Research Article

Chemical-Enhanced Oil Recovery Using *N,N*-Dimethylcyclohexylamine on a Colombian Crude Oil

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Oil recovery was improved using the tertiary amine, *N,N*-dimethylcyclohexylamine (DMCHA), a powerful and promissory switchable solvent, in simulated conditions similar to the Colombian crude oil reserves. Firstly, the Colombian crude oil (CCO) and the soil were characterized completely. Afterwards, an aged crude-rock system was obtained to use DMCHA that gave an oil crude extraction of 80% in our preliminary studies. Thus, a sand-pack column (soil-kaolin, 95 : 5) frame saturated with CCO was used to simulate the conditions, in which DMCHA could recover the oil. After the secondary recovery process, 15.4–33.8% of original oil in place (OOIP) is obtained. Following the injection of DMCHA, the recovery yield rose to 87–97% of OOIP. Finally, 54–60% of DMCHA was recovered and reinjected without affecting its potential in the simulated conditions.

1. Introduction

Due to the reduction of combustible fossil stockpiles, alternative energy solutions are emerging each day; however, crude oil still represents the most used energy source. In 2017, oil demand grew on average by 1.8%, or 1.7 million barrels per day (bpd), becoming the third consecutive year where crude oil demand grew above the 10 year average of 1.2% [1]. Meanwhile, it is projected that 26% of the energy will be derived from petroleum until 2040 [2]. Therefore, petroleum extraction is a practice that is increasing as well as its different processing stages [3]. When a reservoir is found, after the drilling process, production stage begins and primary recovery starts when crude oil rises to the surface naturally due to current reservoir pressure. As reservoir pressure drops, secondary recovery is required by injection of external fluids that normally could be present in the reservoir, such as water and/or gas, mainly to boost the pressure to displace the remaining oil. When no more crude oil is produced in secondary recovery, injection of special fluids such as chemicals and miscible gases and/or the injection of thermal energy are necessary, and this process is called tertiary recovery [4].

By the time the reservoir pressure is depleted, only a 5–15% of original oil in place (OOIP) is recovered [5]; therefore, several strategies have been implemented to access the remaining reserves of approximately 80%. This allows economic equilibrium between investment and commercialization. Therefore, in the secondary phase around 20–30% of oil in place (OIP) is recovered. This artificial drive may look attractive economically, but microscopic capillary forces and sweep efficiency are the main drawbacks of this method. In order to increase sweep efficiency, polymer fluids [6] are used, and surfactant fluids [7] are used to reduce capillary forces. Using these two methods, recovery factor (RF) increases up to 40% of OIP. From these first reports, several polymers [8] and surfactants, including several structural moieties to get higher RF values, have been designed for EOR (enhanced oil recovery) [9].

Despite polymers, alkali, surfactants, or a mixture, SP and ASP methods are currently used [10]; other proposals have been recently evaluated to increase RF. Therefore, dispersion of nanoparticles [11], ionic liquids [12], bio-surfactants [13], microorganisms [14], and deep eutectic solvents [15], among other alternatives, has been used to

increase production in this industry. Due to the technical [16] and environmental [17] drawbacks of these methods, there is constant interest to have new alternatives to increase the RF. One strategy includes the usage of amines because of its capacity to act as interfacial tension reducer agents (ITRA). Thus, these kinds of molecules could be used as precursor for *in situ* surfactant formation and then to act as ITRA [18].

On the other hand, oil-solid separation is a process well known from domestic cleaning to petroleum extraction; therefore, the usage of common solvents like toluene [19], naphtha [20], and xylenes [21], among others, promotes high efficiency in solvent extraction and oil recovery. Nevertheless, these common solvents are normally too volatile and highly toxic; then, Jessop and coworkers proposed a special amine, *N,N*-dimethylcyclohexylamine (DMCHA), as a powerful solvent to extract crude from Canadian oil sands as unconventional ores [22]. Although the capacity of amines to extract crude from porous rock has been proved [23], new amines have been synthesised to be employed like a solvent in oil-solid ore separation; however, DMCHA resulted to be more effective in the extraction process (68%) than synthetic amine (63%) [24]. In addition, due to its switchable polarity, recyclability of DMCHA opens the window towards the synthesis of new kinds of surfactants with tertiary amine moieties. Therefore, the possibility to recover the chemicals after the injection process without changes of crude oil properties and water quality is really attractive.

Colombia is the third largest oil producer in South America (EIA) [25], and the technology of enhanced oil recovery (tertiary recovery) is just in the developing stage. This is illustrated by the fact that only 23 of 280 fields were found in natural depletion. Recovery methods such as water alternated gas (WAG) have been applied, and RF estimated until 2010 was between 0.1 and 65% depending on the injection method [26]. Therefore, we wanted to expose the potential of amines like DMCHA [27] for extraction and recovery of the Colombian crude oil.

2. Materials and Methods

2.1. Materials. The light crude oil sample comes from a Colombian oil reservoir. The characterization of the oil sample is shown in Table 1. Synthetic brine was prepared to 1.5% wt. of NaCl. Carbon dioxide was acquired with 99% purity from a local company. Carbonated water was prepared by bubbling CO₂ via a gas dispersion tube into deionized water at atmospheric pressure. *N,N*-Dimethylcyclohexylamine (DMCHA) was used as Merck reagent degree with 99% purity. The sand used in the sand-pack column was collected from a natural soil.

2.2. Sand-Pack Construction

2.2.1. Sand Washing. Sand was washed according to the modified Mattigod protocol [28]. Briefly, the sand sample was milled and sieved through an 80/100 mesh sieve. Then, the resulting mineral was washed with deionized water,

TABLE 1: Properties of the light oil used before and after injection of DMCHA in sand-pack column.

Physical properties	Before	After
Water content (%)	0.027	0.011
Viscosity (cSt to 30°C)	10.11	9.50
API (@60°F)	29.8	32.1
Relative density	0.8772	0.8671

mixing 67 g of mineral by 1 L of water. This mixture was dispersed using magnetic stirring for 45 min. The pH of this dispersed mixture was adjusted to 9.5 with a NaOH solution 0.1 M. After 15 min of stirring, the dispersed mixture was centrifuged at 3000 rpm for 15 min. The mixture was resuspended in water, and the pH was adjusted to 3 using HCl 0.1 N. Then, the mixture was centrifuged again and washed until pH=5.5. Mineral was dried and preserved under N₂ atmosphere and characterized by SEM-EDS and XRD.

2.2.2. XRD Mineral Characterization. XRD mineral characterization was performed in a Bruker powder diffractometer D8 model with Da Vinci geometry in the range of 3.5° to 70° (2 θ). The sample was milled, homogenized, and brought to a particle size less than 38 μ m. The qualitative analysis of the crystalline phases in the sample was made by comparing the observed profile with the diffraction profiles reported in the database of the ICDD (International Center for Diffraction Data).

2.2.3. SEM and EDS. SEM and EDS were performed with a Tescan model MIRA 3 FEG-SEM and A65cSED, respectively. The samples had to be coated with gold before analysis. SEM images were obtained between 26x to 1000x (scale from 2 mm to 50 microns) up to an electron acceleration voltage of up to 10 kV and an intensive beam of 3.

2.2.4. The Potential of Zero Charge (PZC). PZC was calculated by the salt addition method. Briefly, KCl solution (0.01 M) was added into 11 conical flasks where the pH was adjusted from 2 to 12. A constant weight of mineral (0.2 g) was added to each flask, and then after 24 h, the pH change was measured and PZC was identified in a pH- Δ pH plot when Δ pH = 0 [29] (Figure 1).

2.2.5. Sand-Pack Column Construction. Sand-pack column was created using tubes and caps of PVC material, with Hastelloy fittings. Measures of the sand pack were defined according to protocols established in the literature [30]. Within the tube, a mixture of washed sand (95%) and kaolin (5%) was slowly added and gently compacted in the column looking for a sufficiently tight porous medium with low permeability (Figure 2(a)). After packing the sand tightly, a top sieve and cap were fixed. The caps on both ends of the column were provided with holes for insertion of inlet and outlet tubes. Valves and two manometers were placed, one at the entrance of the tube and one to the outlet of the tube (Figure 2).

FIGURE 1: Mineral PZC plot.

2.3. Extraction of Crude Oil from Oil Moistened Rock. This stage was performed to evaluate the efficiency of the DMCHA like switchable solvent [22].

2.3.1. Oil Moistened Rock. 5 g of mineral was mixed with 2 g of crude oil in a test tube to simulate rock moistened with crude oil. This mixture was maintained in an oven for one week to get older.

2.3.2. Crude Oil Extraction with DMCHA. 10 mL of the switchable hydrophilic solvent DMCHA was added to the oil moistened mineral and stirred for 10 min to 125 rpm. The mix (oil-sand-DMCHA) was divided in two centrifuge tubes, washing each tube with 2.5 mL of DMCHA. These tubes were centrifuged for 30 min at 1500 rpm. Supernatant was decanted and solid was left in the tube.

2.3.3. Solids Treatment. 2.5 mL DMCHA was added to each tube and centrifuged for 30 min to get supernatant separation; this step was performed twice. Next, the solid was washed inside each tube with 7.5 mL of carbonated water (prepared by CO₂ bubbling by 1 h). Solid dispersion was centrifuged, supernatant was separated, and solids were dried.

2.3.4. Organic Supernatant Treatment. Organic supernatant (crude oil and DMCHA collected, approx. 22.5 mL) was mixed with 45 mL of water having a two-phase mixture. Then, it was bubbled with CO₂ for 90 min at atmospheric pressure. Amine switched from hydrophobic to hydrophilic, affording crude oil separation from aqueous phase, now composed of water and DMCHA carbamate salt. This methodology was repeated for different amine : water ratios.

2.3.5. Solvent Recovery. Aqueous fraction composed of carbamate (DMCHA-HCO₃⁻) and water was heated up to 70°C and bubbled continuously for 1 h. It was performed in a round bottom flask fitted with a condenser and air injection system. The solution was converted in a two-phase mixture (DMCHA-water) and was added to a separator funnel. Amine was collected for later reuse, and DMCHA recovery rate (%) was calculated as follows:

$$\% \text{recovered DMCHA} = \frac{\text{recovered DMCHA} \times 100}{\text{total DMCHA}}. \quad (1)$$

2.4. Sand-Pack Flooding Test

2.4.1. Water Saturation. Well simulation was carried out with the construction of sand-pack column (Figure 2). Afterwards, synthetic brine was injected with a continuous flow of 2 mL/min in a vertical ascending manner to ensure that water filled all pores until saturated. Pore volume (PV, cm³), defined as the empty volume of the model, was calculated by measuring the volume of brine required to saturate the column [31].

2.4.2. Crude Oil Injection. Crude oil was injected into the sand-pack column at 2 mL/min until there was no more water coming from the effluent. The volume of oil retained in the column was the original oil in place (OOIP) and was calculated volumetrically. The sand pack was left in equilibrium at room temperature for two days.

2.4.3. Water Flooding. Sand-pack column was flooded with water to simulate the secondary recovery process to remove crude oil excess (S_{orw}). The crude oil was collected until no more oil was observed in the outlet and was determined volumetrically. After this procedure, residual saturation oil (S_{or}) was calculated as follows:

$$S_{or} = \frac{OOIP - S_{orw}}{OOIP} \times 100. \quad (2)$$

2.4.4. DMCHA Flooding. DMCHA was injected (approximately 3 PV) in the sand-pack column as the tertiary recovery process and to obtain amine oil recovery (AmOR, %). Effluent was collected and measured volumetrically to determine extract mixture (crude oil-DMCHA) volume. Then, this extract was mixed with carbonated water (extract-carbonated water, 1:1 ratio) to separate crude oil of the new aqueous phase (water-DMCHA carbamate). The new mixture was stored for the amine recuperation as described in Section 2.3.5. Oil recovery was calculated as follows:

$$\% \text{AmOR} = \frac{\text{Oil without DMCHA} \times 100}{OOIP - S_{orw}}. \quad (3)$$

The ¹H-NMR protocol [32] was used to determine the amount of amine in the final crude oil sample (around 10%), and this amount was subtracted to the oil after cEOR process. Therefore, crude oil was characterized using ¹H-NMR spectra, recorded on Bruker AM-400 or AC-300 spectrometers. Chemical shifts are reported in ppm (δ) relative to the solvent peak (CHCl₃ in CDCl₃ at 7.24 ppm for protons).

3. Results and Discussion

3.1. Mineral Pretreatment. Initially, it was decided to evaluate the chemical composition of the mineral as it was taken

FIGURE 2: (a) Real sand-pack column with fittings valves and manometers; (b) map of the sand-pack column.

from a natural source, and it could be contaminated with other materials (organic and inorganic), potentially voiding test results. Then, natural soil was washed to eliminate interferences, for example, coating of oxides and biodegradable organic matter. Mineral composition was determined by XRD, and qualitative nonclay crystalline phases were identified, analysed in diffraction profile (Figure 3).

According to the spectrum and database, compositional analysis of the mineral does not change after washing process. Therefore, the crystalline phases of both minerals were qualitatively identified, such as calcic albite, sodic anortite, muscovite 2-ITM1, anfibol, orthoclase, quartz, and hematite, among others. To corroborate XRD results, the mineral was studied by SEM-EDS (Figure 4) looking for potential coatings and morphology affectation as environment exposition could interfere in flooding assays.

Elemental analysis (EDS) showed soft variations after washing; however, most important is the identification of iron after pretreatment, passing from 0 to 5% wt. Despite homogenization, several mineral samples from various locations were analysed; this metal was not observed before the washing process. Knowing that Fe minerals, combined with oxygen, can degrade some chemicals like polymers that are currently injected in reservoirs [33], they need to be identified because their potential effects on amines are unknown. On the other hand, oxygen and silicon were softly diminished, perhaps because the washing process reduces the quantity of minerals based on silicon because several of them are present in solid material and can be removed as fines.

3.2. Evaluation of DMCHA in Crude Oil Extraction Process. The capacity of DMCHA to extract crude oil for application in cEOR was optimized evaluating some parameters in the extraction process. After sand was moistened with crude oil, different quantities of amine and different water (brine):

FIGURE 3: XRD profile comparison between washed (WM) and nonwashed mineral (NWM).

amine ratios were used in the extraction process. The extracted crude oil (%), recovered mineral (%), and recovered amine (%) were calculated, comparing their initial and final mass (Table 2).

The mass of the mineral for each test was constant while the adsorbed crude oil was the variable. In the entries 1 and 2, 45 mL of amine was used for the oil crude extraction, and almost three times of water were employed volumetrically (1:2.7, ratio). In spite of the high quantity of carbonated water used during the extraction process and the minimal amount of crude oil used for these cases, extracted crude oil was more than 100% due to amine residues that were detected by ^1H NMR. Thus, 143% of yield for the extract (entry 2) corresponds to crude oil and amine residues combined.

FIGURE 4: SEM micrographs for (a) NWM (26x), (b) NWM (200x), (c) WM (26x), and (d) WM (200x).

TABLE 2: Results obtained from crude oil extraction process using DMCHA as solvent.

Entry	Initial quantities				Ratio DMCHA : W	Obtained results			
	Mineral (g)	O ^b (g)	Amine (mL)	W ^b (mL)		Rec. ^b mineral (%)	Extract (%)	%CV	Rec. ^b amine (%)
1	12	0.75	45	120	1 : 2.7	90.4	112.4	3.7	28.9
						89.8	106.7		27.8
2	12	1.5	45	120	1 : 2.7	89.3	143.5	22.9	57.8
						89.0	103.5		35.6
3	12	1.0	22.5	45	1 : 2	90.7	73.6	17.6	53.3
						86.7	74.0		53.3
						91.7	98.9		48.9
4	12	1.5	22.5	45	1 : 2	88.3	95.7	4.0	53.3
						88.8	88.3		51.1
						89.5	92.5		53.3
5	12	2.5	22.5	45	1 : 2	92.2	69.2	9.7	53.3
						91.8	83.8		55.6
						88.0	74.8		53.3
6	12	2.5	22.5	22.5	1 : 1	91.3	90.2	3.4	62.2
						90.8	84.4		60.0
						91.7	88.7		57.8
7 ^a	12	2.5	22.5	22.5 ^a	1 : 1	87.3	87.7	1.8	62.2
						85.4	90.7		57.8
						92.0	88.2		62.2

^aFor this entry, brine (NaCl, 1500 mg/L) was used instead of water for evaluating the total dissolved solid effects on the extraction process. ^bO: crude oil; Rec.: recovered; W: water.

Additional crude oil was added to the mineral; thus, the amine and water volume were reduced. This led to improved results on the extraction process (entries 3–7) because DMCHA was almost completely eliminated through carbonated water interaction.

The extraction yields were similar for all entries, except for the 7th entry. For the 7th entry, less water and amine were used, having the best behaviour during the extraction process and the most amine recovered (average 60%). Also, the 7th entry was carried out using brine instead of distilled water to simulate the usage of produced water with a total dissolved solids (TDS) value of 1500 ppm. This TDS value was taken as a reference from a physical-chemical data of produced water from a Colombian field. At present, the 7th entry had the best conditions (amine:brine ratio) for the extraction protocol (coefficient of variation $CV < 2\%$). This could be explained because CO_2 is more soluble in brine, and its interaction with amine will be favoured [34].

When more amine was detected in final crude oil sample, it was difficult to take out the carbamate-water from the final mixture, and one more hour of bubbling air was needed. The extraction process could be generating some volatile compounds; thus, they may be eliminated from mixtures after bubbling as fine solids could be dissolved reducing the solid content in the dispersion.

In general, DMCHA demonstrated a good interaction with crude oil, having effective hydrophobic solvent activity, removing almost all crude oil adsorbed over the mineral. Furthermore, a liberation step could occur as the interaction between mineral surface and electron rich region of crude oil molecules could be broken (Scheme 1) [23].

After the crude oil mixture was extracted, brine was added, and the CO_2 bubbling took place to change the solvent polarity to separate petroleum from the amine and brine. Chemistry of DMCHA behaviour is well known, and usage of N_2 and air to separate amine from the brine has been demonstrated (Scheme 2).

As the 1:1 amine:brine ratio yielded the best results, this ratio was used in the DMCHA flooding test.

3.3. DMCHA Flooding Test. As the tertiary amine showed a good efficacy to remove crude oil, it was used to demonstrate its potential in the oil-rock separation, reducing interaction between rock and crude oil in a dynamic test. After brine injection, an average PV of 84 mL was measured. Then, 3 PV of amine was injected in three different runs for the EOR simulation process, using the designed sand-pack system (Table 3).

Pereira et al. performed the same simulations with similar dimensions of the sand pack and obtained a PV between 90 and 94 mL [31]. This value is close to our PV value, 79–90 mL, where a more diluted brine of 1500 ppm was used instead of 20000 ppm used in the study by Pereira et al. [31]. The PV should be higher as lower concentration brine was used. Kaolin was added to reduce the sand-pack porosity and thus to have a less PV values. In the same way, another report showed that for this sand-pack column design, PV was around 90 mL [30]. Therefore, it can be inferred that water saturation was performed under controlled

conditions, and the results obtained are comparable with those in the literature.

Waterflooding process is the most common protocol in secondary oil recovery technologies, and low water salinity flooding can yield better results than seawater injection [35]. However, for brine injection, several parameters, such as rock composition, reservoir temperature, and crude oil properties, among others, have to be known and controlled [36]. Due to the known physicochemical composition of Colombian produced water (TDS values), a brine concentration value of 1500 ppm of NaCl was selected. In the secondary recovery process, S_{orw} between 6.5 and 15.3 mL from the OOIP was achieved, obtaining between 15.5 and 33.8% of crude oil. Oil recovery rates after waterflooding can differ and could be associated with several factors. These include crude oil temperature, brine concentration, and mineral parameters. All these parameters were controlled for all runs. If column is not filled with the crude or the mineral packaging is not well done, preferential roads can be formed in the sand pack, and nonviscous liquid like water will not contact with the crude and will not be able to move it. As crude oil saturation was the same in all three entries, it was considered low sweep efficiency as hypothesis for entries 1 and 3 results because of heterogeneity of our mineral.

In regard to the tertiary recovery using DMCHA, it was observed that the injection process generated an increase in the system's pressure, reaching 60 psi in the inlet during injection. It could be due to crude oil viscosity and hydrophilic-lipophilic interaction. Effluent (mixture crude oil-DMCHA) was collected and was of lower viscosity compared with original crude oil. The interaction between amine and the crude oil results appears to be favourable, where amine acts like an efficient solvent for washing our impregnated crude oil mineral. After effluents were collected, they (amine-crude) were bubbled with CO_2 looking for crude oil separation from the nitrogen compound. This process generates an emulsion, but after a few minutes, it disappeared, and recovery crude oil was calculated as % AmOR (amine oil recovery) for the 3 entries with higher values up to 87%.

Oil-solid separation with switchable solvents can occur through dissolution or via interfacial tension (IFT) reduction, reducing the capillary number. In this last case, amine is used as carbonated salt in water solution. In this study, DMCHA was used as a solvent, not as a amine-water mixture, and the IFT was not taken into account. However, it has been demonstrated that amines such as triethyl amine (Et_3N) can be mixed with water until 11% wt., reducing the IFT between water and crude oil from $33.7 \text{ m}\cdot\text{Nm}^{-1}$ to $13.2 \text{ m}\cdot\text{Nm}^{-1}$ [37], demonstrating potential dual activity as solvent and as surfactant.

The oil recovery factor depends on several conditions, and crude oil has been obtained between 5 and 80% of yield with an estimated average value of 37% [26]. In this preliminary research, in the usage of tertiary amines as switchable solvent (DMCHA) for tertiary recovery simulation on Colombian crude oil, amine allowed us to obtain an average crude oil extraction of 87%.

The crude oil was left to room temperature, and the effect of this parameter on amine behaviour was not evaluated as

SCHEME 1: Mechanism proposal for crude oil-DMCHA interaction based on preliminary studies and the results obtained.

SCHEME 2: DMCHA extraction activity and switchability process.

TABLE 3: Summary of the results obtained in the sand-pack experiments using DMCHA.

Subject	Entry		
	1	2	3
PV (mL)	90	79	82
OOIP (mL)	42	45.2	44.4
S _{orw} (mL)	6.5	15.3	9.9
S _{or} (%)	84.5	66.2	77.7
(OOIP-S _{orw}): oil in production (mL)	35.5	29.9	34.5
Oil without DMCHA (mL)	34.59	26.1	31.5
%AmOR	97.4	87.3	91.3
Recovered DMCHA (%)	58	60	54

the same as thermal stability related to the field's temperature at Colombia. As the crude oil was obtained from the Llanos basin in Colombia, where field temperatures are lower than 80°C (maximum temperature registered for a Colombian field) [38] and the boiling point of DMCHA has been determined (162°C), thermal stability should not be a drawback. However more studies of heavy crude oil cEOR at different temperatures are being investigated.

Regarding the extracted petroleum physical properties, they were slightly affected after the injection process (Table 1).

To understand the interaction between mineral, crude oil, and DMCHA, the PZC of the model rock was used (Figure 1). Therefore, PZC was observed, pH = 7, meaning that the crude oil will not be strongly adsorbed on mineral

surface; further interaction of amine-rock will also not be favourable. At the same time, when amine was injected, pH increased and PZC was negative, favouring rejection of electron rich region in crude oil molecules and mineral. On the other hand, amine and crude oil will interact favourably.

At the end of the flooding process, crude oil was analysed by NMR to identify any modification of the crude oil composition or chemical changes in crude oil molecules. In addition, a test was carried out to determine if amine could remain in the final effluent after CO₂ bubbling. For this experiment, a methodology proposed by Molina and co-workers [32] was applied, considering different kinds of protons that were related to the original crude oil and each effluent after the recovery process (Table 4).

Variation in relative percentage of protons in the crude oil characterization was determined and compared between each spectrum for each effluent. In general, minor variations between recovered crude oils were observed. The crude oil contained mostly protons which were found in intervals related with H6, H7, and H8 type (Table 5). According to the statistics, integration comparison between original crude oil and effluents of the research gave noteworthy information about reduction of molecules associated to the protons H7 and H8.

Therefore, all effluents had a reduction in CH₃ paraffinic hydrogens γ and β to aromatic systems and alkyl termination. That reduction of hydrogen was also affected by DMCHA content that was identified for all spectra effluents.

TABLE 4: Kind of hydrogen and NMR intervals for crude oil characterization.

δ (ppm)	Name	Chemical group	Kind of hydrogen
9.0–12.0	H1	$H_{Ald} + H_{Carb}$	Aldehydic and carboxylic hydrogens.
7.2–9.0	H2	H_{Ar}^{pa}	Aromatic hydrogens joined to di or polyaromatic compounds.
6.0–7.2	H3	H_{Ar}^{ma}	Aromatic hydrogens joined to monoaromatic compounds.
4.5–6.0	H4	H_{Ole}	Olefinic hydrogens.
2.0–4.5	H5	$H_{Par}^{\alpha-Ar} + H_{Nap}^{\alpha-Ar} + H_{OH} + H_{SH}$	CH, CH ₂ , and CH ₃ , paraffinic and naphthenic hydrogens, joined to aromatics system in α position. Other groups in this region could be -OH and -SH.
1.5–2.0	H6	$H_{Nap-CH_2}^{\beta-Ar}$	CH ₂ naphthenic hydrogens, β to aromatic systems.
1.0–1.5	H7	$H_{Par-CH_3}^{\beta-Ar}$	CH ₃ paraffinic hydrogens β to aromatic systems and alky termination.
0.1–1.0	H8	$H_{Par-CH_3}^{\gamma-Ar}$	CH ₃ paraffinic hydrogens γ to aromatic systems.

TABLE 5: Relative percent of protons H1–H8 (SD ± 0.1 –0.2%).

Run	Kind of protons, intervals of integration							
	H8 0.1–1.0	H7 1.0–1.5	H6 1.5–2.0	H5 2.0–4.5	H4 4.5–6.0	H3 6.0–7.2	H2 7.2–9.0	H1 9.0–12.0
0*	27.9094	51.0579	10.2186	7.3183	0.0772	1.4271	1.8763	0.1152
1	23.9674	50.9290	9.5293	14.2041	0.1314	0.4722	0.5869	0.1797
2	21.5855	49.0126	12.9885	13.1245	0.0766	1.2192	1.8494	0.1438
3	23.1838	48.5673	11.1138	12.9427	0.1870	1.6852	2.2135	0.1067

*Original crude oil.

FIGURE 5: Expansion of NMR spectra of effluent 3 (blue) and original crude oil (black).

After defining the area between 0.1 and 1 ppm for H8, the integration region was taken for the amine protons (1.5–1.9 ppm) giving to an integration that corresponded to an

average of 9.7% for all effluents as relative amine composition [27]. This amine value was previously reported in the bitumen recovery process with DMCHA (Figure 5) [22].

This analysis showed the potential of NMR as an analytical tool in the study of bench flooding test.

Analysis of the process showed that DMCHA was useful to move trapped Colombian crude oil and can be recycled and reused in the EOR protocols. This compound could be a model molecule to design new surfactants and polymers with tertiary amine groups.

4. Conclusion

A switchable solvent, DMCHA, was used as a solvent in the oil-solid separation and oil recovery process. Oil recovery process was simulated through a sand-pack column and a mineral with kaolin up to 5% wt. as a solid phase. Amine showed excellent properties as a solvent and extracted oil reached 90% yield with an amine:water ratio of 1:1. This ratio was used in the DMCHA flooding process to obtain 97% crude oil recovery through a dissolution mechanism process. After the cEOR methodology, the crude oil contained 9.7% residual amine; however, the physical properties were only slightly affected. Therefore, amine showed excellent efficiency in this oil-solid separation, and 60% of its original amount was recovered after injection methodology.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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