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The effect of CO2-philic thickeners on gravity drainage mechanism in gas invaded zone

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The effect of CO_2-philic thickeners on gravity drainage mechanism in gas invaded zone

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Abstract

The rate of mass transfer between the fractures and matrix in gas invaded zone can significantly influence on the oil recovery during the forced gravity drainage process. However, in this study, a new approach was suggested to improve the gravity drainage process in gas invaded zone. Poly(fluoroacrylate) (PFA), as a CO_2-philic thickener, was injected into the gas invaded zone to illustrate the impact of interfacial mechanisms such as gas diffusion coefficient and interfacial tension (IFT) on oil recovery. Also, the cloud point pressures were measured to ensure that the PFA did not come out of the solution due to a phase change during IFT, gas diffusion coefficient, and gravity drainage experiments. Results showed that the CO_2-PFA thickener (20000 ppm) could decrease the IFT from 56 to 24 dyne/cm compared to the pure CO_2 scenario, improving the gravity drainage mechanism in the gas invaded zone. In addition, the CO_2 diffusion coefficients were increased approximately more than two times during CO_2-PFA injection in comparison with pure CO_2 injection in both porous media and bulk oil phase scenarios at reservoir

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conditions. Also, an incremental oil recovery of 16 percent was achieved during PFA/CO_2 compared to pure CO_2 injection in the gas invaded zone. Therefore, gas gravity drainage is the most important mechanism once gas thickener or CO_2 enters the fractures in the gas invaded zone.

Keywords: Gas invaded zone, Gas thickeners, CO_2 diffusion coefficients, Gravity drainage, Matrix-fracture system, Cloud point pressure

Introduction

CO_2 injection in naturally fracture reservoirs is the process of storing and capturing atmospheric carbon dioxide combined with enhanced oil recovery. It is one method of decreasing the amount of CO_2 in the atmosphere with the goal of reducing global climate change (Hassanpouryouzband et al., 2021 and 2018). Naturally fractured carbonate reservoirs (NFRs) hold a significant portion of the global oil reserves. Gravity is the only conceivable economic driving mechanism in widely fractured reservoirs because extremely conductive fractures create shortcuts for the injected fluids. In the production from fractured carbonate reservoirs, three zones can be recognised: (1) a gas invaded zone with oil-filled matrix and gas-filled fractures, (2) an oil rim with oil-filled matrix and fractures, and (3) a water invaded zone with water-filled fractures and oil-filled matrix (Li et al., 2018; Kharrat et al., 2021; Farrokhrouz et al., 2022). The oil flow in the gas invaded zone will be largely through the matrix due to the gravity drainage mechanism. When gas from gas-saturated fractures moves oil in the matrix, gas gravity drainage occurs. The gas gravity drainage is derived from the difference in density of the oil and gas phases. By injecting gas or gas thickeners into the fracture-matrix system, these contact with insitu fluid through diffusion. This makes the oil to swell, and consequently lessens the oil viscosity, absorbs the light component, and drops the IFT. Therefore, the gas diffusion coefficient and IFT can affect the gravity drainage mechanism in the gas invaded zone. Therefore, it is significantly important to fully understand these mechanisms under actual reservoir conditions (Guo et al., 2022; Aghabarari et al., 2022). The diffusion coefficient is a key parameter in controlling the mixing rate of the injected gas and insitu fluids. Gas dissolution will change the insitu fluid properties significantly including the reduction in oil viscosity and oil swelling which consequently result in the improvement of oil mobility and enhancing the oil recovery (Gao et al., 2019). In Berea cores saturated with n-hexadecane, Li et al. (2006 and 2009) estimated the effective CO_2 diffusion coefficient. They came to the conclusion that the readings were slightly affected by pressure changes ranging from 2.3 to 6.3 MPa. Li et al. (2016) investigated the impacts of oil saturation and tortuosity on CO_2 diffusivity in porous media with poor permeability. The diffusion coefficients were found to be highly influenced by the oil saturation and permeability of the porous medium. Gao et al. (2019) used tortuosity to link the CO_2 mass transfer coefficient to the permeability of porous media. They discovered that the high tortuosity can slow down the CO_2 diffusivity by restricting gas solubility. The prior measurements of diffusion coefficients, on the other hand, still need to be extended by using gas thickeners. In addition, several field performance analyses (Al-Shibli et al., 2022; Zobeidi et al., 2021; King et al., 1970; Carlson, 1988) and laboratory experiments (Saidi et al., 1993; Clemens et al., 2001; Sajjadian et al., 1999, Zobeidi et al., 2018) showed that the oil recovery factor could be significantly enhanced if gravity drainage process is the leading production mechanism. Carlson (1988) also came to the conclusion that high oil recovery after a gas drive operation is attributable to gravity forces reflected by considerable differences in density between the oil and gas. However, the obtained conclusion ignores the process's numerous side consequences. Laboratory studies of gravity drainage in fractured rock were conducted by Sajjadian et al. (1999). They reported that capillary continuity and re-infiltration could improve oil recovery factor. Clemens et al. (2001) demonstrated that when there are no fractures in the horizontal plane and the oil must flow sideways into the fracture system, the drainage rate is further lowered, resulting in lower drainage rates. Ameri et al. (2013) investigated the effect of miscibility on the gas-oil gravity drainage in naturally fractured reservoirs. The findings show that injecting a non-equilibrium gas with a larger scale of solubility into the oil phase causes a zone of reduced oil viscosity, leading to enhanced gravity-mediated recovery. Zobeidi et al. (2018) investigated the impact of gravity drainage on the block to block interactions in NFRs. Their findings showed that oil penetration into lower blocks occurs rapidly. Hasanzadeh et al. (2021) investigated the forced and free-fall gravity drainage mechanism in a fractured physical model. Results reveal that the forced gravity drainage performs better under controlled process conditions than the free-fall gravity drainage. Karimaie et al. (2010) investigated gas-oil gravity drainage process in fractured carbonate rock with low IFT and gas injection. They showed that even after water injection, low IFT gravity drainage may recover a large amount of oil in NFRs. Ameri et al. (2015) evaluated the rate of mass-transfer between the fractures and the matrix while a gas solvent is injected into a fracture system. Their findings revealed that matrix wettability has no effect on solvent injection performance, and that the remaining oil in the matrix may be recovered using an increased gravity drainage procedure. Kahrobaei et al. (2012) illustrated that transfer rates of solvent between fracture and matrix is a function of the rock permeability, oil viscosity and the density of both oil and solvent. Consequently, based on the previous works, the data of CO_2 diffusion coefficients and gravity drainage mechanism in hydrocarbon fluids and crude oil is still undersupplied at the actual reservoir conditions. Also, a large portion of the recorded data are within a limited temperature range (<60 ^{o}C) and pressures (<2500 psi), and the effect of gas thickeners on gas diffusivity coefficient and gravity drainage mechanism is not reported. Moreover, several experimental and theoretical studies are conveyed in the literature to study the efficacy of a gas or solvent injection in NFRs under static conditions. Still, few pieces of work have focused on the mas transfer mechanisms between matrix and fracture under dynamic conditions. In addition, the gas diffusion coefficient is still a controversial challenge during gas-based EOR for improving the gravity drainage mechanism in the gas invaded zone. However, the gas thickener scenario can be one of the new approaches for improving the mass transfer processes under flow conditions between fracture and matrix. Recently, several pieces of research have been done to improve the oil recovery by polymer thickeners for gas-based EOR in the conventional reservoir (Gandomkar et al., 2021; Gandomkar et al., 2020a; Dai et al., 2018; Alhinai et al., 2017; Lee et al., 2016; Zhang et al., 2011). The dissolution of polymer thickeners in gases can cause a series of gas properties changes such as IFT reduction, gas diffusivity coefficient improvement, and viscosity enhancement, which can promote the gravity drainage mechanism in the gas invaded zone. Therefore, in this study, this new approach was considered to investigate the effect of gas thickener on gravity drainage mechanism in the gas invaded zone. Furthermore, polymer thickeners can improve gas characteristics in two ways: 1) by dissolving heavy polymers (high molecular weight) in gases, and 2) by dissolving the small molecules as direct thickeners. The substantial amount of co-solvent (toluene) in the case of heavy gas thickeners, on the other hand, is troublesome and makes field application of this mixture unfeasible. Furthermore, fluorous-based thickeners with high molecular weights are still the only agents shown to dissolve in CO_2 without the need of a co-solvent. Therefore, except for the fluorous based thickeners, it is adequate to utilise low molecular weight thickeners (without adding co-solvents), as these are more economically agents during gas-based enhanced oil recovery (Enick et al., 2012 and 2018; Dhuwe et al., 2016). Though, according to previous studies, it was indicated that several gas thickeners such as poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVOH), poly(styrene) (PS), poly(phenylene oxide) (PPO), poly(acrylic acid) (PAA), poly(hydroxy alkanoates) (PHAA), poly(vinyl acetate) (PVAC), and poly(isobutylene) (PIB), are seriously CO_2-phobic agents. On the contrary, poly(dimethyl siloxane) (PDMS) and poly(fluoroacrylate) (PFA) are significantly CO_2-philic candidates (Xu et al., 2001; Kikic et al., 2009; Mohamed et al., 2011; Enick et al., 2012 and 2018; Zaberi et al, 2020; Mao et al., 2013; Talebian et al., 2014; Gandomkar et al., 2021). Therefore, in this study, PFA was used as a CO_2-philic gas thickener to improve the gravity drainage mechanism during gas injection in the gas invaded zone. PFA is an amorphous, viscous, clear homopolymer that dissolves in CO_2 at temperatures and pressures that are appropriate for CO_2-assisted oil recovery. Furthermore, there is no extensive investigation of the mass transfer process in the literature for CO_2-PFA thickener injection. Therefore, the goal of this paper is to recognize the governing oil-recovery mechanisms during CO_2 thickener injection in the gas invaded zone such as CO_2 diffusion coefficient, IFT, and gravity drainage.

Materials and methods

- **Rock and fluid properties**

All laboratory experiments employed reservoir crude oil with an API of 32 from one of the Middle Eastern oil fields. The oil filtration was performed to separate particles and impurities from the oil to reduce any experimental complications. In addition, original formation water (172000 ppm) was considered for gravity drainage tests. The properties of both formation water and reservoir crude oil are reported in Table 1. Also, the carbonate reservoir rock was used for gravity drainage and CO_2 diffusion coefficients tests. The chemical composition of carbonate rock was determined using the XRD (X-Ray Diffraction) technique. According to the observations, the crushed material contains roughly 80 % calcite ($CaCO_3$), 11 % dolomite ($CaMg(CO_3)_2$), 5 % anhydrate ($CaSO_4$) and 4% clay. The corresponding error values for the XRD results were lower than ± 0.5 %. In addition, during the gravity drainage and gas diffusion coefficient processes, the connate water saturation and the wettability of the core is set to those of their reservoir conditions.

Table 1

- **Cloud point measurement**

In this study, the poly(fluoroacrylate) gas thickener was synthesized by our team following the synthesis that has been previously described in detail elsewhere (Zaberi et al., 2020); the average molecular weight of the polymer was 550000 g/mol. PFA is a CO_2-philic agent which is monomer based and has six fluorinated carbons (not eight), thus eradicating the environmental concerns that are associated with possible degradation products. The gas thickeners solubility in CO_2 was measured by the HPHT visual cell described in our previous works (Gandomkar et al., 2020a, 2020b; Azizkhani and Gandomkar, 2019). However, a specific amount of PFA must be weighed and injected into the window cell first. The sample was then given a certain amount of carbon dioxide to achieve the appropriate composition. A magnetic stirrer was utilised to create a revolving magnetic field from a pressurised mixture with a constant overall composition (2000 rpm). It was repeated until the window cell produced transparent, single-phase solutions at a suitable temperature and pressure. Finally, all samples were subjected to pressure reductions at intervals of 20 psi. The equilibrium condition took roughly two hours to identify any visual changes, and the poor solubility thickeners may take more time. Generally, the cloud point pressures of gas/thickeners in the fog form were determined in the bulk sample by visual monitoring. The measurements were taken at least three times, with a ±5 psi repeatability. This process was implemented for different PFA concentrations such as 5000, 10000, 20000, and 30000 ppm. Next, the mixtures were used for all experiments, such as IFT measurements, CO_2 diffusion coefficient calculations, and gravity drainage tests.

- **IFT measurement**

The interfacial tension of oil/CO_2 and oil/CO_2-PFA were measured using the HPHT IFT 700 equipment. The pendant drop technique is state of the art and precise method for determining the IFT. During IFT measurements, a drop of oil is formed from the capillary needle's tip, which CO_2 or CO_2-PFA bounds at the reservoir conditions (P_{res}=3000 psi and T_{res} = 100 ^oC). Furthermore, the IFT error was computed using the standard deviation of four repeat measurements of each mixture and was around 0.1 (Gandomkar et al., 2020b; Azizkhani and Gandomkar, 2019).

- **CO_2 diffusion coefficients measurement in the matrix-fracture system**

Figure 1 shows a schematic design of the experimental setup for determining CO_2 diffusion coefficients. Diffusion cell, gas/oil supply system, HPLC pump, data gathering system, and temperature maintenance system were the primary components. The fluids and porous media were held in a diffusion cell with an ID of 5 cm and a depth of 10 cm. The diffusion cell was built to withstand pressures of up to 8000 psi and temperatures of up to 150^{o}C. In this study, the gas thickener or CO_2 diffusivity coefficients in bulk oil and porous media are measured in the same diffusion cell. Therefore, for the diffusivity of the gas in the oil, the diffusion cell is filled with gas thickeners (or CO_2) and oil with a suitable contact interface between the oil and gas thickeners. This scenario was created to test diffusivity without the use of porous media. In addition, a core that was initially saturated was inserted into the diffusion cell in the instance of gas diffusivity in porous media. As a result, the annulus space provided a larger region for gas diffusion into the core. It simulating the situation in which CO_2/gas thickeners are injected into gas invaded zone. In the case of the bulk oil phase, all the containers were cleaned, and then all cylinders were vacuumed for two hrs. After that, a required volume of oil was pumped into the diffusion cell. Gas thickeners or CO_2 were transferred to a cylinder, and then the HPLC pump pressurised it to the desired pressure. The system was maintained at a desirable temperature for 2 hrs. At the beginning of the diffusion test, the pressurised gas thickeners or CO_2 was transferred to the diffusion cell. The pressure was logged by the pressure transducer connected to data acquisition in the cell. When the diffusion process achieved a steady-state condition, it came to an end. Furthermore, the approach for the gas diffusion experiment on porous media was identical to scenario 1. Rather than injecting the oil straight into the cell, the diffusion cell was filled with a core saturated with formation fluids. The core saturation was carried out in a separate coreflooding setup, described in our previous works in detail (Gandomkar and Rahimpour 2015, 2017). The core is prepared during the gas diffusion coefficient process based on the idea that the core's saturation state (connate water saturation) and wettability (aging process) are restored to their original state. The core sample C5 from Table 2 was used for the gas diffusion coefficient process. The gas diffusion coefficient tests were repeated for pure CO_2 and CO_2/PFA in different PFA concentrations such as 5000, 10000, 20000, and 30000 ppm. The pressure decay method is widely used to measure the CO_2/gas thickeners diffusion coefficient and thus was applied in this work (Gao et al., 2019; Li et al., 2006). The CO_2 or gas thickener diffusion coefficient will be estimated by mathematical model based on the measured instantaneous pressure data. The mathematical description of CO_2 or gas thickener diffusion in the porous medium could be defined as follows based on the Fick's law (Li et al., 2016; 2009):

$$\frac{\partial C(r,t)}{\partial t} = D_{eff}\frac{\partial^2 C(r,t)}{\partial r^2} \qquad (1)$$

The boundary and initial conditions are:

$$C(r,t) = 0 \text{ at } 0 < r < r_0 \qquad (2)$$

$$C(r,t) = 0 \text{ at } t \geq 0 \text{ and } r = r_0 \qquad (3)$$

Where C(r,t) are the gas thickener or CO_2 concentration during the diffusion process, mol.m^{3}; t is the diffusing time, s; D_{eff} is the effective diffusion coefficient, m^{2}.s^{-1}; r_0 is the core radii, m; and r is the CO_2 diffusion radius, $0 < r < r_0$, m. The analytical solution to diffusion equation is:

$$C = C_0\left[1 - \frac{2}{r_0}\sum_{n=1}^{\infty}\frac{J_0(ra_n)exp(-D_{eff}a_n{}^2t)}{a_nJ_1(r_0a_1)}\right] \qquad (4)$$

Changing equation (4) in the form of mass and integrating it with r, and then replacing the real gas equation of state (ΔPV = ZΔnRT) into equation 4, could be presented in the form of the instant pressure change among the square root of time:

$$\Delta P = \frac{4M_{\infty}ZRT\sqrt{D_{eff}}}{r_0V\sqrt{\pi}}\sqrt{t} = k\sqrt{t} \qquad (5)$$

Where K can be calculated through the simple linear regression, the gas thickener or CO_2 diffusion coefficient is determined by equation (6) (Chai et al., 2019; Li et al., 2006):

$$D_{eff} = \frac{\pi}{16}\left(\frac{r_0kV}{M_{\infty}ZRT}\right)^2 \qquad (6)$$

Where:

- ❖ r_0 : porous media's radii, m;
- ❖ k : the gradient of the pressure change v.s the square root of time;
- ❖ V: gas thickener or CO_2 volume in the annulus area between the core and the cell, m^3;
- ❖ M_∞ : CO_2 or gas thickener dissolved in the porous medium, mole;
- ❖ Z : Gas thickener or CO_2 deviation factor, dimensionless;
- ❖ R: gas constant,
- ❖ T : temperature in Kelvin.

Also, in the bulk oil phase, the molar flux of gas thickener or CO_2 diffusing into an oil column can be presented based on Fick's law (Hoteit et al., 2009; Zhang et al., 2000). The procedure is similar to the mathematical model described for porous media. Therefore, based on the Fick's law, the relationship between the pressure and time is:

$$P(t) = P_{eq} + a_1 \exp(-b_1 t) + a_2 \exp(-b_2 t) \qquad (7)$$

Where all the constants a_1, b_1, a_2, b_2 and P_{eq} can be calculated through the non-linear regression of the experimental data. After that, the gas thickener or CO_2 diffusion coefficient in the bulk oil phase can be calculated as follows:

$$D_{AB} = \frac{4 b_1 H^2}{\pi^2} \qquad (8)$$

where the liquid height in the cell is shown as H, m; and D_{AB} is the gas thickener or CO_2 diffusion coefficient, $m^2.s^{-1}$.

Figure 1

- **Gravity drainage process in gas invaded zone**

The experimental setup, shown in Figure 2, simulated the vertical gravity drainage mechanism in a matrix block-fractured system in gas invaded zone. The main parts of the experimental setup are a vertically-mounted core holder, BPR, oven, data acquisition, HPLC pump, transfer vessel, and separator. The core holder has several pressure gauges to display the critical parameters linked with oil recovery from the cores. A total length of 72.9 cm carbonate cores (4 carbonate cores) with 4 inches (10.16 cm) in diameter was centered in the middle of a core holder with an internal diameter of 11 cm; 0.84 cm larger than the carbonate core. The annular space of 0.42 cm can simulate the experimental model's vertical fracture. It should be noted that oil recovery by gravity drainage in gas invaded zone is a function of capillary continuity between matrix blocks. Several authors have addressed this phenomenon reporting different results (Firoozabadi et al., 1990, 1994; Saidi, 1991). Therefore, the horizontal fracture opening was considered 30 μm to provide the capillary continuity between blocks in fractured reservoirs. Moreover, the carbonate core samples were initially saturated by formation water (Table 2). Reservoir crude oil was then injected to create connate water saturation. The core saturation procedure was made in a self-governing coreflooding setup, described in our previous works in detail (Gandomkar and Rahimpour, 2015 and 2017; Gandomkar et al., 2013; Nematzadeh et al., 2012). During gravity drainage tests, the cores are also prepared with the intention of restoring the connate water saturation and the wettability of the core (aging process) to their reservoir conditions (Zendehboudi et al., 2011). After that, the saturated oil-wet cores were centered vertically in the middle of a core holder. The system was obtained to the desired temperature, and then gas thickener or CO_2 was inserted into the 0.42 cm wide annulus, to simulate the fractures between the core samples and core holder. The system was pressurised by gas thickener or CO_2 injection to the desired pressure, and finally, oil recovery versus time was documented. Other researchers have already used the described model to simulate the oil recovery from gas invaded zone experimentally (Schechter et al., 1996; Pooladi-Darvish et al., 2000; Babadagli et al., 2003). It should be highlighted that oil recovery by gravity drainage in gas invaded zone significantly depends on capillary and gravity forces. Therefore, to experimentally simulate the gravity drainage process in the gas invaded zone, gas thickener or CO_2 was injected from the top of the column at a constant frontal advance rate. At the same time, the capillary number was controlled to be lower than its critical value (less than 10^{-5}) to establish the capillary force dominating the flow process (Babadagli et al., 2003; Firoozabadi et al., 1990, 1994; Saidi 1991). Two different scenarios, including CO_2/PFA and pure CO_2 injection, were considered to study the impact of gas thickener on oil recovery in the gas invaded zone. In addition, the oil recovery factors were measured based on the original oil in place.

Figure 2

Table 2

Results and discussion

This study investigates the effect of CO_2-philic polymeric thickener (PFA) on the gravity drainage mechanism in the gas invaded zone during CO_2 injection through the synergy of the interfacial mechanisms. First, the dissolution of PFA in CO_2 was conducted for different PFA concentrations, 5000, 10000, 20000, and 30000 ppm, via cloud point pressure measurements. After that, these new resolutions were used for all other tests. Therefore, the effect of PFA-thickened carbon dioxide on IFT measurements was estimated at various temperatures. After that, the CO_2 diffusion coefficients in porous and non-porous media were calculated during pure CO_2 and PFA-CO_2 scenarios. Finally, the oil recovery was illustrated through a gravity drainage mechanism during CO_2 thickener injection in the gas invaded zone under reservoir conditions (i.e. T_{res} = 100 ^oC and P_{res} = 3000 psi). These results have been presented as follows.

- **The dissolution of gas thickener in CO_2**

The dissolution of PFA in CO_2 was examined by calculating cloud point pressures. The cloud point appears as the pressure at which the single-phase solutions were achieved at favourable temperature and pressure. After that, the resulting single-phase mixtures were used for all other tests in the gas invaded zone. The cloud point pressures of CO_2/PFA solutions with four different PFA concentrations, 5000, 10000, 20000, and 30000 ppm, for temperatures of 40, 70, and 100 ^oC were reported in Figure 3. The cloud point pressure measurements were 2250 to nearly 3100 psi. These results show that increasing temperature and PFA concentration generally raise the cloud point pressures. These were 2260, 2420, and 2680 psi at different temperatures of 40, 70, and 100 ^oC, respectively, for 5000 ppm PFA concentration. Also, these were 2680, 2810, 2950, and 3100 psi for different concentrations of 5000, 10000, 20000, and 30000 ppm, respectively, at 100 ^oC. The results highlighted that the lower temperatures provided higher thickeners solubility in CO_2. Moreover, the high concentrations of PFA (30000 ppm) increased the cloud point pressures to 3100 psi at 100 ^oC. In addition, Figure 4 illustrates the effect of PFA concentrations on the cloud point pressure at 40, 70, and 100 ^oC. From this result, it increases approximately linearly with increasing in PFA concentrations. Also, it showed that the cloud point pressure was higher than it by increasing the temperature at the same PFA concentration. It is known as the entropy of mixing, and it has the ability to control this condition. The density of PFA is almost unchanged with temperature, whilst the density of gas rises as temperature decreases. As a result, the density difference widens and the entropy of mixing decreases, causing the temperature to behave inversely during the thickened gas phase (Azizkhani and Gandomkar 2019). Enick et al. (2018) showed that the PFA is remarkably soluble in CO_2, requiring only about 1450 psi to dissolve 30000 ppm of PFA in CO_2 at 24°C. The main difference between their results and our measurements is referred to as PFA molecular weight and temperature conditions. However, our cloud point measurements have a good consistency with their results. PFA solubility in CO_2 was determined, and single-phase solutions were employed for all subsequent studies in the gas invaded zone. As a result, in the remaining trials in this work, the pressure was always kept above the cloud point pressure to guarantee that the PFA did not come out of the solution because of phase change.

Figure 3

Figure 4

- **The effect of gas thickener on IFT**

Karimaie et al. (2010) investigated the gravity drainage mechanism in fractured carbonate rock during gas injection in low IFT. They reported that the gas-oil gravity drainage at low IFT is an efficient oil recovery technique at secondary and tertiary injection in the gas invaded zone. Therefore, in this study, the CO_2/PFA solutions were considered to examine the performance of gas thickeners on gravity drainage by IFT reduction. The impact of PFA thickener on oil and CO_2 interfacial tension was measured at reservoir pressure (3000 psi). Also, the cloud point pressure for 30000 ppm PFA at 100 ^{o}C was higher than reservoir pressure (3100 psi). Therefore, only at this point, the IFT was conducted at a pressure higher than reservoir pressure (3200 psi) to guarantee that the PFA did not come out of the solution due to a phase change. The results (Table 3) displays that the high molecular weight of PFA can meaningfully decrease the IFT. For example, the IFT between the pure CO_2 and reservoir fluid was 56 dyne/cm, and it was lowered to 24 dyne/cm for 20000 ppm CO_2/PFA scenario at reservoir conditions. Also, the IFTs were increased by increasing temperature, but while PFA dissolved to the CO_2, it was increased lower than that compared to pure CO_2 scenarios. Moreover, Figure 5 illustrates the effect of PFA concentrations on IFTs between CO_2/PFA and reservoir crude oil at the reservoir conditions. The findings indicated that the IFTs were reduced by increasing PFA concentrations. It could be considered as a rise in gas density in the attendance of thickeners (Harrison et al., 1996). Figure 6 shows the MMPs of crude oil and CO_2/thickener estimated using the vanishing interfacial tension (VIT) approach using interfacial tension data (Ghorbani et al. 2019 and 2020; Gandomkar et al., 2020b). The MMPs were 3510 and 3320 psi for pure CO_2 and 20000 ppm PFA, respectively, at reservoir temperature. The results show that the CO_2 thickener could meaningfully decrease the minimum miscibility pressure. Consequently, the MMP for pure carbon dioxide and PFA-thickened CO_2 (20000 ppm) were more than the reservoir pressure (P_{res}=3000 psi). So the immiscible injection will happen under reservoir conditions during the gravity drainage and gas diffusion coefficient experiments.

Table 3

Figure 5

Figure 6

- **Gas diffusion in matrix block during CO_2/thickener injection**

The gas diffusion coefficient is a key parameter to control the mixing rate of the injected gas and crude oil. By injecting gas into the gas invaded zone, gas associates with the oil through diffusion, that result in change in different properties such as drop in IFT and viscosity, and oil swelling, which can improve the oil recovery in the gas invaded zone. Thus, it is vital to explore the gas diffusivity under real reservoir conditions during CO_2/PFA scenarios. Table 4 shows the gas diffusion coefficients for the CO_2–oil and CO_2/PFA–oil systems in porous media and bulk oil phase scenarios. At reservoir conditions, the pure CO_2 diffusion coefficients in the bulk oil phase and porous media were 11.8 and 0.24 * 10^{-9} $m^2.s^{-1}$, respectively. Results showed that the pure CO_2 diffusion coefficient in the bulk oil phase was higher than that in porous media. In other words, the CO_2 pressure drop in the bulk oil phase system was more significant than that in porous media, demonstrating a higher volume of CO_2 was dissolved. The enlargement of the contact area between oil and CO_2 in bulk oil phase system compared to porous media system significantly improved the gas diffusivity coefficient. Therefore, mass transfer between fracture-matrix decreases, resulting in low CO_2 reaching inside the porous media compared to the oil phase system. In the porous media case, the mass transfer was decreased due to heterogeneity compared to the bulk oil phase. CO_2 penetrates the thin oil film first and then disperses the oil in the porous media. Furthermore, the pores of varied diameters are twisted and interlinked in carbonate reservoirs due to the complex geological sedimentation processes. The path for a gas molecule to diffuse via the pores is complex and tortuous. As a result, reaching the inside porous media would take the longest, corresponding to the pressure decrease in the system (Zhang et al., 2000; Chai et al., 2019). Based on Figure 7, the CO_2 diffusion coefficients were increased during PFA/CO_2 injection in both scenarios. For example, these were 33.8 and 0.56 * 10^{-9} $m^2.s^{-1}$ for 20000 ppm polymer thickener in the bulk oil phase and porous media systems, respectively, at reservoir conditions. Renner (1988) illustrated that the diffusion coefficient is extremely reliant on both solvent and solute viscosity (oil and CO_2 respectively), that highlights the impact of temperature, pressure and fluid composition. Therefore, it can be rationalised by bearing in mind two distinctive phenomena from the aspect of the gas thickener enhanced oil recovery technique; 1) a reduction in oil viscosity due to CO_2 diffusion, and 2) increasing gas viscosity due to polymer thickener dissolution in CO_2. Additionally, these two phenomena may improve the CO_2

diffusion coefficient during CO_2/PFA injection. During the gas-based enhanced oil recovery, the porous media's properties are of great importance in analysing the gas diffusion process in a fractured-matrix system. Therefore, the relationship of CO_2 diffusion between the bulk oil phase and porous media can be described as the effective diffusion coefficient (Li et al., 2006; Hoteit et al., 2009):

$$D_{eff} = \frac{\varphi D_{bulk}}{\tau} \tag{9}$$

Where:

- D_{eff} : gas diffusion coefficient in porous media;
- D_{bulk} : gas diffusion coefficient in the bulk oil phase;
- φ : porosity;
- τ: touristy of the porous media;

Table 4

Figure 7

- **Enhanced oil recovery in gas invaded zone during CO_2/thickener injection**

Gravity drainage is one of the most critical mechanisms in gas invaded zone, and it plays a significant impact on oil recovery during gas-based methods. Moreover, the synergy of the aforementioned mechanisms on oil recovery was investigated by two different sets of gravity drainage scenarios: pure CO_2 and PFA/CO_2 (20000 ppm) injection. Figure 8 illustrates the ultimate oil recovery factor based on the gravity drainage process in the gas-vented zone at reservoir conditions. The pure CO_2 and PFA/CO_2 scenarios indicated that about 36 and 52 percent oil recovery factor was produced in the gas invaded zone during the gravity drainage process. Therefore, an incremental oil recovery of 16 percent was achieved during PFA/CO_2 compared to pure CO_2 injection in the gas invaded zone. The lower oil recovery achieved in the pure CO_2 scenario is due to a high capillary hold-up zone. The density difference and low interfacial tension between the phases also contribute to the substantial oil recovery efficiency recorded during the gravity drainage test. In this study, the gas and oil density to increase by dissolution of PFA in CO_2 and also more gas in solution, respectively which caused a change in density difference and consequently improving oil recovery. The principal force countered by the matrix capillary pressure is the density difference between pure CO_2 or CO_2/PFA in the fracture and the oil in the matrix. Furthermore, the interfacial tension between oil and CO_2/PFA lowers, resulting in a decrease in capillary hold-up. The remaining oil saturation above the new hold up zone will also diminish in this instance, especially if the interfacial tension goes below one dyne/cm (Karimaie et al., 2010). Additionally, it should be highlighted that in cases where high CO_2 solubility in the oil phase increases the oil density, the higher density leads to unavoidable natural convection and, consequently, higher oil recovery. Accordingly, the high CO_2 mass transfer and IFT reduction during the gas thickener injection compared to pure CO_2 scenario can improve the oil recovery in gas invaded zone. This is consistent with the findings of other researchers (Pedrera et al., 2002; Shahidzadeh et al., 2003).

Figure 8

Conclusion

- Lower temperatures provided higher PFA solubility in CO_2. Also, the high concentration of PFA (30000 ppm) increased the cloud point pressure to 3100 psi at 100 ^oC.
- The high molecular weight of PFA thickener could enhance the oil recovery in gas invaded zone due to a decrease in the IFTs.
- The CO_2 thickener could significantly reduce the minimum miscibility pressure and may be improved oil recovery during the gravity drainage process.

- The CO_2 pressure drop in the bulk oil phase system was more significant than that in porous media, indicating a higher amount of CO_2 diffusion coefficient.
- The mass transfer was decreased due to heterogeneity compared to the bulk oil phase during the CO_2 diffusion tests.
- The CO_2 diffusion coefficients were increased during PFA/CO_2 injection in both scenarios at reservoir conditions.
- An incremental oil recovery of 16 percent was achieved during PFA/CO_2 compared to pure CO_2 injection in the gas invaded zone.

Nomenclature

API	American Petroleum Institute
EOR	Enhanced Oil Recovery
HPHT	High Pressure-High Temperature
HPLC	High Pressure Liquid Chromatography
IFT	Interfacial Tension
MMP	Minimum Miscibility Pressure
PAA	poly(acrylic acid)
PDMS	poly(dimethyl siloxane)
PEO	poly(ethylene oxide)
PFA	poly(fluoroacrylate)
PHAA	poly(hydroxy alkanoates)
PIB	poly(isobutylene)
PPO	poly(phenylene oxide)
P_{res}	Reservoir Pressure
PS	poly(styrene)
PVAC	poly(vinyl acetate)
PVOH	poly(vinyl alcohol)
rpm	Revolutions Per Minute
T_{res}	Reservoir Temperature
VIT	Vanishing Interfacial Tension
XRD	X-Ray Diffraction

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List of Tables

Table 1

Formation water		Crude oil	
Ions	Concentrations (ppm)	Hydrocarbon Type	mole percent
Na^+	57441	N.Paraffins	36.4
Mg^{2+}	1783	Iso.Paraffins	21.5
Ca^{2+}	9704	Naphthenes	24.7
Cl^-	103021	Aromatics	15.2
HCO_3^-	28	Saturates C_{15}^+	1.2
SO_4^{2-}	6	Aromatics C_{15}^+	1.0
K^+	13	Total sum	100.0
Br^-	4	S.G (60°F), ASTM D40452	0.8
TDS (ppm)	172000	Molecular weight, g/mol, IP-86	106.3

Table 2

Carbonate cores	**Length (cm)**	**D (in)**	**PV (cc)**	**Porosity (%)**	**Permeability (md)**	**S_{wc} (%)**
C1	15.7	4	145.1	11.4	5.8	27.5
C2	17.1	4	188.5	13.6	6.4	28.3
C3	18.7	4	159.2	10.5	6.8	29.0
C4	21.4	4	196.1	11.3	7.5	28.2
C5*	6.3	1.5	7.8	10.6	6.2	27.6

*This core was used to CO_2 diffusion coefficients tests in porous media

Table 3

Injection Gas	PFA (ppm)	IFT (dyn/cm)		
		40 ºC	70 ºC	100 ºC
CO_2	0	30.0	42.0	56.0
CO_2/PFA	5000	23.0	31.0	41.0
	10000	14.0	26.0	33.0
	20000	05.0	12.0	24.0
	30000	00.5	06.0	15.0*

*IFT was conducted at pressure higher than reservoir pressure (3200 psi) to ensure that the PFA did not come out of the solution due to a phase change. Because of the cloud point pressure of these conditions (30000 ppm and 100 ºC) was higher than reservoir pressure (3100 psi).

Table 4

Scenarios	**Gas diffusion coefficients (10^{-9} $m^2.s^{-1}$)**	
	Bulk oil phase	Porous media
Pure CO_2	11.80	0.24
CO_2/PFA (5000 ppm)	21.10	0.41
CO_2/PFA (10000 ppm)	28.40	0.50
CO_2/PFA (20000 ppm)	33.80	0.56
CO_2/PFA (30000 ppm)	36.70	0.61

List of Figures

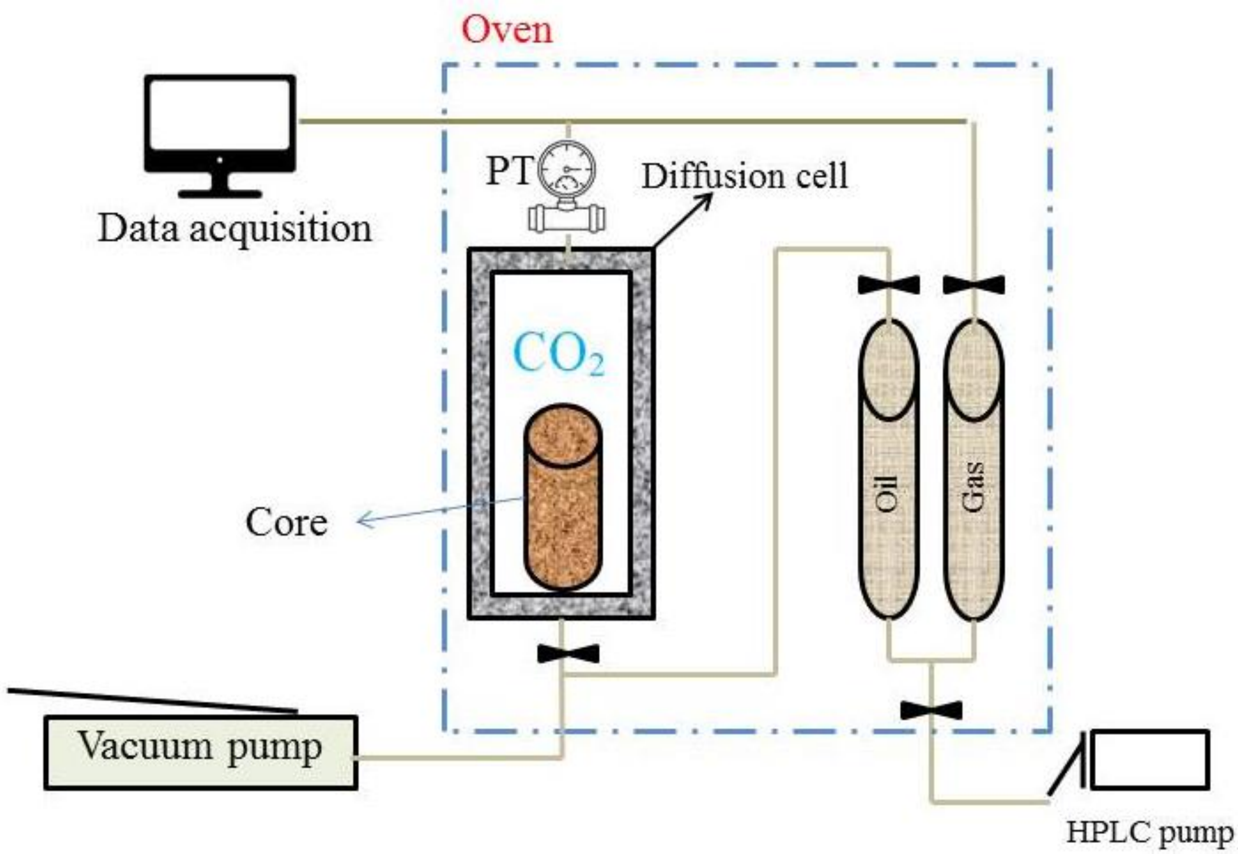
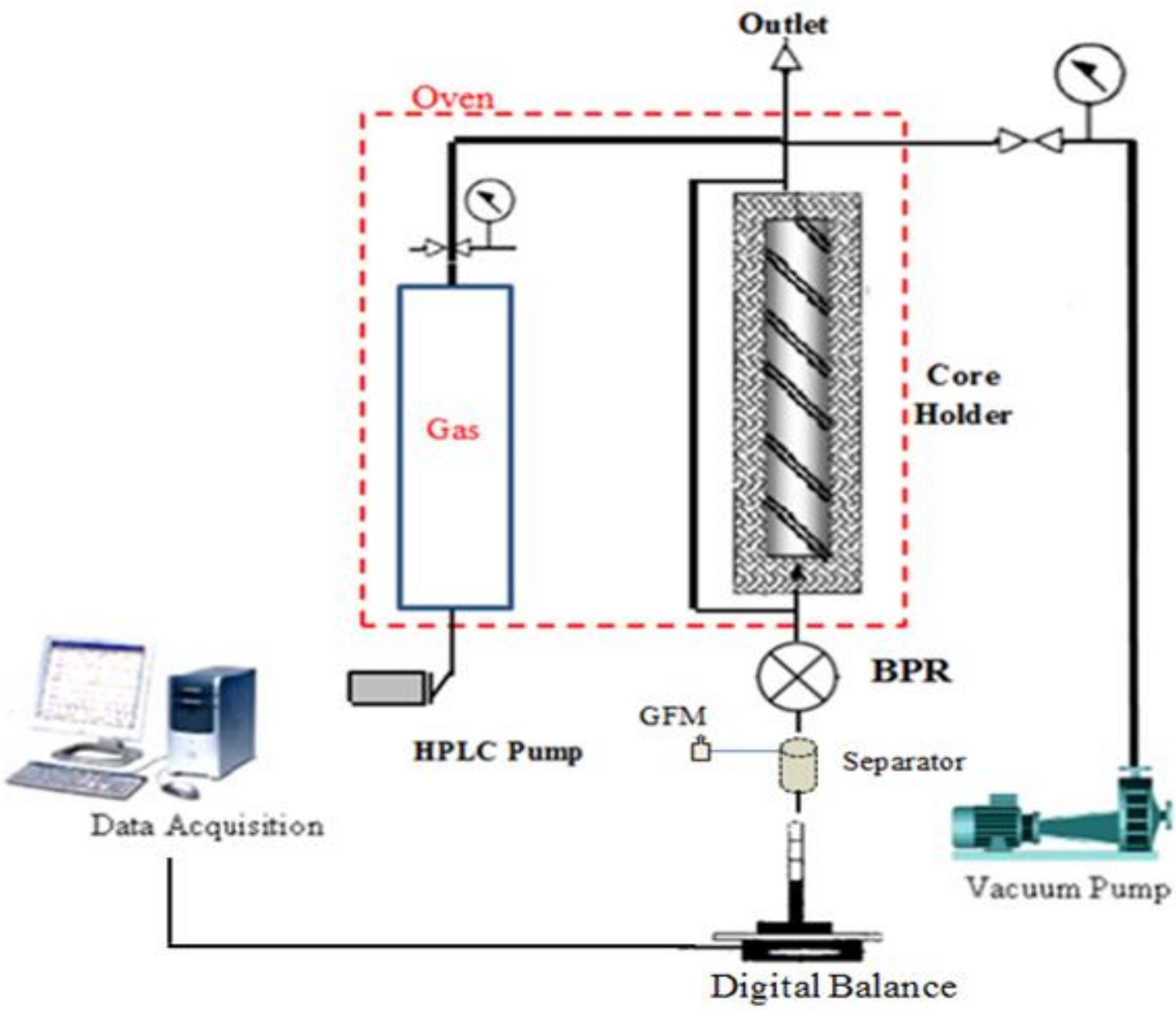

Oven
Data acquisition
PT
Diffusion cell
CO_2
Core
Oil
Gas
Vacuum pump
HPLC pump

Figure 1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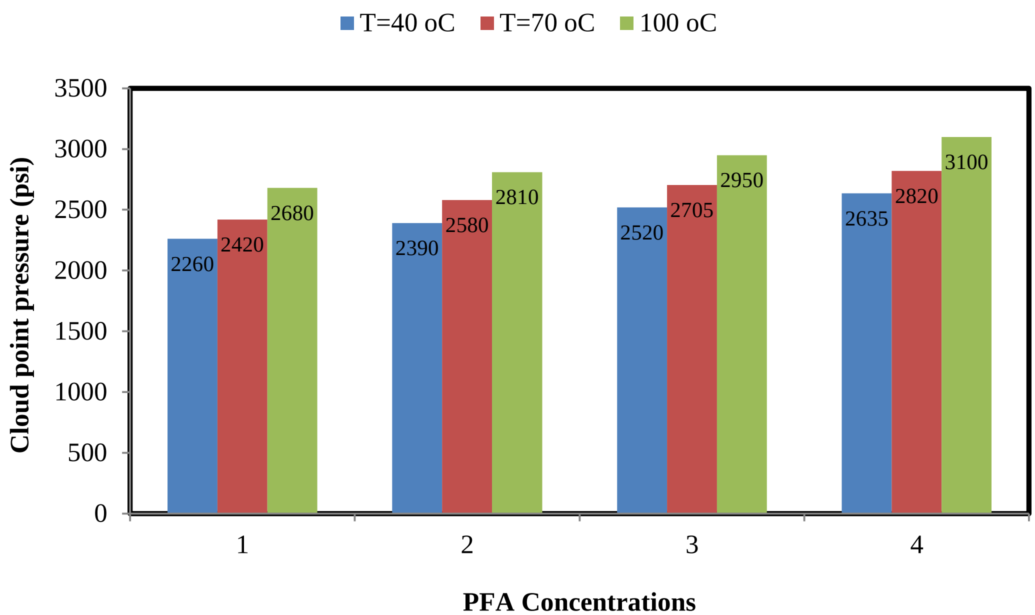
Gas
Core
Holder
BPR
GFM
Separator
HPLC Pump
Data Acquisition
Vacuum Pump
Digital Balance

Figure 2



T=40 oC
T=70 oC
100 oC
Cloud point pressure (psi)
3500
3000
2500
2000
1500
1000
500
0
2260
2420
2680
2390
2580
2810
2520
2705
2950
2635
2820
3100
1
2
3
4
PFA Concentrations

Figure 3

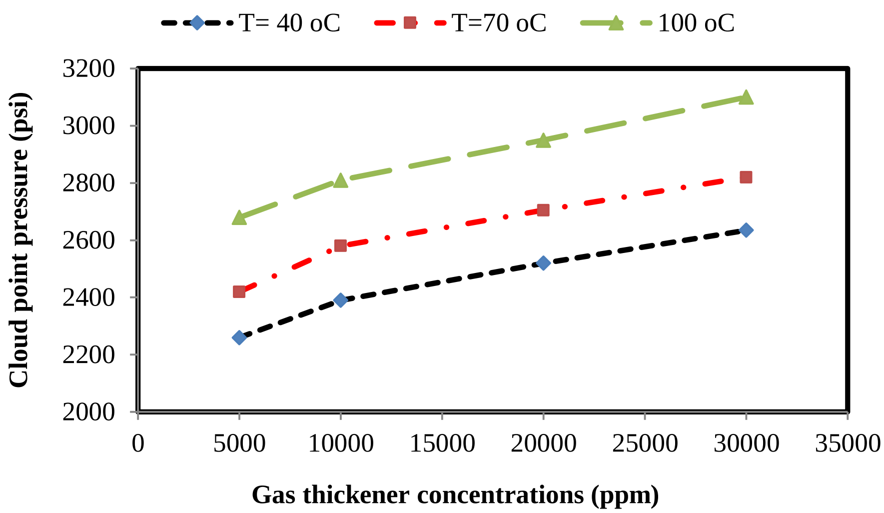
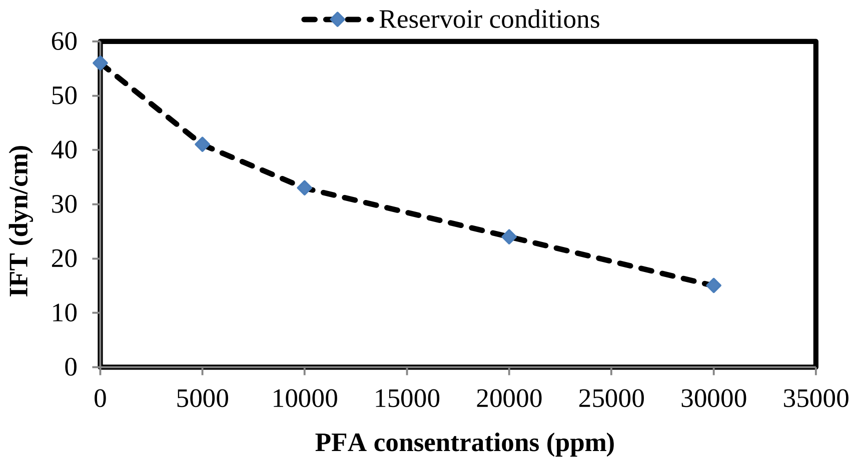

T= 40 oC
T=70 oC
100 oC
Cloud point pressure (psi)
3200
3000
2800
2600
2400
2200
2000
0
5000
10000
15000
20000
25000
30000
35000
Gas thickener concentrations (ppm)

Figure 4



Reservoir conditions
IFT (dyn/cm)
0
10
20
30
40
50
60
0
5000
10000
15000
20000
25000
30000
35000
PFA consentrations (ppm)

Figure 5

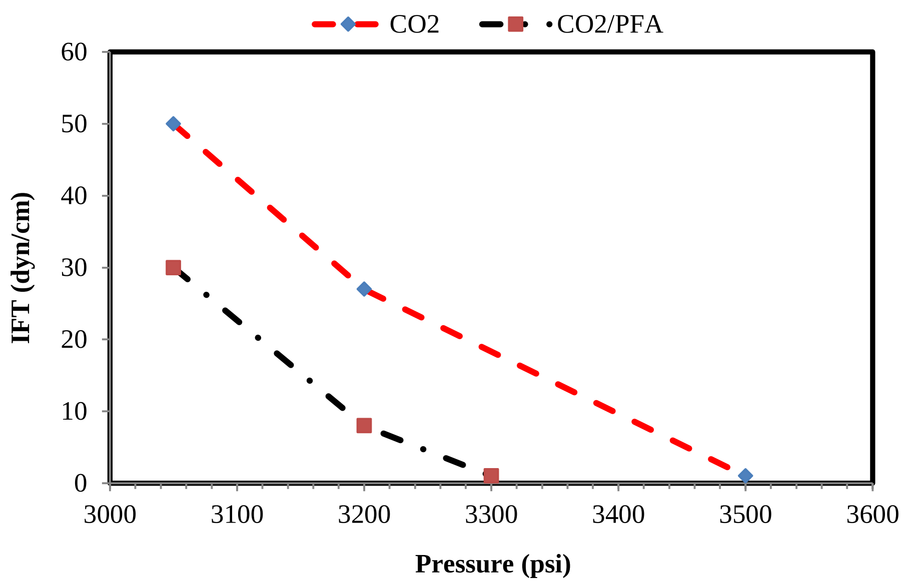

CO2
CO2/PFA
IFT (dyn/cm)
60
50
40
30
20
10
0
3000
3100
3200
3300
3400
3500
3600
Pressure (psi)

Figure 6

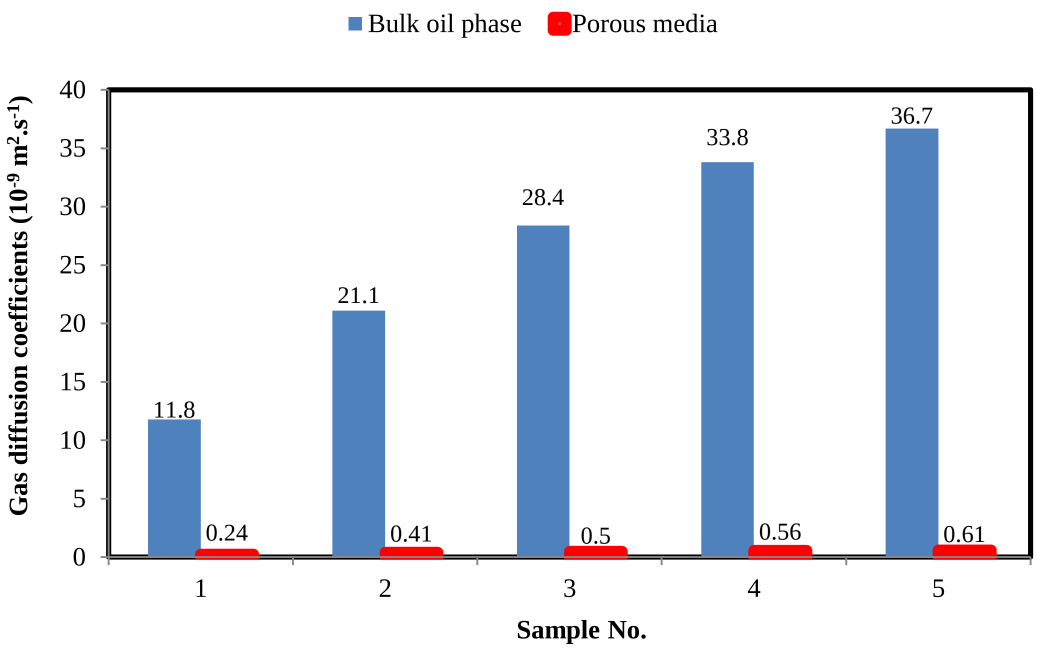

Bulk oil phase
Porous media
Gas diffusion coefficients (10^{-9} $m^2.s^{-1}$)
40
35
30
25
20
15
10
5
0
11.8
21.1
28.4
33.8
36.7
0.24
0.41
0.5
0.56
0.61
1
2
3
4
5
Sample No.

Figure 7

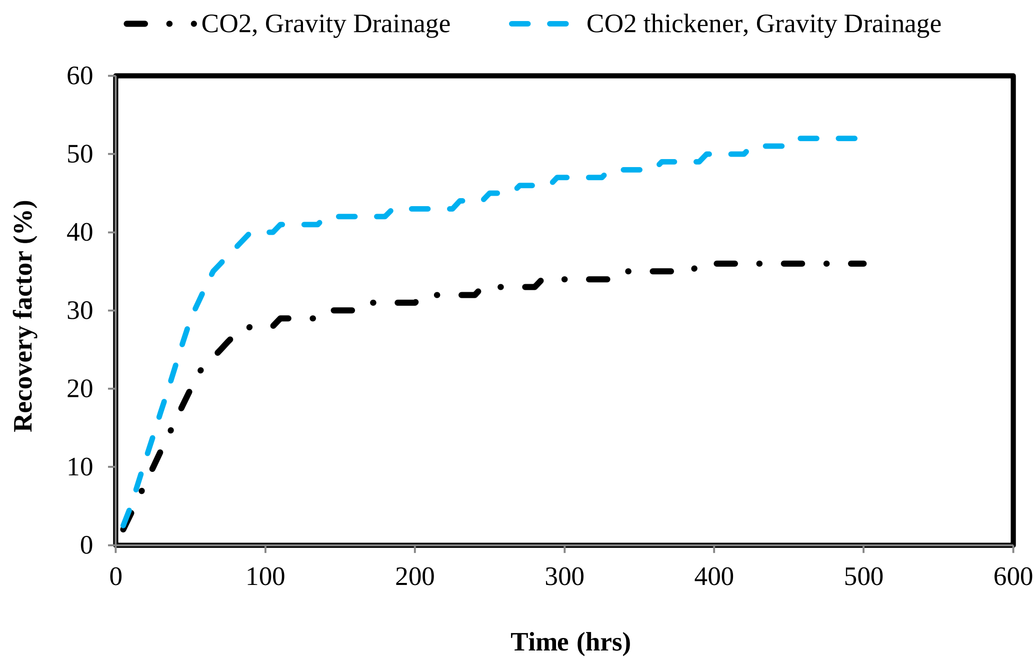

CO2, Gravity Drainage
CO2 thickener, Gravity Drainage
Recovery factor (%)
0
10
20
30
40
50
60
0
100
200
300
400
500
600
Time (hrs)

Figure 8

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Credit author statement

Asghar Gandomkar: Conceptualization, Methodology, Validation, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision, Project administration. **Hamidreza Nasriani:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Visualization. **Robert M. Enick:** Conceptualization, Methodology, Investigation, Writing - Original Draft, Writing - Review & Editing. **Farshid Torabi:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Visualization.