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Experimental Investigation of Asphaltene Deposition and its Impact on Oil Recovery in Eagle Ford Shale during Miscible and Immiscible Co2huff-N-Puff Gas Injection

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Experimental Investigation of Asphaltene Deposition and Its Impact on Oil Recovery in Eagle Ford Shale during Miscible and Immiscible CO_2 Huff-n-Puff Gas Injection

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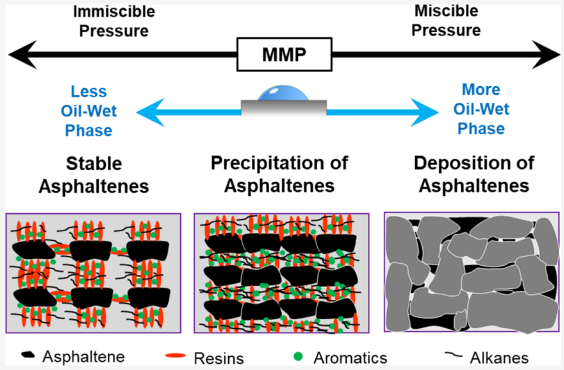
ABSTRACT: One of the challenges in extracting oil from unconventional resources using hydraulic fracturing and horizontal drilling techniques is the low primary recovery rate, which is caused by the ultra-small permeability of these resources. Consequently, it is essential to investigate gas injection methods to produce the trapped oil in shale formations. However, the injection process can cause asphaltene depositions inside the reservoir, leading to plugging of pores and oil recovery (OR) reduction. There has been limited research on using gas injection techniques to improve oil production in tight/unconventional resources, although carbon dioxide (CO_2) and gas-enhanced oil recovery methods have been used in conventional resources. In order to determine whether or not the cyclic (huff-n-puff) CO_2 process improves OR and aggravates asphaltene precipitation, a rigorous experimental investigation was undertaken utilizing filter membranes and Eagle Ford shale cores. After the minimum miscibility pressure was calculated for CO_2, various injection pressures were selected to perform CO_2 huff-n-puff experiments. Investigations were carried out at 70 °C on injection pressure, cycle number, production time, and huff-and-puff mode injection. The results demonstrated that when the pore size structure of the membranes used was smaller and gas injection cycles increased, a higher asphaltene weight percent (wt %) was determined during the static experiments (i.e., employing filter paper membranes). Miscibility improved OR in dynamic testing (i.e., using shale cores), but a more oil-wet system was detected in wettability measurements taken following CO_2 huff-and-puff tests. The plugging impact of asphaltene particles on the pore structure was studied using optical microscopy and scanning electron microscopy imaging. Following the huff-and-puff tests, a mercury porosimeter revealed how severely the pores were plugged, and after the CO_2 tests, the pore size distribution reduced as a consequence of asphaltene deposition. This study examines the significance of CO_2 injection in OR under miscible/immiscible conditions to identify the critical parameters that could impact the effectiveness of CO_2 huff-n-puff operation in unconventional formations.



1. INTRODUCTION

Tight oil and gas have come into the forefront in the United States in recent years as conventional oil reserves have been depleted. Unconventional resources, such as shale reservoirs, are well-known to have ultra-small permeability and very low porosity.[1] Only 4−6% of the trapped oil may be retrieved using multi-stage hydraulic fracturing and horizontal well drilling methods,[2−6] and oil production decreases after months attributable to the ultra-small permeability of such reservoirs.[7−27] The water flooding technique is one applicable method that can increase oil recovery (OR) from conventional reservoirs; however, this technique is not the optimal choice for tight reservoirs due to their poor injectivity, poor sweep potency, and clay swelling issues.[28,29] Gas injection has become a widespread technology that improves oil production in unconventional reservoirs in the United States and could be the best reliable method to unlock the remaining oil percentage.[30] Huff-n-puff gas injection has a more advantageous impact in increasing OR compared to gas flooding techniques, especially in ultra-tight reservoirs with the matrix permeability under 0.001 mD.[31,32] Because kerogen renders the surface of the pores oil-wet, extracting the oil from inside tight reservoirs is restricted by the presence of a high total organic carbon (TOC).[33] In multiphase-flow operations, the mixture of scales and multiphase fluids, such as gas and oil,

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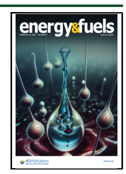

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may result in several challenges, such as the deposition of wax and asphaltene, the creation of hydrates, slugging, and the generation of emulsions.[34] Particles made mostly of organic hydrocarbons that settle in oil and gas reservoirs might cause a number of flow-assurance concerns during oil extraction. Increased resistance to flow caused by these materials might decrease productivity or possibly plug pipelines.[35,36] Asphaltene precipitation and deposition is a difficult aspect of huff-and-puff gas injection into shale formations because it causes pore plugging in the shale and changes the wettability of the formation, which in turn reduces OR. In crude oil, asphaltene is a solid-phase material that dissolves in aromatics like toluene but not in light *n*-alkanes such as *n*-pentane.[37] The stability of asphaltenes in the crude oil decreases due to the interaction between the gas injected into the shale reservoir and the oil.[38] Injecting gas into crude oil causes changes that affect the oil's solubility. Therefore, asphaltene starts to precipitate and flocculate because of the unstable condition of the colloidal suspension in the crude oil.[39,40] Various studies have investigated the effect of a number of factors on asphaltene deposition in conventional reservoir cores on permeability reduction.[41−46] Many investigations have been conducted to highlight the impact of gas injection on asphaltene deposition using nitrogen (N_2) and CO_2.[47−57] The asphaltene instability in shale/unconventional resources during the miscible/immiscible CO_2 huff-n-puff operation is still not fully understood. To do so requires investigating the conditions under which the asphaltene may deposit and precipitate in tight shale resources during the CO_2 huff-n-puff injection process.

Recently, gas huff-n-puff and flooding processes have been studied extensively in shale resources by various approaches, including experimental studies,[58−75] field pilots,[76,77] and simulation work.[78−87] Using N_2 and Eagle Ford shale cores, Yu and Sheng[60] carried out an experimental investigation. They used mineral oil to saturate the cores and to perform the study. The majority of the oil was extracted in the first 2 h of production, during the "puff" phase, proving that N_2 was successful in enhancing OR. There was a weakness in their research, however, since they did not utilize crude oil but mineral oil instead, so avoiding the impact of asphaltene precipitation on the performance of OR. To examine how water saturation influences OR using CO_2 and N_2 huff-n-puff processes, Altawati[61] saturated Eagle Ford outcrops with oil of decane and brine with a percentage of 15%. Altawati[59] discovered that cores that were slightly wet with water had a lower recovery factor (RF) than those that were not saturated with water. OR during the CO_2 huff-and-puff process was studied by Li et al.,[88] who looked at the impact of the MMP. All 15 tests utilized Wolfcamp cores, and the findings revealed an improvement in OR at injection pressures higher than the MMP. Tovar et al.[89] used 11 Wolfcamp shale cores in a number of tests to study the impact of CO_2 and N_2 injections on the performance of OR. MMP, soaking length, and injection-gas mixtures were all variables investigated. Injecting CO_2 instead of N_2 was shown to increase OR because CO_2 can evaporate a wider range of hydrocarbons. OR increased with increasing pressure and soaking duration beyond the miscibility limits for CO_2. Evaluating the OR in tight resources was the focus of experiments done by Bougre and Gamadi,[90] who compared the results of flooding with CO_2, N_2, and a CO_2-N_2 mixture. All of the tests utilized the same oil-soaked core sample from the Eagle Ford shale. Each experiment included washing and resaturating the sample. The CO_2 gas injection produced the best OR, followed by the CO_2-N_2 mixture with a relatively slow breakthrough. The findings of OR from the huff-and-puff injection of CO_2 are controversial since a literature study reveals that the influence of asphaltene attributable to CO_2 miscible injection was not evaluated.

Recent years have seen a few studies looking at the effects of asphaltene precipitation during huff-and-puff gas injection.[91−95] Shen and Sheng[91] researched the impact of CO_2 huff-n-puff injection on the permeability and pore plugging due to asphaltene plugging in Eagle Ford shale. Results demonstrated that after six CO_2 cycles, pore diameters in the 100−800 nm range decreased as well as pore sizes below 100 nm. In addition, a decrement of 47.5 nD of permeability was determined after six cycles of the CO_2 huff-n-puff process compared to the original permeability of 126 nD. Based on their results, pore plugging and asphaltene adsorption in shale cores were significant during the CO_2 huff-n-puff injection process. Mohammad et al.[93] used computer simulations to estimate the formation of asphaltene in low-permeability reservoirs after huff-and-puff CO_2 injection. They aimed to optimize CO_2 injection by including brine in the huff-and-puff CO_2 injection in order to decrease asphaltene issues. Shen and Sheng.[94] conducted a simulation study to provide a better idea of the main factors that might affect asphaltene deposition and precipitation in hydraulically fractured shale reservoirs under the CO_2 huff-n-puff injection process. They found that asphaltene deposition can be different in the rock matrix and fractured network, and thus, the permeability reduction will also differ. Li et al.[95] performed experimental research to highlight the impact of the CO_2 huff-n-puff process on a shale outcrop using four cycles and two oil samples. Their findings revealed that the greatest amount of asphaltene was deposited in the first cycle. Despite the aforementioned studies' emphasis on a variety of variables that influence oil production from shale formations using the gas huff-and-puff technique, there is a lack of comprehensive studies on how to evaluate asphaltene precipitation issues and how to determine its impact on oil production performance in shale resources using the gas huff-n-puff technique (especially below and above MMP). The novelty of the work lies in presenting a comprehensive experimental evaluation of asphaltene instability in tight shale reservoirs during miscible and immiscible conditions using shale cores and filter paper membranes. This study further expands the work of Elturki and Imqam,[96−99] who evaluated the effect of continuous and huff-n-puff immiscible/miscible N_2 injections on the deposition of asphaltenes. The ultimate goal of this research is to highlight the process of asphaltene damage during the miscible and immiscible CO_2 huff-n-puff process, especially in ultra-small-permeability reservoirs (mainly unconventional reservoirs). A better understanding of the factors impacting asphaltene instability during miscible and immiscible CO_2 huff-n-puff injections in tight-shale resources must therefore contribute from the completion of this extensive comparative study.

2. MATERIALS AND METHODOLOGY

There were three primary parts to the laboratory work. First, MMP determination experiments. Second, CO_2 huff-n-puff gas injection tests. Third, asphaltene deposition and pore plugging analysis. Initial investigations determined the MMP for CO_2 huff-n-puff tests. The miscible and immiscible pressures of the huff-n-puff gas injection tests were selected based on the findings of MMP. Figure 1 illustrates the experimental design for the primary tests and analysis presented in this research. Table 1 provides a summary of the study's primary materials and their suppliers.

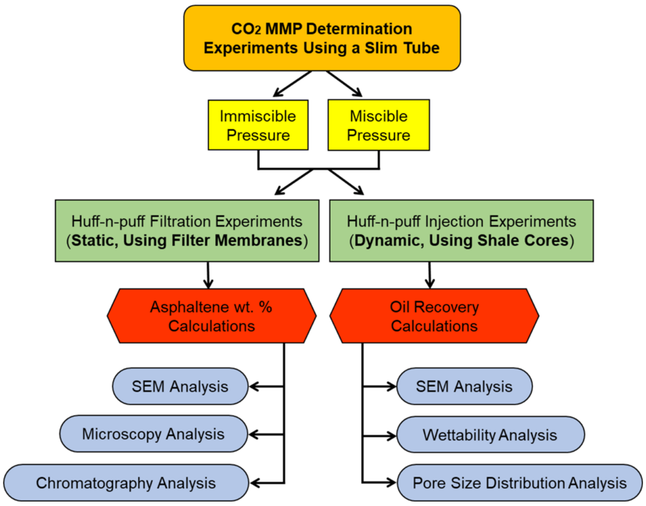

Figure 1. Flowchart of experimental design.

Table 1. List of Chemical/Material Suppliers Used in This Research

material/equipment	type/size	supplier/company
crude oil		Western Missouri Oil Field
solvent of *n*-heptane	chemical formula: C_7H_{16}, purity: ≥99%)	Lab Alley Powering
Whatman filter paper	size: 2.7 μm	OFITE
filter paper membranes	pore size structure: 50, 100, and 450 nm	Foxx Life Sciences
oven	LBB2-27-2	Despatch

2.1. Experimental Materials. Shale outcrops from the Eagle Ford formation were completely saturated with western Missouri oil (viscosity: 19 cP, density: 0.864 g/cc, and American Petroleum Institute (API): 32). The crude oil's composition was analyzed utilizing gas chromatography and mass spectrometry (GC−MS), and the findings are presented in Table 2. For the MMP tests, the western Missouri oil was used to saturate the slim tube, and then the gas (i.e., CO_2) was injected to determine the MMP, more details will be discussed in the following section. For the huff-and-puff filtration studies, 450, 100, and 50 nm filter papers were used. The gas injection for the slim tube and huff-and-puff trials was supplied from CO_2 gas cylinders with a 99.9% purity level. During the huff-and-puff tests, the cores were placed in a specially made vessel (length: 15.25 cm, inside diameter: 5.0 cm, and outside diameter: 7.63 cm). During the MMP tests, the temperature was controlled through an oven. Figure 2 shows core sample dimensions after the saturation process. Their diameter and length, respectively, were 2.5 and 5 cm. The average permeability and porosity were 0.000198 mD and 5.7% (helium porosity), respectively. Figure 3 shows the cores' XRD (X-ray diffraction) results. Finlay, the TOC (total organic carbon) of the Eagle Ford samples was 5.5% (measured by Rock-Eval pyrolysis).

2.2. Slim Tube Experiments. In order to carry out the MMP tests, we used a slim tube that was filled with sand as well as three accumulators. The slim tube has the following dimensions: length, 13.10 m; inside diameter, 0.21 cm; and outside diameter, 0.41 cm. Figure 4 highlights the primary parts of the setup. The first phase was cleaning the slim tube, the second step was saturating the slim tube with the oil, and the third step was injecting gas into the slim tube. Therefore, the first accumulator stored the crude oil that was going to saturate the slim tube, the second accumulator contained the *n*-heptane solvent that was utilized to wash the slim tube, and the third

Table 2. Elemental Composition of Crude Oil

carbon number	mass %
C_1	0.000
C_2	0.000
C_3	0.000
C_4	0.003
C_5	0.063
C_6	0.430
C_7	0.540
C_8	64.48
C_9	0.278
C_{14}	0.309
C_{15}	0.349
C_{16}	0.425
C_{17}	3.490
C_{18}	0.196
C_{19}	1.166
C_{20}	3.596
C_{21}	0.926
C_{22}	2.662
C_{24}	1.973
C_{27}	5.395
C_{28}	7.225
C_{29}	1.322
C_{30+} (including asphaltene)	5.170
total	100.0

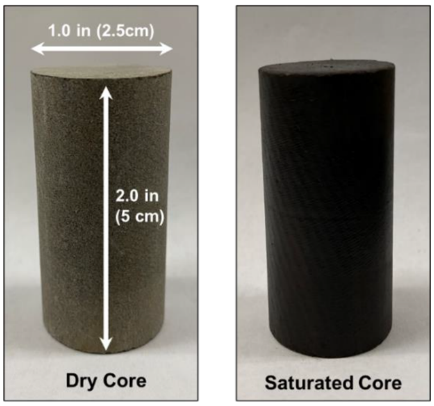

Figure 2. Core taken before and after the saturation phase.

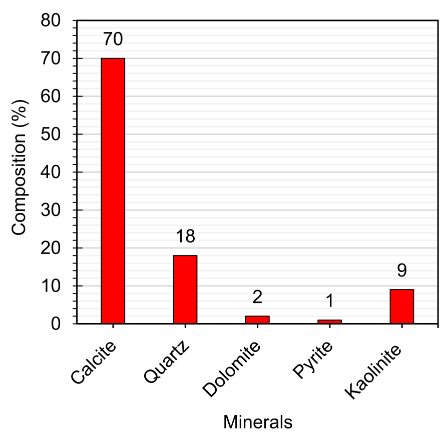

Figure 3. Eagle Ford XRD results.

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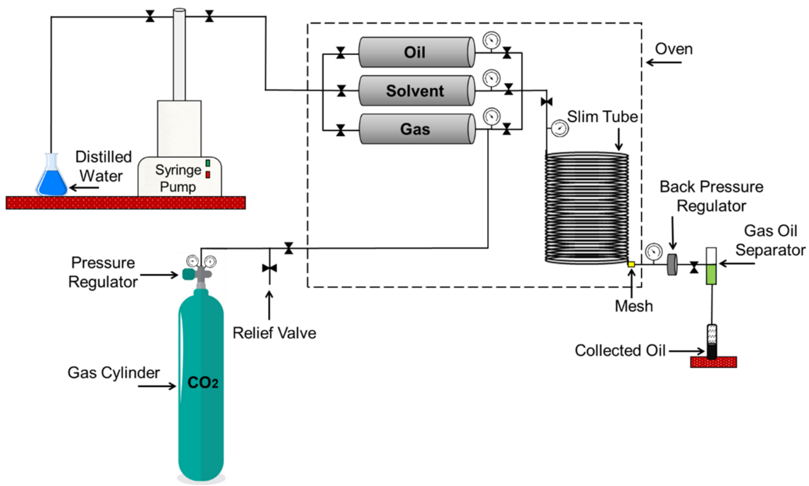

Figure 4. Slim tube apparatus for CO_2 MMP.

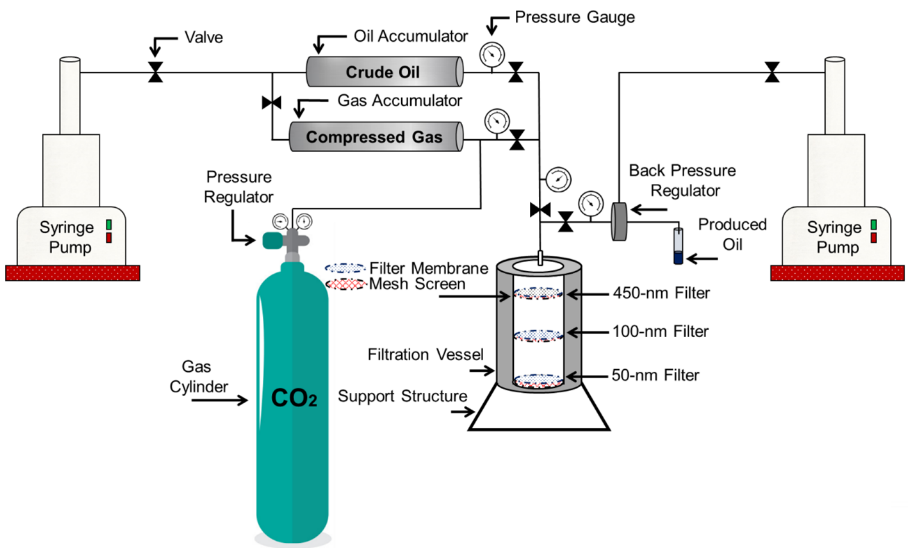

Figure 5. Huff-n-puff filtration test setup.

accumulator contained the gas that was pumped into the slim tube throughout the tests. The methodology for carrying out the tests began with the preparation of the slim tube, which included completely filling it with distilled water. Constant injections of crude oil at a rate of 0.25 mL/min were conducted until the tube was saturated with oil. This can be confirmed at the outflow of the slim tube, which only received oil as a fluid. This insured that the whole slim tube was completely filled with oil. The gas accumulator was loaded with CO_2, and after that, the syringe pump's constant pressure mode was used to inject gas at a pressure that had been previously determined. When the gas breaks through or a 1.2 pore volume of gas was injected, the test was stopped. The MMP may be calculated by generating a graph that compares the pressure of the gas injection to the total amount of oil recovered. After each experiment, the slim tube setup was given a thorough cleaning using the solvent xylene. This was done to guarantee that there was no oil residue left in the slim tube, which may have had an impact on the following experiment.

2.3. Huff-n-Puff Filtration Technique (Static Mode). The primary parts of the huff-n-puff tests using the static mode are shown in Figure 5. Due to the low outlet pressure of the CO_2 cylinder, an accumulator was used to store the CO_2 and pump it directly into the vessel utilizing a syringe pump to accomplish high-pressure levels. Various filter-paper membranes with pore sizes of 50, 100, and 450 nm were used to represent the structure of shale reservoirs and to examine the influence of variable sizes. Utilizing a filtration vessel with three mesh screens as a means of protecting the filter papers and avoiding the possibility of the sheets breaking at higher pressures. The mesh screens were built with porous structures to allow the oil to flow across them freely. One transducer was used to record and monitor the pressure during the experiments. The following steps were taken to perform the static mode experiments:

- The vessel was loaded with 50, 100, and 450 nm filter membranes and then was closed and attached to the gas source/cylinder in order to fill the accumulator of gas. Next, the pressure regulator was used to secure the gas cylinder.
- The gas cylinder was opened using the pressure regulator at the desired pressure after 30 mL of crude oil was injected into it by utilizing a syringe pump attached to the accumulator of oil.
- During the "huff" stage, the gas was able to mix with the crude oil for a set period of time (in this case, 6 h).
- The temperature within the vessel was adjusted to 70 °C by operating a heating jack.
- When the soaking time was over, the pressure inside the vessel was released. This is known as the "puff" phase.
- After taking the oil from the effluent and opening the vessel, a sample of the crude oil that had been filtered through the membranes was taken for asphaltene examination. Next, the oil that had been filtered through the paper membranes was carefully returned for yet another new cycle.

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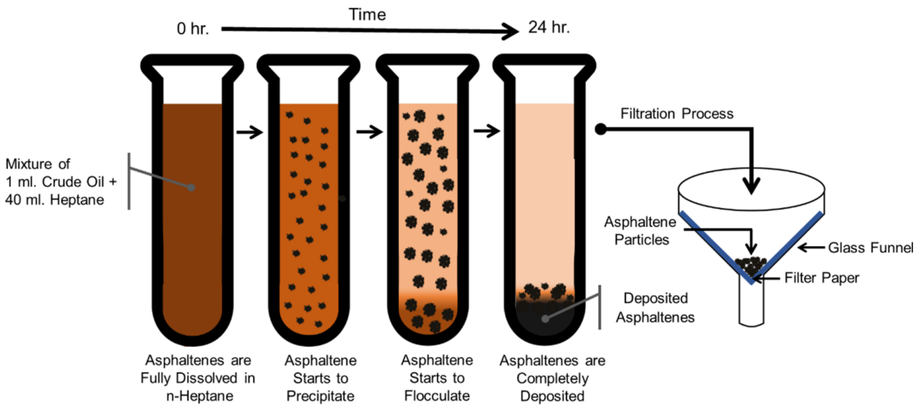

Figure 6. Simple sketch of test tube showing the process of asphaltene precipitation, flocculation, and deposition in *n*-heptane over 24 h to quantify the weight of asphaltenes after filtration huff-n-puff tests.

- Without changing the filter membranes, the aforementioned procedures were carried out once again to create a new huff-and-puff process.

Figure 6 shows a simple sketch of the test tube and the process of asphaltene deposition to quantify the weight of asphaltenes after mixing 1 mL of crude oil with 40 mL of *n*-heptane (ratio of 1:40). Before measuring the asphaltene wt %, 1 mL of oil from each filter paper was mixed with 40 mL of *n*-heptane in a test tube (ratio of 1:40). Filter paper (2.7 μm) was used to filter the mixture. The asphaltene wt % determined using the following equation:

$$\text{Asphaltene wt\%} = \frac{\text{wt}_{\text{asphaltene}}}{\text{wt}_{\text{oil}}} \times 100$$

where asphaltene wt % is the asphaltene weight percentage; $\text{wt}_{\text{asphaltene}}$ is the asphaltene particles' weight on the filter paper; wt_{oil} is the weight of oil sample.

2.3.1. Huff-n-Puff Filtration Technique Scope of Work. Two filtration huff-n-puff experiments were conducted utilizing one miscible pressure (i.e., 1750 psi) and one immiscible pressure (i.e., 1000 psi). Various filter paper membranes were used in each test as shown in Table 3. All experiments were carried out at 70 °C and for 6 h soaking time. The purpose of these tests was to examine how gas condition influences the asphaltene stability and the structure of filter membranes. These tests were implemented to highlight and evaluate how CO_2 conditions can influence the asphaltene stability and the membranes' pore structure. These tests will provide an understanding of how asphaltene affects ultra-pore structures, which represent real tight shale structures. Table 3 summarizes the operating conditions used in this section.

Table 3. CO_2 Huff-n-Puff Filtration Experiments' Operating Parameters

test no.	filter membrane's pore size (nm)	gas used	soaking time (h)	injected pressure (psi)	CO_2 condition
1	450	carbon dioxide (CO_2)	6	1000	immiscible
	100				
	50				
2	450		6	1750	miscible
	100				
	50				

2.4. Huff-n-Puff Process Using Eagle Ford Cores (Dynamic Mode). Eagle Ford outcrops (8 cores) were used to conduct immiscible/miscible CO_2 huff-n-puff tests based on the findings of MMP tests. Figure 7 illustrates the setup used in the dynamic mode tests. A high-pressure vessel was utilized for accommodating the cores. A syringe pump is attached directly to the accumulator of gas for holding and boosting the pressure of CO_2 gas. Finally, to mimic the real shale temperature during the experiments, a heat jacket was used.

Prior to the saturation step, 12 Eagle Ford cores were labeled and saturated with the same properties of crude oil used in the MMP tests. An accumulator was used to accommodate the core, and then they were subjected to high pressure and high temperature for a period of 10 months to guarantee that the cores will be saturated. The saturation process was discontinued after 10 months since the cores' weight did not change during the last 2 months of the saturation time, demonstrating that the outcrops were completely saturated. Figure 8 illustrates the weight change of three selected cores throughout the saturation step.

Spaces surrounding the core improved gas flow during the tests after inserting it in the vessel. Figure 9 displays a top view of the actual vessel. The experiments were conducted using the following steps:

- Following the placement of the core inside the vessel, the vessel was then closed after being attached to the CO_2 cylinder and the gas accumulator.
- The CO_2 was pumped into the vessel at the specified pressure during the huff stage, and then the CO_2 was allowed to soak the saturated core for the amount of time that was set for the soaking process.
- For the temperature, a heating jacket was used to boost the temperature to mimic the reservoir temperature (i.e., 70 °C).
- Depressurizing the vessel after the end of soaking time is called the "puff" stage.
- The core was collected in order to determine the RF at certain production durations by applying the following formula:

$$\text{Oil recovery factor (RF)} = \frac{\text{wt}_1 - \text{wt}_2}{\text{wt}_1 - \text{wt}_{\text{dry}}}$$

where wt_1 is the saturated core weight; wt_2 is the core weight after production time; wt_{dry} is the core weight when it is dry. After calculating the RF from the previous gas cycle, a new cycle was started, and the cycles were terminated when no cumulative OR was calculated/determined. Once all the required cycles were completed, the Eagle Ford cores were tested for asphaltene precipitation, alteration in pore size distribution, and wettability phase.

2.4.1. Huff-n-Puff Tests Using Shale Cores Scope of Work. In this part, eight Eagle Ford outcrops were utilized to study the effect of CO_2 miscibility on OR performance and asphaltene precipitation using the huff-n-puff injection technique. Extra four-reference cores that were only saturated (no CO_2 gas exposure) were used to measure their wettability phase and pore size structure range. Various factors were examined such as soaking time, injection pressure, and production time. Table 4 summarizes the operation conditions. In order to investigate how the soaking period influences the amount of oil that can be extracted, many cores were exposed to a gas huff-n-puff pressure of 2000 psi and a range of soaking durations (i.e., 1, 6, 12, and 24 h). Two techniques were used to investigate the influence of

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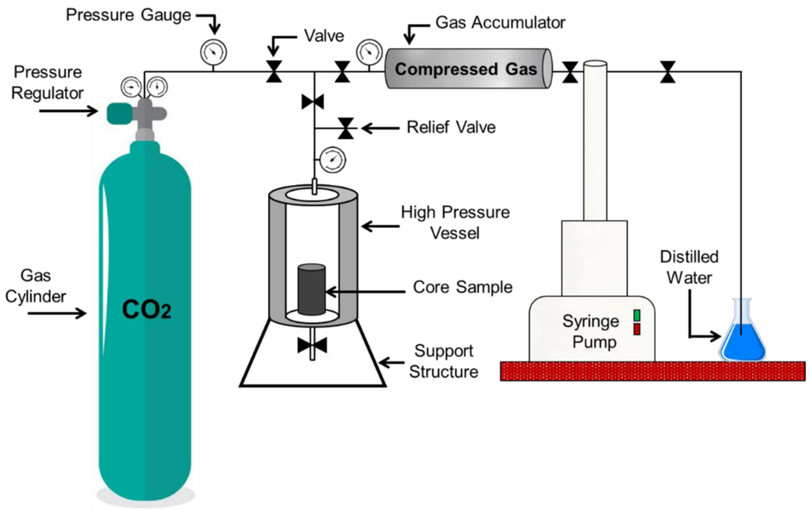

Figure 7. Huff-n-puff experiment setup.

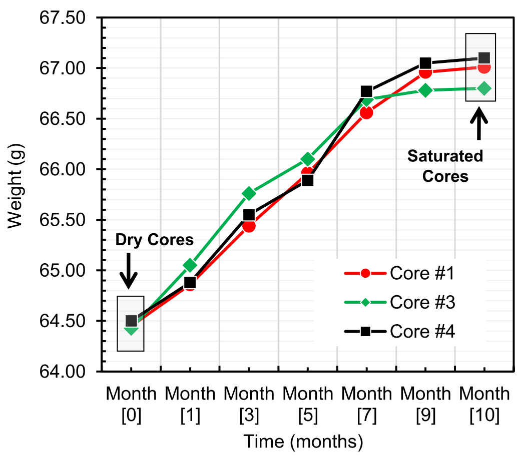

Figure 8. Core saturation examples during a 10-month period.

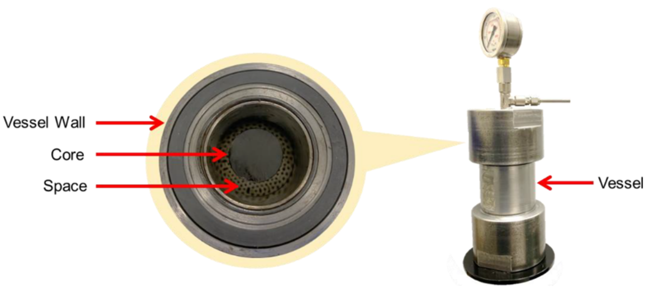

Figure 9. Real vessel top view.

soaking time: one core for all soaking durations (test no. 5) and utilizing various cores for each soaking time (test nos. 6–8) to evaluate the influence of re-soaking procedure on the performance of OR (more details in the following sections). The temperature for all the tests was maintained at 70 °C. For each test, the cycle number ranged, but the cycles were stopped when there was no observation of oil (i.e., no OR recorded/calculated). For both miscible and immiscible scenarios, the production times (i.e., the time when the core was weighed after finishing the huff-n-puff cycle) were defined as 15, 60, and 90 min. Finally, slim tube results were the reference for selecting the CO_2 miscible and immiscible pressures.

Table 4. CO_2 Huff-n-Puff Experiments' Operating Parameters[a]

test no.	core no.	gas used	soaking time (h)	injected pressure (psi)	production time (min)
1	#1	carbon dioxide (CO_2)	6	1000	15, 60, and 90
2	#2		6	1300	
3	#3		6	1750[b]	
4	#4		6	2000[b]	
5	#5		1, 6, 12, and 24	2000[b]	15
6	#6		1	2000[b]	
7	#7		12	2000[b]	
8	#8		24	2000[b]	

[a]Four additional cores, numbered #9, #10, #11, and #12, were used as references for the wettability assessment and pore size distribution measurements. [b]Miscible pressure condition.

3. FINDINGS AND DISCUSSION

3.1. Minimum Miscibility Pressure (MMP) Results. The gas injection process can occur in either condition—miscible or immiscible; however, miscibility had a significant influence on the performance of OR. The MMP is the pressure at which a gas becomes miscible with the crude oil at the conditions of the reservoir such as temperature.[100−103] Nine tests were performed to estimate the CO_2 MMP at pressures of 400, 600, 800, 1000, 1200, 1500, 1750, 1850, and 2000 psi at 32 and 70 °C, as shown in Figure 10. As a point of reference of the MMP findings, the first MMP tests were carried out at 32 °C. The cumulative OR at each of the CO_2 pressures is shown in Table 5. The MMP of CO_2 was estimated to be 1450 and 1650 psi at 32 and 70 °C, respectively. The MMP findings were utilized to determine which miscible and immiscible pressures of CO_2 that could be selected for the static and dynamic CO_2 huff-n-puff tests.

3.2. Results of Huff-n-Puff Filtration Tests. The huff-and-puff filtration methodology was used to perform two sets of huff-and-puff tests (i.e., static mode). In order to examine the influence of CO_2 pressures (i.e., above and below MMP) on asphaltene deposition, two scenarios were designed. Pressures of 1000 and 1750 psi were considered for immiscible and miscible circumstances, respectively. For both tests, the temperature and soaking time were fixed to be 70 °C and 6 h,

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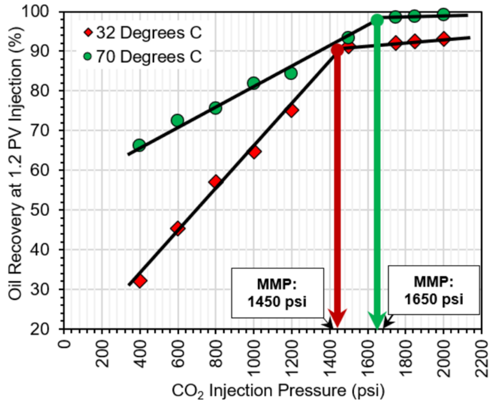

Figure 10. Results of CO_2 MMP experiments at 32 and 70 °C.

respectively. The findings of the CO_2 huff-n-puff filtration tests are presented in Figure 11. These findings suggest that asphaltenes in crude oil were impacted by varying degrees of aggregation during the first two cycles. The figure reveals that the asphaltene wt % in the 450 nm filter upsurged considerably from 8.89 to 10.23% when comparing the first cycle to the second cycle, respectively, with an immiscible CO_2 pressure of 1000 psi. The asphaltene wt % increased considerably as the number of cycles increased until the fifth cycle, demonstrating that asphaltene particles were affected at a higher pace in the early cycles. Because of the ultra-small pore structure, the 50 nm filter was identified to have a more asphaltene wt % than the other filters. For example, a significant increase was observed in the fifth cycle in which the asphaltene wt % climbed to 18.21% compared to 14.22% in the first cycle. The asphaltene wt % started growing slowly to 19.68% in the sixth cycle, then stabilized after the seventh cycle. However, the miscible CO_2 pressure of 1750 psi dramatically increased the asphaltene wt % in all filter membranes, indicating that the miscibility notably disrupted the connections between asphaltene particles and resins in the crude oil. For example, the asphaltene wt % in the 50 nm filter was 24.98% during the first cycle, however by the fifth cycle, it had dramatically jumped to 35.5%. The asphaltene wt % remained nearly constant at 35.98% during the subsequent cycles. To sum up, the asphaltene wt % went up in all huff-and-puff experiments as the pore size structure of the membranes became smaller in the first cycle of the huff-and-puff process. According to these findings, CO_2 causes more rates of asphaltene deposition and flocculation, especially at miscible gas conditions, which have strong light component extraction.[104] This could occur because CO_2 has high solubility, thus, the mass transfer potential of CO_2 is very strong.

3.2.1. Results of Chromatography Analysis. Following the completion of the last cycle of the filtration tests, samples of crude oil were taken from the oil that was produced in order to analyze the alteration in its elemental composition using GC−MS (GC6890-MS5973). This step will ensure that the structure of filter membranes and gas cycles have an influence on heavy components in crude oil, such as asphaltenes. Figure 12 reveals the oil composition of the produced oil after miscible and immiscible CO_2 huff-and-puff tests. The findings demonstrated that CO_2 injection at miscible scenarios had a substantial influence on crude oil, as shown by the increased mole fraction of both the intermediate and heavy components (C_{15}−C_{30}). Partial extraction was observed for the light components (C_8−C_{14}) as CO_2 had a considerable light extraction mechanism. More heavy components (i.e., C_{31+}) were detected after CO_2 tests, including asphaltenes, due to the high mass transfer mechanism of high CO_2 pressure. Moreover, miscible pressure had weakened the connections between asphaltene particles and resins in the crude oil, resulting in an increase in asphaltene deposition and heavy components.[105,106]

3.2.2. Microscope and Scanning Electron Microscopy (SEM) Analysis. A Hirox digital microscope was used in order to investigate the pore structure plugging that resulted in the filter membranes as an outcome of the buildup of asphaltenes. After completing immiscible and miscible CO_2 tests (static mode), microscopic photos showing the filter membranes' pore structure (i.e., 450, 100, and 50 nm) were taken at a magnification of 500 μm, as shown in Figure 13. Before the photos were captured, the filter paper membranes were cleaned and exposed to the solvent of heptane for 24 h. The figure reveals that asphaltene clusters plugged more spots in the 50 nm filter during miscible CO_2 pressure, resulting in more asphaltene depositions. This is due to the smaller pore structure of the 50 nm filter paper. This observation confirms the above results in previous sections. To provide a clear picture of filter membranes, SEM was used for high-resolution photos of the membrane's structure. As shown in Figure 14, different photos of the membranes were captured to highlight the asphaltene deposition and its severity in pore plugging. The same sizes of the filter membranes were selected (i.e., 450, 100, and 50 nm) in both conditions of miscible and immiscible gas injections. Similar observations of the digital microscope were noticed in all filter membranes. For example, more asphaltene particles were found in the filter paper of 50 nm compared to the 450 nm filter as the former has a smaller pore structure. Moreover, the photos show that darker colors were found during miscible CO_2 pressure. These results provide support to the observations that CO_2 has a high solubility and high extraction of light-hydrocarbon compounds in the oil, both of which have the potential to cause asphaltenes' related issues.

3.3. Results of Huff-n-Puff Gas Injection Using Shale Cores. *3.3.1. Effect of Injected Pressure.* The influence of CO_2 huff-n-puff injection pressure on the performance of OR using eight Eagle Ford shale cores will be discussed. Table 6 presents the cumulative RF results that were determined after each cycle for each test for CO_2. Four sets of tests (test nos. 1−4) were designed to evaluate the impact of CO_2 miscible conditions on the performance of OR. The tests were carried out utilizing pressures both below and above the CO_2 MMP with a fixing soaking time of 6 h. At different production intervals of 15, 60, and 90 min, the OR performance was measured, and the production time was evaluated. When there

Table 5. CO_2 Slim Tube Cumulative Oil Recoveries (%)

pressure injected (psi)	400	600	800	1000	1200	1500	1750	1850	2000
cumulative OR at 32 °C	32.20	45.40	57.10	64.71	75.20	91.30	92.10	92.50	93.12
cumulative OR at 70 °C	66.30	72.50	75.60	81.90	84.40	93.30	98.50	98.80	99.10

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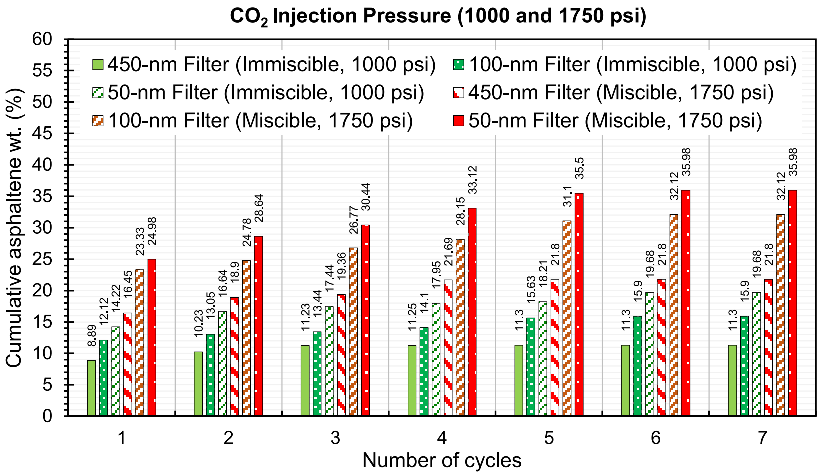

Figure 11. Asphaltene wt % in all filter membranes after seven CO_2 cycles at 70 °C.

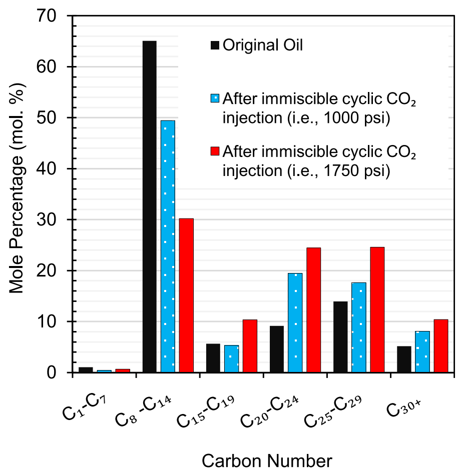

Figure 12. Crude oil carbon number before and after CO_2 huff-n-puff filtration tests.

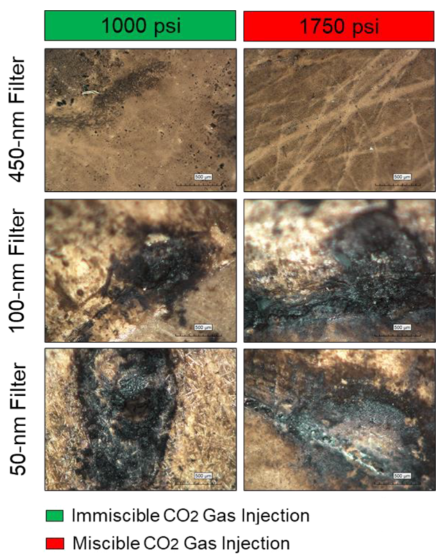

Figure 13. Microscopic photos at a magnification of 500 μm showing the structure of 450, 100, and 50 nm membranes following the last cycle of immiscible and miscible CO_2 injections.

was no OR recorded, the cycles were ended, and a new experiment was started. Figure 15 demonstrates that at

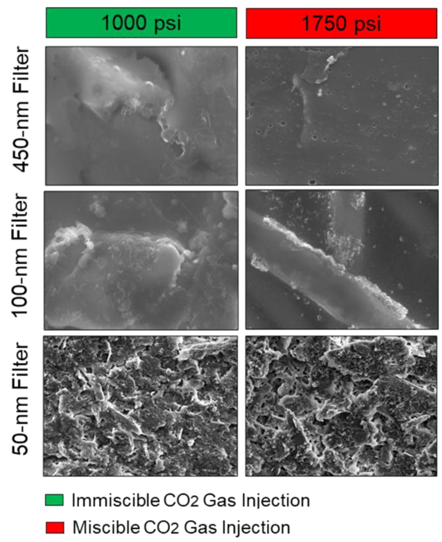

Figure 14. SEM photos at a magnification of 500 μm showing the structure of 450, 100, and 50 nm membranes following the last cycle of immiscible and miscible CO_2 injections.

immiscible huff-n-puff conditions, OR was significantly lower than under miscible conditions. The OR performance significantly improved as the pressure continued to increase, as seen in the first cycle. According to the findings, oil can be recovered during the first five cycles in both scenarios, but after the sixth cycle, no more oil can be collected. These findings, therefore, confirm that miscible pressures were more effective and advantageous over immiscible pressure in terms of improving OR. Similar results were obtained for the miscibility conditions, where miscibility positively impacted the OR more than immiscible conditions. The possible explanation is that miscible CO_2 has a good solubility, which decreases the viscosity of oil, resulting in more oil extraction and recovery. Under miscible CO_2 pressure, hydrocarbon contents can be evaporated at a quicker pace, resulting in an increased OR factor at higher pressures. The steady cumulative OR in the last cycles indicates that asphaltene precipitation started to impact OR performance in later cycles. During conditions of immiscibility (i.e., low pressure), asphaltene clusters started to deposit mostly in the larger pores.[107] During miscible conditions, asphaltenes started to fill both large and small

Table 6. Cumulative Recovery Factor (%) Summary Determined after CO_2 Huff-n-Puff Tests

test no.	soaking time (h)	pressure (psi)	production time (min)	cycle 1	cycle 2	cycle 3	cycle 4	cycle 5	cycle 6	cycle 7	cycle 8	cycle 9
1	6	1000	15	4.14	10.66	12.30	13.93	13.93	13.95	13.98		
			60	4.55	11.29	12.93	14.57	14.57	14.59	14.60		
			90	4.76	11.72	13.82	15.69	15.69	15.69	15.70		
2	6	1300	15	9.10	10.72	11.66	12.24	13.24	13.24	13.24		
			60	9.07	11.16	12.36	13.09	14.09	14.09	14.10		
			90	9.28	12.07	13.75	14.48	15.48	15.48	15.48		
3	6	1750	15	10.26	15.40	17.42	20.30	22.81	22.81			
			60	11.38	17.08	18.42	21.53	25.08	25.08			
			90	12.67	16.97	18.99	22.52	26.08	26.08			
4	6	2000	15	7.87	18.08	29.40	34.96	39.30	39.30			
			60	9.26	22.39	31.01	37.42	41.57	41.57			
			90	11.11	25.56	32.90	39.87	43.14	43.14			
5	1	2000	15	11.16	13.25	18.68	21.74	24.30	25.20	26.40	26.20	26.19
	6	2000	15	27.46	31.46	40.03	44.03	45.61	47.36	47.10	47.41	47.41
	12	2000	15	47.50	61.79	68.93	71.30	73.22	75.46	75.60	75.61	75.61
	24	2000	15	76.06	81.66	85.47	90.12	91.54	92.33	93.11	93.12	93.12
6	1	2000	15	2.26	8.94	12.61	15.13	16.33	18.01	19.25	20.33	20.35
7	12	2000	15	17.93	25.43	32.48	41.13	45.12	46.32	47.10	47.11	47.11
8	24	2000	15	31.01	37.39	47.69	53.44	59.12	61.31	61.32	61.32	61.32

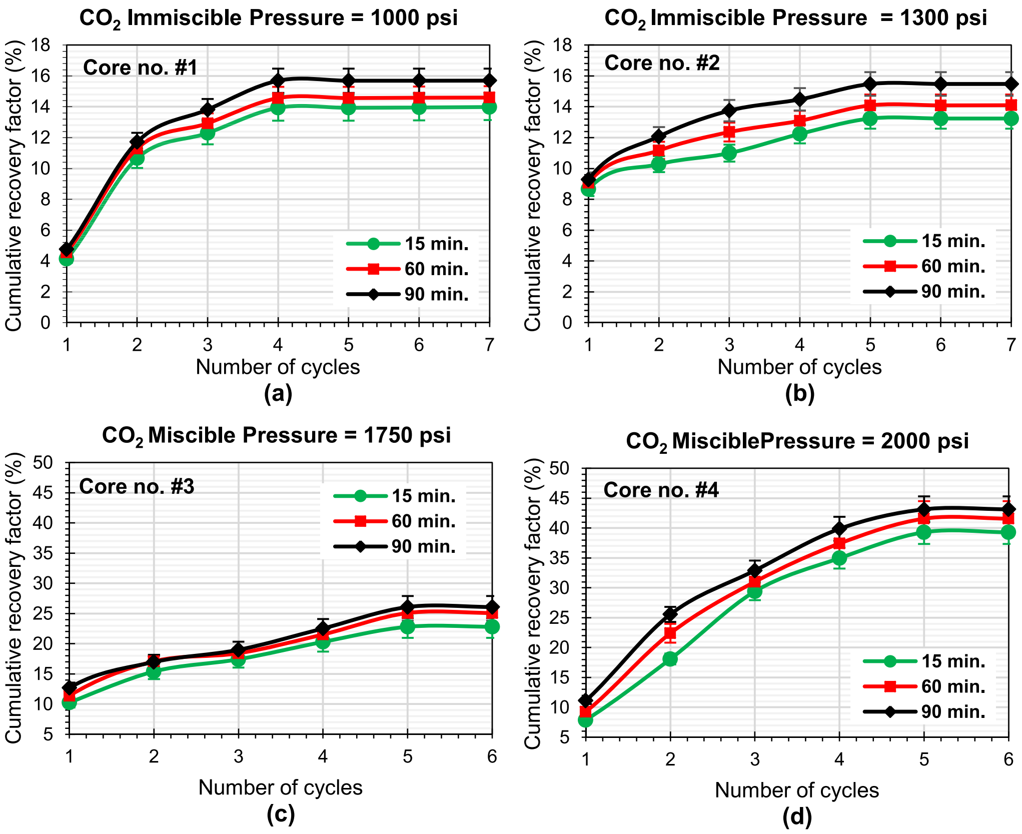

Figure 15. (a−d) Cumulative oil recovery factor of CO_2 huff-n-puff pressures (6 h soaking time).

pores, especially after several cycles of huff-n-puff pressures; thus, the pore plugging rate in the shale structure increased. This finding suggests that OR existed primarily in early cycles, when asphaltenes were not yet fully deposited and blocked all pore spaces in the cores, in terms of production time shown in the figures which is the time when the cores were collected from the vessel after the cycle phase and then left for a certain period of time for weighing. At 15, 60, and 90 min of production time, the OR was calculated, and every cycle's soaking period was set at 6 h. Figure 15 presents the findings of the CO_2 huff-and-puff experiments with different production periods. The figure reveals that for all CO_2 huff-n-puff cycles the recovery slightly increased in all production periods. After the second immiscible CO_2 cycle, the influence on OR was most considerable. This was because more soaking time led to more interactions between the crude oil and the CO_2; thus, a higher solubility occurred, which led to a higher performance of OR. A slight increase in OR was determined during the

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second cycle, which increased from 10.66 to 11.71% during the 1000 psi CO_2 gas injection for 15 and 90 min of production time, respectively. The OR increased from 13.95 to 15.69% in the fifth cycle (conditions: 1000 psi, 15 and 90 min production time). For miscible conditions (i.e., higher pressures), the change in OR performance was seen from the second cycle, especially for the 2000 psi injection pressure. The previously discussed findings indicated that production time had a slightly positive influence on the performance of the RF during the process of CO_2 huff-n-puff.

3.3.2. Soaking Time Mode. The impact of the soaking step will be discussed in this section using different techniques at a pressure of 2000 psi. The first technique is referred to as Mode I, and it involved using many cycles on the same core with changing soaking times of 1, 6, 12, and 24 h. The second technique, known as Mode II, is defined by the use of a separate core for each soaking time, as well as multiple cycles. Figure 16 illustrates the difference between these two modes.

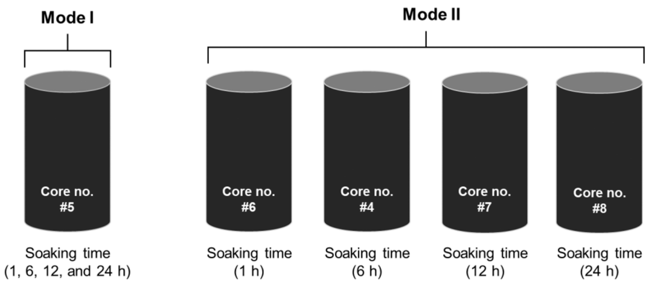

Figure 16. Soaking time mode illustration.

Test no. 5 was conducted using the Mode I technique, and one core was used for all soaking time and cycle parameters. To implement Mode II, three more tests were designed (test nos. 6–8) and each soaking time had its separate core. The results for the fourth test (soaking time of 6 h) were addressed in an earlier section. All experiments used a constant production period of 15 min and a miscible injection pressure of 2000 psi. As demonstrated in Figure 17a, nine CO_2 cycles using Mode I were sufficient to extract more than 90% of the crude oil (soaking time of 24 h). On the other hand, using Mode II resulted in a maximum OR of 61% after seven cycles, as shown in Figure 17b. The optimal number of cycles was found to be eight, beyond which there was no more recovery recorded. According to these findings, increasing the soaking duration resulted in a larger amount of recovery, especially in Mode I. This could be because of the high rate of hydrocarbon evaporation that was encountered while employing Mode I with a range of soaking times. The findings showed that carbon dioxide (CO_2) is effective for increasing OR from shale cores for two main reasons: (1) because CO_2 can condense at a higher concentration in crude oil and (2) because CO_2 can vaporize more hydrocarbon from the shale cores, mainly in miscible conditions. Both of these advantages were demonstrated by the findings of this study. Based on the findings, it appears that a higher proportion of OR could be achieved by beginning with a short soaking time, during which asphaltene would not have time to completely precipitate in the core. Figure 18 shows the core samples (for Mode I and Mode II) following CO_2 huff-n-puff experiments with a 24 h soaking period and a 2000 psi injection pressure.

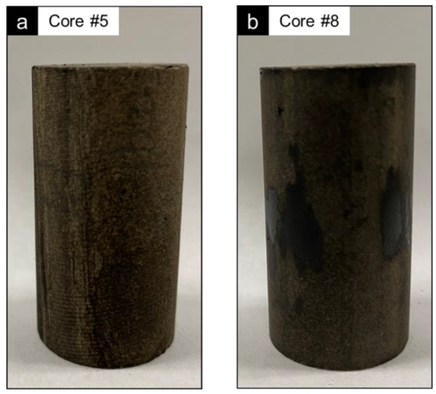

Figure 18. Photos of cores following huff-n-puff gas injection tests at 2000 psi (a) after a Mode I CO_2 test and (b) after a Mode II CO_2 test (24 h soaking period).

3.3.3. Wettability Analysis due to Asphaltene Precipitation. Wettability can be defined as "the tendency of fluids to adhere to the surface".[108] Wettability changes during enhanced OR are a critical characteristic for oil production, specifically in unconventional reservoirs. During gas injection processes, asphaltene may be deposited and precipitated, which have the possibility of changing the wettability of shales and, as a result, the efficiency of OR. Capillary pressure in shale rocks is relatively high because of the small permeability of the shale structure. The wettability of shale rocks is variable; it is not necessarily oil-wet as has been commonly believed but can be water- or oil-wet.[108] However, some studies have indicated that

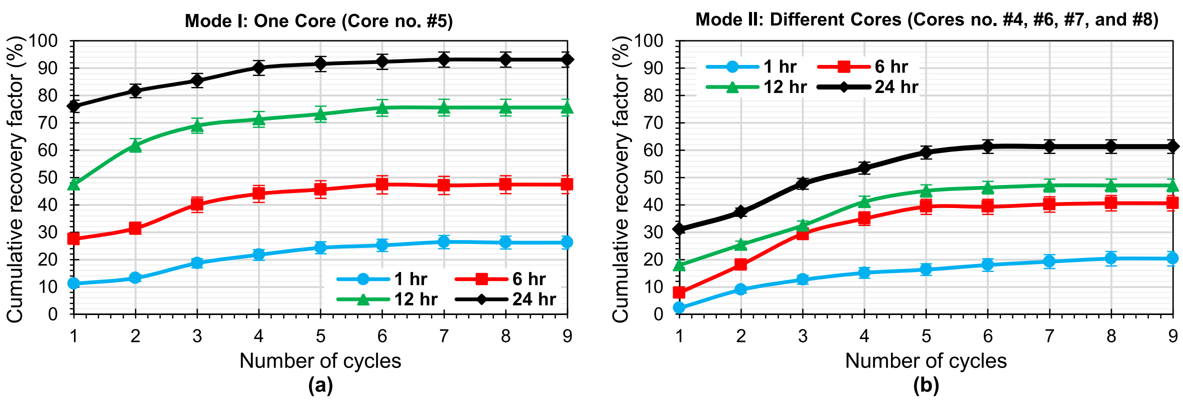

Figure 17. Cumulative recovery factor of CO_2 (a and b) huff-n-puff injections using Modes I and II at a 2000 psi CO_2 huff-n-puff pressure.

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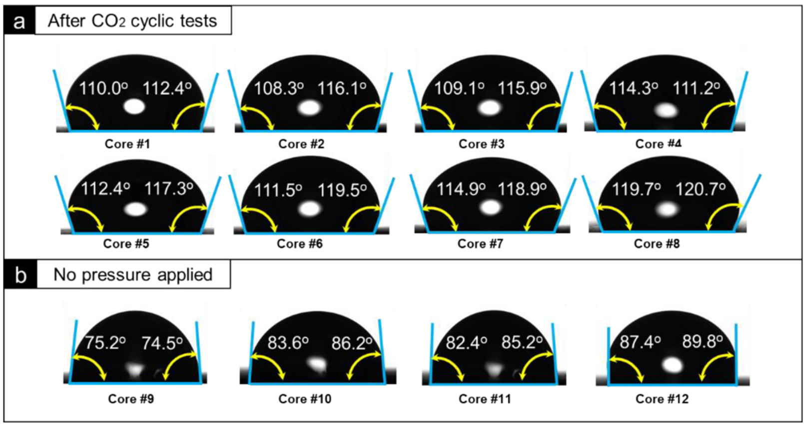

Figure 19. Contact angle determination using brine droplets (a) after CO_2 huff-n-puff tests and (b) no pressure exposure.

Table 7. Contact Angle Determination[a]

stage	CO_2 condition	test no.	pressure used (psi)	average contact angle (°)	status of wettability[b]	total average
four separate cores			no pressure exposure	83.80	neutrally wet	82.95
				74.50	neutrally wet	
				88.60	neutrally wet	
				84.90	neutrally wet	
after CO_2 huff-n-puff tests	immiscible	1	1000	111.20	weakly oil-wet	114.51
		2	1300	112.20	weakly oil-wet	
	miscible	3	1750	112.50	weakly oil-wet	
		4	2000	112.75	weakly oil-wet	
		5	2000	114.85	weakly oil-wet	
		6	2000	115.50	weakly oil-wet	
		7	2000	116.90	weakly oil-wet	
		8	2000	120.20	weakly oil-wet	

[a]Based on definitions from Arif et al.[119] and Anderson.[123] [b]Wettability was classified as the following: 0° = completely water-wet; 0−50° = strongly water-wet; 50−70° = weakly water-wet; 70−110° = neutrally wet; 110−130° = weakly oil-wet; and 130−180° = strongly oil-wet.

shale rocks tend to have more oil-wet phase wettability.[109,110] The asphaltenic components and the TOC content both have an impact on the wettability phase of shale rocks.[111−113] This study implemented an air-liquid-rock system to examine the Eagle Ford cores' wettability before and after CO_2 huff-and-puff experiments. Figure 19 displays equilibrated droplets of brine on all shale samples before and after the CO_2 huff-and-puff experiments. Before CO_2 huff-n-puff gas injection experiments, the contact angle was measured using four separate saturated cores, which were used as a reference (Figure 19b). The four cores were saturated with crude oil, and the average contact angle was determined to be 82.95° (neutral wettability phase). After completing CO_2 huff-and-puff tests in both scenarios, the contact angles of all shale cores were measured as presented in Table 7. After the CO_2 huff-n-puff testing, the cores were found to have an average wettability of 114.17° (i.e., weakly oil-wet). These findings show that CO_2 had a greater influence on the asphaltene precipitation in Eagle Ford cores. When CO_2 gas was injected at miscible injection pressures, the contact angle increased, suggesting that miscibility may promote a weak oil-wet to the moderate oil-wet system during CO_2 huff-n-puff tests. Asphaltene deposition has affected the surface structure of the shale, making it harder, leading to an increase in contact angle measurements.[114,115] Our results were consistent with the results of other researchers, who reported that an increase in gas injection pressure led to an increase in the contact angle.[116−121] When injecting miscible CO_2 gas into shale basins, more oil-wet systems may be observed. Moreover, our results indicate that reduction of OR and asphaltene precipitations mostly found and accumulated during the later cycles. This is due to the fact that a decrease in OR was observed in the last two cycles of the majority of CO_2 huff-and-puff tests. More cycles increased the pace at which asphaltene clusters began to fill the larger spaces in the core's structure,[104] and more asphaltenes were precipitated in the cores with an increase in the plugging rate. Following CO_2 huff-and-puff tests, the OR factor decreased, and more cycles revealed that asphaltene deposition and precipitation had a negative influence on the OR's performance.[122] To sum up, our results suggested that the CO_2 huff-and-puff method, particularly at miscible conditions, affected the asphaltene's stability and severely damaged the strong connection between asphaltenes and resins, leading to an increase in asphaltene plugging rate.

3.3.4. SEM Examination. The main objective of utilizing SEM was to detect alterations in the structure of shale formations caused by asphaltenes. The SEM examinations may provide further details on asphaltene particles inside the shale core and also give a precise image of the ultra-small pores that were plugged with asphaltenes. The gas injection may break the bonds between the resins and asphaltene molecules in crude oil, resulting in an increase in asphaltene instability and an increase in pore plugging. A SEM was utilized (100 μm) to show the severity of asphaltene's pore plugging of the cores used, as shown in Figure 20. After the CO_2 huff-and-puff tests, three cores were selected for SEM evaluation in this study,

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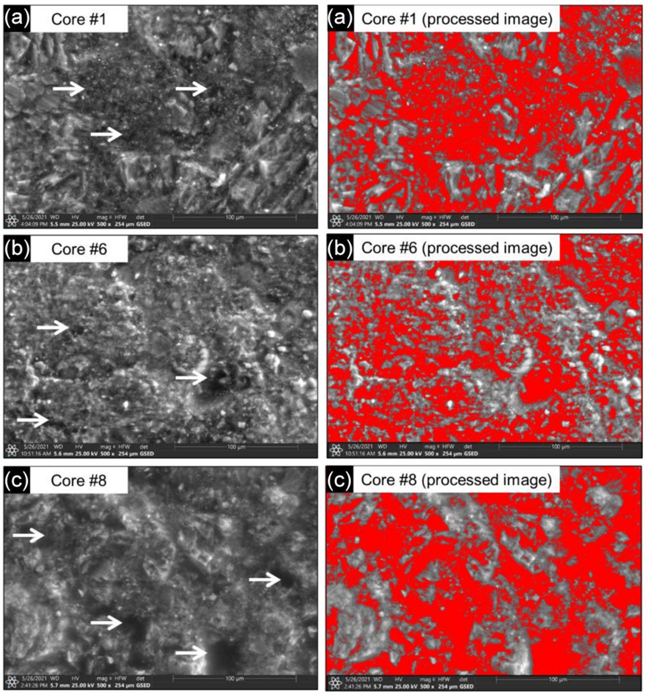

Figure 20. Scanning electron microscope (SEM) pictures (100 μm) of (A−C) three cores after CO_2 huff-n-puff gas injection tests.

with the findings presented in Figure 20a−c. Asphaltene particles appeared to fill some spots in the shale cores, as demonstrated by the SEM pictures. For instance, pictures (a) and (c) demonstrated a higher level of asphaltene pore blockage in comparison to sample (b). This might be because pictures (a) and (c) were exposed to longer soaking periods of 6 and 24 h, respectively. Furthermore, the degree and distribution of the blocked pores in all samples were never identical. Finally, image-processing software was utilized to show the asphaltene areas from SEM photos, as shown in red color in Figure 20.

3.3.5. Change of Pore Size Distribution due to Asphaltenes. Permeability reduction is one of the crucial challenges produced by asphaltene plugging in shale resources during the huff-n-puff gas process. This test was designed to determine how the pore size distribution altered as a result of the increasing asphaltene deposition after the CO_2 huff-and-puff process. Using a PoreMaster mercury porosimeter, the pore size distribution of two Eagle Ford cores was measured. A sample was picked among those that were fully saturated with oil, but no pressure was exposed to them. Another sample after the huff-n-puff CO_2 test (i.e., test no. 8) of the Eagle Ford outcrops sample was selected to compare the results. Because it was necessary to have very little pieces of each sample, each outcrop was broken into smaller pieces prior to the tests performed. During the measurement, a high pressure of 60,000 psi was applied to evaluate the cores' microstructure pores and throats. At each intrusion pressure, the PoreMaster determined and recorded precisely the volume of mercury intruded. Pore size distribution results are shown in Figures 21 and 22. Huff-n-puff gas injection altered the oil's composition and resulted in asphaltene deposition. Asphaltene aggregated and generated a solid material that started to settle and fill the pores within the cores and on the surface of the cores.[124−128] Compared to after huff-n-puff tests, the samples before the test showed larger pore size diameters. Figure 21 indicates that the pore size peaks of two samples occur in completely separate ranges, showing that the major pore diameter in the samples significantly varies. The pore size distribution's peak was determined to be between 0.03 to 40 μm before CO_2 huff-n-puff tests, while the peak was changed to be between 0.01 and 10 μm after CO_2 huff-n-puff tests. Based on these findings, it can be concluded that the asphaltene particles that were injected into the cores had an influence on the pore throats. Due to the presence of asphaltenes, more pore plugging was found after using the CO_2 huff-n-puff gas technique during the EOR process.

3.4. Further Discussion (the CO_2 vs N_2 Huff-n-Puff Process). The performance of OR under CO_2 and N_2 gas injections, as well as the effect of asphaltene deposition, is comprehensively compared in this section. The results of OR under N_2 gas injection are from our previous work.[98] For the comparison, two immiscible pressures (i.e., 1000 and 1300 psi) and two miscible pressures (i.e., 1750 and 2000 psi) for the two gases were selected with a production time of 15 min and 6 h soaking time, as summarized in Table 8. Figure 23 shows the performance of OR during immiscible and miscible CO_2 and N_2 injections. The difference between the cumulative OR for both gases started from the first cycle in all pressures. The huff-n-puff process was more effective to extract more oil from shale cores under CO_2 gas compared to lower performance using N_2 as CO_2 can reduce the interfacial tension at a higher rate than N_2. For both gases, more recovery was seen in the first three cycles before it started to stabilize or slightly increase. For instance, using CO_2 immiscible pressure of 1000

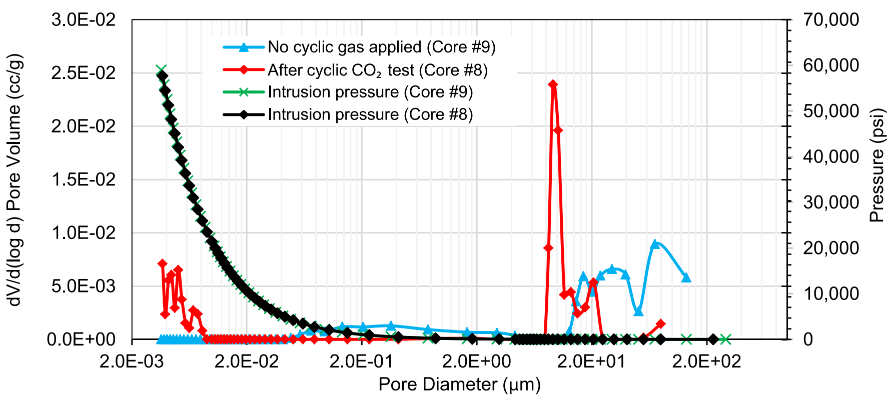

Figure 21. Pore size distribution results.

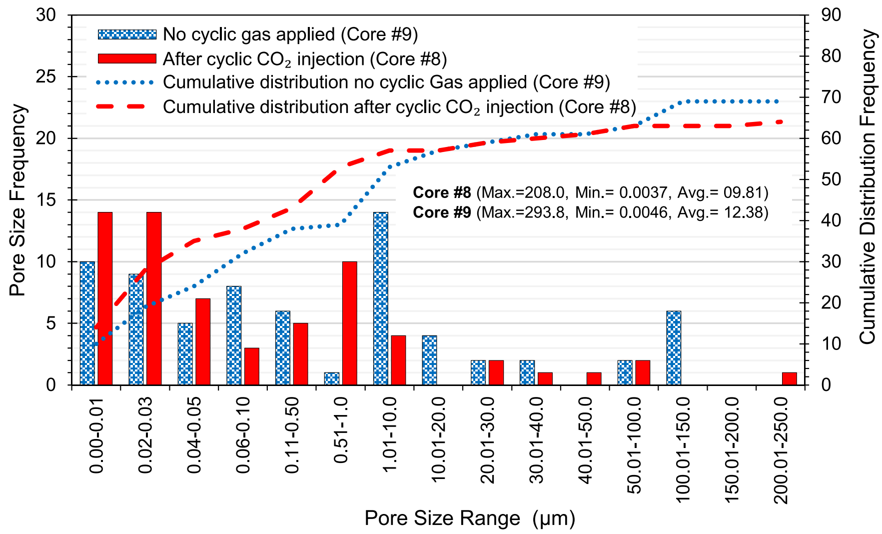

Figure 22. Pore size distribution comparison.

Table 8. Results of Cumulative Oil Recovery Factor (%) after (CO_2) and (N_2)[98] Huff-n-Puff Tests

test no.	Test #1		Test #2		Test #3		Test #4	
pressure (psi)	1000		1300		1750		2000	
condition	immiscible				miscible			
gas	N_2	CO_2	N_2	CO_2	N_2	CO_2	N_2	CO_2
Cycle 1	1.81	4.14	8.88	9.10	9.08	10.26	5.38	7.87
Cycle 2	2.64	10.66	10.33	10.72	11.10	15.40	9.00	18.08
Cycle 3	3.38	12.30	11.43	11.66	12.82	17.42	13.33	29.40
Cycle 4	4.63	13.93	12.03	12.24	15.24	20.30	15.81	34.96
Cycle 5	4.85	13.93	12.03	13.24	15.24	22.81	16.01	39.30
Cycle 6	4.85	13.95		13.24		22.81		39.30
Cycle 7		13.98		13.24				

psi resulted in cumulative OR of about 4.14%, which increased to 12.30% in the third cycle. After that, it began to rise gradually, reaching 13.93% and reaching 13.98% in the latest cycle. Under N_2 gas injection, the same observation was obtained, but the cumulative OR was much lower. Interestingly, the cumulative OR for both gases was close to each other under immiscible pressure of 1300 psi gas injection, but CO_2 gas still had a higher cumulative recovery. This might be a result of the oil being trapped in the deep core's pores during test #2 of CO_2, which prevented the gas from evaporating more of the crude oil's light hydrocarbons and lowering cumulative recovery. Miscible huff-n-puff pressure had better OR performance in both gases. For example, using miscible 2000 psi CO_2 pressure led to 39.30% cumulative OR compared to 16.01% when using N_2 gas at the same pressure. The OR factor in all of the experiments decreased in the later cycles, which is clear from the earlier results and suggests that asphaltene deposition had an immediate impact after the first cycle but accumulated over the subsequent cycles. Our finding suggests that the CO_2 huff-and-puff process in shale reservoirs can extract more oil than the N_2 process, but additional cycles may lead to accumulated issues with asphaltene deposition. More research must be done in order to scale up these laboratory-scale findings to actual shale resources.

4. CONCLUSIONS

In this research, asphaltene instability under the CO_2 huff-and-puff process was investigated experimentally using Eagle Ford shale cores and ultra-small membranes. Examinations were conducted on the effects of pressure, miscibility, and soaking duration. The wettability study and pore size distribution examination of the cores provided a comprehensive picture of the impact of asphaltene's related pore plugging during CO_2 huff-and-puff operations. When using the static mode (i.e., filter paper membranes), the asphaltene wt % climbed as the pressure increased and the influence of the huff-n-puff gas process on the instability of asphaltene particles was found in the first five cycles and accumulated in later cycles. The results showed that more asphaltene wt % resulted in the 50 nm filter paper due to the ultra-small pore structure. During the static mode experiments, chromatography analysis revealed the influence of CO_2 on the asphaltene wt %, with the findings revealing that CO_2 generated more accumulated heavy hydrocarbon components after the last CO_2 huff-n-puff injection, especially under miscible conditions. The results of the dynamic mode (i.e., using Eagle Ford shales) indicated that the OR improved when both the miscible high pressure and more cycles were achieved. The findings of the dynamic mode suggested that starting with a shorter soaking time led to more OR. Longer soaking durations induced asphaltenes to accumulate within the cores, which accelerated the decline in OR. Our results show that oil reduction and asphaltene

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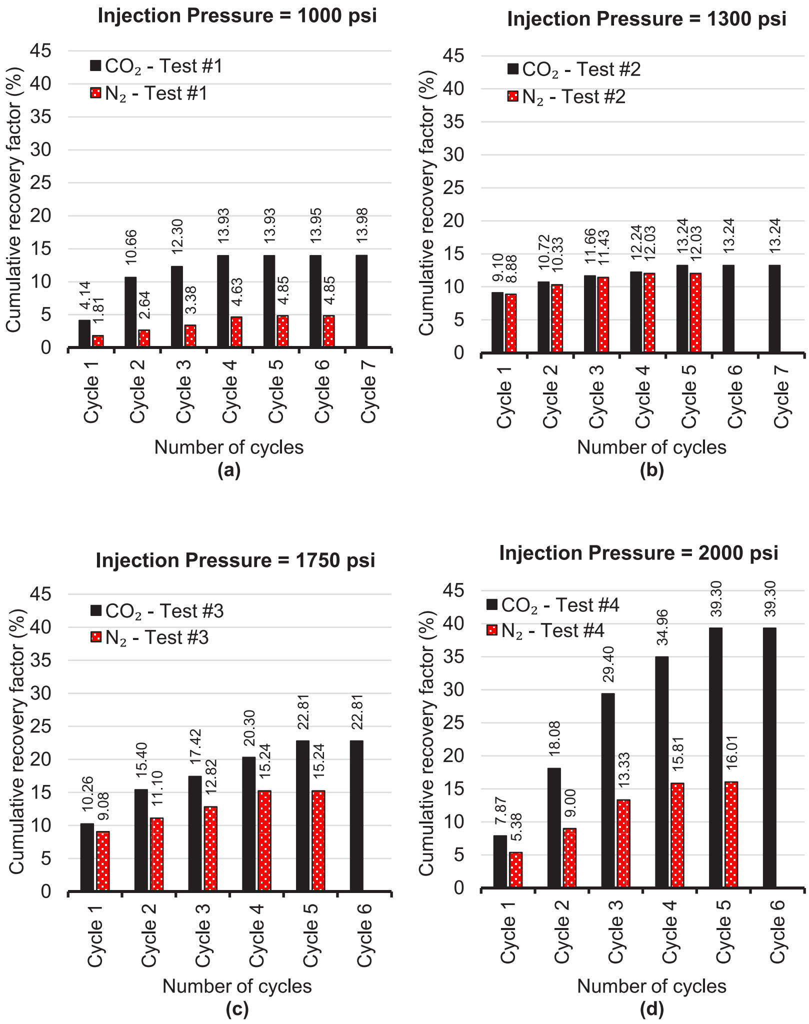

Figure 23. (a–d) Comparison of oil recovery performance during immiscible and miscible CO_2 and N_2 huff-n-puff injection pressures.

deposition accumulated mostly in the later cycles as a result of the fact that the final two cycles in the majority of CO_2 huff-and-puff experiments revealed a decrease in the volume of oil recovered during those cycles. As the number of cycles increased, asphaltene clusters started to fill the bigger pores at a higher pace, altering the wettability of the shale cores to be an oil-wet phase. After CO_2 huff-and-puff experiments on Eagle Ford cores, a PoreMaster mercury porosimeter revealed a reduction in pore size distribution related to asphaltene deposition. Our finding suggests that the CO_2 huff-and-puff process in shale reservoirs can extract more oil than the N_2 process, but additional cycles may lead to issues with asphaltene deposition. More research must be done in order to scale up these laboratory-scale findings to real shale resources and to highlight other variables/factors that may influence the effectiveness of such operations in tight-shale resources.

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Notes

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