 °C indicating that at higher

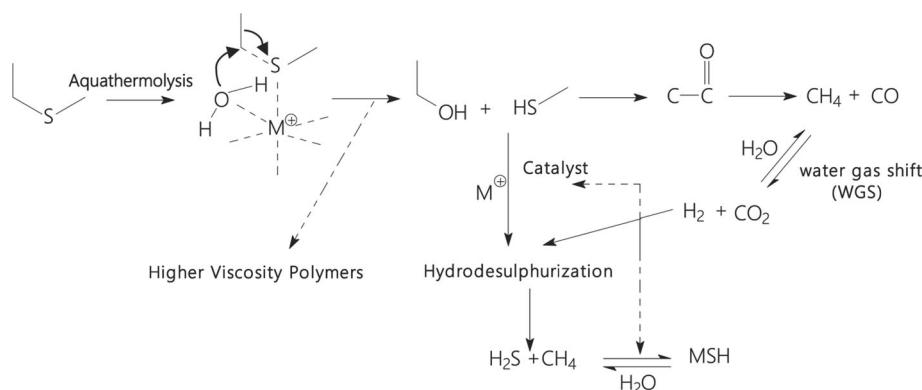


**Figure 10.** Average molecular parameters for the original oil and the upgraded oils obtained for each temperature.



**Figure 11.** Distribution of aromatic hydrogen for the original oil and the upgraded oils obtained for each temperature.

temperatures, the reactions of alkyl chains cleavage (Figure 10). Nevertheless, the aromaticity factor (fa) increased between 240 and 270 °C, and then decreased significantly. This trend occurs by condensation reactions as indicated the increase of bridge carbons ( $RCH_2$ ) between aromatic rings, the decrease of mono-aromatic species, and the formation of polycyclic aromatic species (Figure 11). On the other hand, the formation of condensed rings at 300 °C decreased slightly by the formation of lighter fractions. The increase of both the aromaticity factor and the temperature was mainly associated to the change in the relationship between aromatic and alkyl proportions in the new species. Additionally, a slight decrease in the content of rings substituted (r) by alkyl chains was observed. This is because the cleavage of alkyl chains takes place without affecting significantly the



**Figure 12.** Reaction mechanism in catalytic aquathermolysis. (Núñez-Méndez 2021).

aromatic structure of the new species (Figure 12) (Hyne 1986; Li et al. 2019<sup>i</sup>; Aliev et al. 2021).

The formation of polyaromatic structures may be attributed to increased formation of free radicals to which the temperature was increased. On the other hand, the decrease in the number of substituted rings and the increase in the aromaticity factor of hydrogen are consequences of the dealkylation reactions and the carbon content reduction in the alkyl chains of the produced molecular species. Therefore, during the aquathermolysis process, an increase in the number of aromatic rings may be associated with the aggregation of resin species and asphalt, as determined by other authors (Yi et al. 2009; Vakhin et al. 2018).

#### 4. Conclusions

Iron naphthenate generated better results on the Colombian heavy crude oil upgrading than the other catalysts. Viscosity reduction and API° gravity increase are associated with changes in the chemical structure, due to dealkylation and hydrogenation reactions and the variation of the aromaticity factor.

The molecular parameters obtained by NMR and the variation of the aromatic species show that each catalyst has different selectivity. Therefore, it is possible to indicate that the chemical composition of crude oil and the catalyst type have a direct influence on its physicochemical properties.

Temperature was found to be the most significant effect on aquathermolysis reactions. The levels involved in the experimental design showed that the conversion and change of the upgraded oil properties depend on temperature variations at which the reaction occurs. While at 270 °C, the 300 °C + fraction conversion was 1.4%, at 300 °C+, 8.6% was reported.

As temperature increases, the compositional variation in the poly-aromatic structures formation was produced thanks to increased formation of

free radicals. Moreover, the decrease in the number of substituted rings and the increase in the aromaticity of hydrogen were consequences of dealkylation reactions as well as a decrease in carbon content in alkyl chains of new molecular species. Therefore, during the aquathermolysis process, an increase in the number of aromatic rings is identified, which may be associated to the aggregation of species of resins and asphaltenes.

The inclusion of a catalyst in aquathermolysis reactions consolidates the generation of an additional recovery mechanism during steam injection processes. The production of lighter hydrocarbons and permanent changes in viscosity, density, and composition could generate an additional increase of production.

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## Nomenclature

API	American Petroleum Institute
SAGD	Steam-Assisted Gravity Drainage
NMR	Nuclear Magnetic Resonance
SARA	Saturate, Aromatic, Resin, and Asphaltene
TGA	Thermogravimetric Analysis
$^1\text{H}$ NMR	Proton nuclear magnetic resonance
ASTM	American Society for Testing and Materials
ppm	parts per million
rpm	revolutions per minute
$\text{H}_\gamma$	$\text{H}_\gamma$ to aromatic ring/terminal $\text{CH}_3$
$\text{H}_\beta$	$\text{H}_\beta$ to aromatic/in paraffinic CH and $\text{CH}_2$
$\text{H}_\alpha$	$\text{H}_\alpha$ to aromatic ring
Har	Aromatic proton
Hm	Mono-aromatic proton
$\text{H}_{\text{D-T}}$	Di-aromatics and some tri-tetra-aromatics
$\text{R}_{\text{CH}_2}$	Hydrogen atoms in $\text{CH}_2$ carbons ( $\text{CH}_2$ bridges between aromatic rings)
Fa	Aromaticity factor
n	Average length of paraffinic chain
r	Substituted rings