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

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Corresponding Author:	Asghar Gandomkar, Ph.D Shiraz University Shiraz, IRAN, ISLAMIC REPUBLIC OF
First Author:	Asghar Gandomkar, Ph.D
Order of Authors:	Asghar Gandomkar, Ph.D
	Hamid Reza Nasriani, PhD
	Robert M. Enick, PhD
	Farshid Torabi, PhD
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 CO2-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 CO2-PFA thickener (20000 ppm) could decrease the IFT from 56 to 24 dyne/cm compared to the pure CO2 scenario, improving the gravity drainage mechanism in the gas invaded zone. In addition, the CO2 diffusion coefficients were increased approximately more than two times during CO2-PFA injection in comparison with pure CO2 injection in both porous media and bulk oil phase scenarios at reservoir conditions. Also, an incremental oil recovery of 16 percent was achieved during PFA/CO2 compared to pure CO2 injection in the gas invaded zone. Therefore, gas gravity drainage is the most important mechanism once gas thickener or CO2 enters the fractures in the gas invaded zone.
Suggested Reviewers:	Dandina Rao, PhD Professor, Louisiana State University dnrao@lsu.edu
	Hamid Hosseinzade Khanamiri, PhD Research Associate, Norwegian University of Science and Technology hamid.hosseinzade@ntnu.no
	Edris Joonaki, PhD Research Associate, TUV SUD Ltd NEL ej5@hw.ac.uk
	Aliakbar Hassanpouryouzband, PhD Research Associate, The University of Edinburgh Hssnpr@ed.ac.uk
	Riyaz Kharrat, PhD Professor, University of Mining Leoben riyaz.kharrat@unileoben.ac.at

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

*Asghar Gandomkar¹, Hamid Reza Nasriani², Robert M. Enick³, Farshid Torabi⁴

 ¹Department of Petroleum Engineering, Faculty of Chemical and Material Engineering, Shiraz Branch, Islamic Azad University, Shiraz, Iran
 ²School of Engineering, Faculty of Science and Technology, University of Central Lancashire, Preston PR1 2HE, United Kingdom
 ³Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA, 15261, United States
 ⁴Faculty of Engineering and Applied Science, University of Regina, Regina, SK S4S 0A2, Canada

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14 Abstract

The rate of mass transfer between the fractures and matrix in gas invaded zone can significantly 15 influence on the oil recovery during the forced gravity drainage process. However, in this study, 16 a new approach was suggested to improve the gravity drainage process in gas invaded zone. 17 Poly(fluoroacrylate) (PFA), as a CO₂-philic thickener, was injected into the gas invaded zone to 18 illustrate the impact of interfacial mechanisms such as gas diffusion coefficient and interfacial 19 20 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, 21 22 and gravity drainage experiments. Results showed that the CO_2 -PFA thickener (20000 ppm) 23 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 CO₂ diffusion coefficients 24 were increased approximately more than two times during CO₂-PFA injection in comparison 25 with pure CO₂ injection in both porous media and bulk oil phase scenarios at reservoir 26

^{*} Corresponding Author: Email Addresses: agandomkar@shirazu.ac.ir (Asghar Gandomkar)

conditions. Also, an incremental oil recovery of 16 percent was achieved during PFA/CO₂ 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, CO₂ diffusion coefficients, Gravity drainage,
Matrix-fracture system, Cloud point pressure

33 Introduction

34 CO₂ injection in naturally fracture reservoirs is the process of storing and capturing atmospheric 35 carbon dioxide combined with enhanced oil recovery. It is one method of decreasing the amount of CO₂ in the atmosphere with the goal of reducing global climate change (Hassanpouryouzband 36 et al., 2021 and 2018). Naturally fractured carbonate reservoirs (NFRs) hold a significant portion 37 38 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 39 40 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 41 matrix and fractures, and (3) a water invaded zone with water-filled fractures and oil-filled 42 matrix (Li et al., 2018; Kharrat et al., 2021; Farrokhrouz et al., 2022). The oil flow in the gas 43 invaded zone will be largely through the matrix due to the gravity drainage mechanism. When 44 gas from gas-saturated fractures moves oil in the matrix, gas gravity drainage occurs. The gas 45 gravity drainage is derived from the difference in density of the oil and gas phases. By injecting 46 gas or gas thickeners into the fracture-matrix system, these contact with insitu fluid through 47 diffusion. This makes the oil to swell, and consequently lessens the oil viscosity, absorbs the 48

49 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 50 to fully understand these mechanisms under actual reservoir conditions (Guo et al., 2022; 51 Aghabarari et al., 2022). The diffusion coefficient is a key parameter in controlling the mixing 52 rate of the injected gas and insitu fluids. Gas dissolution will change the insitu fluid properties 53 significantly including the reduction in oil viscosity and oil swelling which consequently result 54 in the improvement of oil mobility and enhancing the oil recovery (Gao et al., 2019). In Berea 55 cores saturated with n-hexadecane, Li et al. (2006 and 2009) estimated the effective CO_2 56 57 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 58 saturation and tortuosity on CO₂ diffusivity in porous media with poor permeability. The 59 diffusion coefficients were found to be highly influenced by the oil saturation and permeability 60 of the porous medium. Gao et al. (2019) used tortuosity to link the CO₂ mass transfer coefficient 61 to the permeability of porous media. They discovered that the high tortuosity can slow down the 62 CO_2 diffusivity by restricting gas solubility. The prior measurements of diffusion coefficients, on 63 the other hand, still need to be extended by using gas thickeners. In addition, several field 64 65 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, 66 Zobeidi et al., 2018) showed that the oil recovery factor could be significantly enhanced if 67 68 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 69 reflected by considerable differences in density between the oil and gas. However, the obtained 70 71 conclusion ignores the process's numerous side consequences. Laboratory studies of gravity

72 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) 73 demonstrated that when there are no fractures in the horizontal plane and the oil must flow 74 sideways into the fracture system, the drainage rate is further lowered, resulting in lower 75 drainage rates. Ameri et al. (2013) investigated the effect of miscibility on the gas-76 77 oil gravity drainage in naturally fractured reservoirs. The findings show that injecting a nonequilibrium gas with a larger scale of solubility into the oil phase causes a zone of reduced oil 78 viscosity, leading to enhanced gravity-mediated recovery. Zobeidi et al. (2018) investigated the 79 80 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 81 forced and free-fall gravity drainage mechanism in a fractured physical model. Results reveal 82 that the forced gravity drainage performs better under controlled process conditions than the 83 free-fall gravity drainage. Karimaie et al. (2010) investigated gas-oil gravity drainage process in 84 fractured carbonate rock with low IFT and gas injection. They showed that even after water 85 injection, low IFT gravity drainage may recover a large amount of oil in NFRs. Ameri et al. 86 (2015) evaluated the rate of mass-transfer between the fractures and the matrix while a gas 87 88 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 89 recovered using an increased gravity drainage procedure. Kahrobaei et al. (2012) illustrated that 90 91 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 92 data of CO₂ diffusion coefficients and gravity drainage mechanism in hydrocarbon fluids and 93 94 crude oil is still undersupplied at the actual reservoir conditions. Also, a large portion of the

95 recorded data are within a limited temperature range ($<60 \text{ }^{\circ}\text{C}$) and pressures (<2500 psi), and the effect of gas thickeners on gas diffusivity coefficient and gravity drainage mechanism is not 96 reported. Moreover, several experimental and theoretical studies are conveyed in the literature to 97 study the efficacy of a gas or solvent injection in NFRs under static conditions. Still, few pieces 98 of work have focused on the mas transfer mechanisms between matrix and fracture under 99 dynamic conditions. In addition, the gas diffusion coefficient is still a controversial challenge 100 during gas-based EOR for improving the gravity drainage mechanism in the gas invaded zone. 101 However, the gas thickener scenario can be one of the new approaches for improving the mass 102 103 transfer processes under flow conditions between fracture and matrix. Recently, several pieces of 104 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; 105 106 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 107 coefficient improvement, and viscosity enhancement, which can promote the gravity drainage 108 109 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. 110 111 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 112 direct thickeners. The substantial amount of co-solvent (toluene) in the case of heavy gas 113 114 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 115 agents shown to dissolve in CO₂ without the need of a co-solvent. Therefore, except for the 116 fluorous based thickeners, it is adequate to utilise low molecular weight thickeners (without 117

118 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 119 studies. it indicated that several thickeners poly(ethylene 120 was gas such as 121 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 122 poly(isobutylene) (PIB), are seriously CO₂-phobic agents. On the contrary, poly(dimethyl 123 siloxane) (PDMS) and poly(fluoroacrylate) (PFA) are significantly CO₂-philic candidates (Xu et 124 al., 2001; Kikic et al., 2009; Mohamed et al., 2011; Enick et al., 2012 and 2018; Zaberi et al., 125 2020; Mao et al., 2013; Talebian et al., 2014; Gandomkar et al., 2021). Therefore, in this study, 126 PFA was used as a CO₂-philic gas thickener to improve the gravity drainage mechanism during 127 gas injection in the gas invaded zone. PFA is an amorphous, viscous, clear homopolymer that 128 129 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 130 CO₂-PFA thickener injection. Therefore, the goal of this paper is to recognize the governing oil-131 132 recovery mechanisms during CO_2 thickener injection in the gas invaded zone such as CO_2 diffusion coefficient, IFT, and gravity drainage. 133

134

135 Materials and methods

136

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 141 and reservoir crude oil are reported in Table 1. Also, the carbonate reservoir rock was used for gravity drainage and CO₂ diffusion coefficients tests. The chemical composition of carbonate 142 rock was determined using the XRD (X-Ray Diffraction) technique. According to the 143 observations, the crushed material contains roughly 80 % calcite (CaCO₃), 11 % dolomite 144 (CaMg(CO₃)₂), 5 % anhydrate (CaSO₄) and 4% clay. The corresponding error values for the 145 146 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 147 of their reservoir conditions. 148

149

Table 1

150

Cloud point measurement

151 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 152 153 molecular weight of the polymer was 550000 g/mol. PFA is a CO₂-philic agent which is 154 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 155 CO₂ was measured by the HPHT visual cell described in our previous works (Gandomkar et al., 156 2020a, 2020b; Azizkhani and Gandomkar, 2019). However, a specific amount of PFA must be 157 weighed and injected into the window cell first. The sample was then given a certain amount of 158 159 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 160 rpm). It was repeated until the window cell produced transparent, single-phase solutions at a 161 162 suitable temperature and pressure. Finally, all samples were subjected to pressure reductions at 163 intervals of 20 psi. The equilibrium condition took roughly two hours to identify any visual

164 changes, and the poor solubility thickeners may take more time. Generally, the cloud point 165 pressures of gas/thickeners in the fog form were determined in the bulk sample by visual 166 monitoring. The measurements were taken at least three times, with a ± 5 psi repeatability. This 167 process was implemented for different PFA concentrations such as 5000, 10000, 20000, and 168 30000 ppm. Next, the mixtures were used for all experiments, such as IFT measurements, CO₂ 169 diffusion coefficient calculations, and gravity drainage tests.

170

IFT measurement

The interfacial tension of oil/CO₂ and oil/CO₂-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 CO₂ or CO₂-PFA bounds at the reservoir conditions (P_{res} =3000 psi and T_{res} = 100 °C). 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).

179

• CO₂ 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°C. In this study, the gas thickener or CO_2 diffusivity coefficients in bulk oil and porous media are measured in the 186 same diffusion cell. Therefore, for the diffusivity of the gas in the oil, the diffusion cell is filled 187 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 188 addition, a core that was initially saturated was inserted into the diffusion cell in the instance of 189 gas diffusivity in porous media. As a result, the annulus space provided a larger region for gas 190 191 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 192 cylinders were vacuumed for two hrs. After that, a required volume of oil was pumped into the 193 194 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 2 195 hrs. At the beginning of the diffusion test, the pressurised gas thickeners or CO₂ was transferred 196 197 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 198 an end. Furthermore, the approach for the gas diffusion experiment on porous media was 199 200 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 201 202 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 203 on the idea that the core's saturation state (connate water saturation) and wettability (aging 204 205 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_2 206 and CO₂/PFA in different PFA concentrations such as 5000, 10000, 20000, and 30000 ppm. The 207 208 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 CO₂ or gas thickener diffusion coefficient will be estimated by mathematical model based on the measured instantaneous pressure data. The mathematical description of CO₂ or gas thickener diffusion in the porous medium could be defined as follows based on the Fick's law (Li et al., 2016; 2009):

213
$$\frac{\partial C(r,t)}{\partial t} = D_{eff} \frac{\partial^2 C(r,t)}{\partial r^2}$$
(1)

214 The boundary and initial conditions are:

215
$$C(r,t) = 0 \text{ at } 0 < r < r_0$$
 (2)

216
$$C(r,t) = 0 \text{ at } t \ge 0 \text{ and } r = r_0$$
 (3)

Where C(r,t) are the gas thickener or CO₂ concentration during the diffusion process, mol.m³; t is the diffusing time, s; D_{eff} is the effective diffusion coefficient, m².s⁻¹; r₀ is the core radii, m; and r is the CO₂ diffusion radius, $0 < r < r_0$, m. The analytical solution to diffusion equation is:

220
$$C = C_0 \left[1 - \frac{2}{r_0} \sum_{n=1}^{\infty} \frac{J_0(ra_n)exp(-D_{eff}a_n^2 t)}{a_n J_1(r_0 a_1)} \right]$$
(4)

221 Changing equation (4) in the form of mass and integrating it with r, and then replacing the real 222 gas equation of state ($\Delta PV = Z\Delta nRT$) into equation 4, could be presented in the form of the 223 instant pressure change among the square root of time:

224
$$\Delta P = \frac{4M_{\infty}ZRT\sqrt{D_{eff}}}{r_0 V \sqrt{\pi}} \sqrt{t} = k \sqrt{t}$$
(5)

225

226 Where K can be calculated through the simple linear regression, the gas thickener or CO_2 227 diffusion coefficient is determined by equation (6) (Chai et al., 2019; Li et al., 2006):

228
$$D_{eff} = \frac{\pi}{16} \left(\frac{r_0 kV}{M_{\infty} ZRT} \right)^2$$
(6)

Where:

230	• r_0 : porous media's radii, m;
231	\bigstar k : the gradient of the pressure change v.s the square root of time;
232	• V: gas thickener or CO_2 volume in the annulus area between the core and the cell, m^3 ;
233	♦ M_{∞} : CO ₂ or gas thickener dissolved in the porous medium, mole;
234	\bigstar Z : Gas thickener or CO ₂ deviation factor, dimensionless;
235	✤ R: gas constant,
236	✤ T : temperature in Kelvin.
237 238	Also, in the bulk oil phase, the molar flux of gas thickener or CO ₂ diffusing into an oil column
239	can be presented based on Fick's law (Hoteit et al., 2009; Zhang et al., 2000). The procedure is
240	similar to the mathematical model described for porous media. Therefore, based on the Fick's
241	law, the relationship between the pressure and time is:

242
$$P(t) = P_{eq} + a_1 \exp(-b_1 t) + a_2 \exp(-b_2 t)$$
(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 CO₂ diffusion coefficient in the bulk oil phase can be calculated as follows:

246
$$D_{AB} = \frac{4b_1 H^2}{\pi^2}$$
 (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, m².s⁻¹.

249 Figure 1

250

• 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, 254 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 255 cores) with 4 inches (10.16 cm) in diameter was centered in the middle of a core holder with an 256 internal diameter of 11 cm; 0.84 cm larger than the carbonate core. The annular space of 0.42 cm 257 can simulate the experimental model's vertical fracture. It should be noted that oil recovery by 258 gravity drainage in gas invaded zone is a function of capillary continuity between matrix blocks. 259 Several authors have addressed this phenomenon reporting different results (Firoozabadi et al., 260 1990, 1994; Saidi, 1991). Therefore, the horizontal fracture opening was considered 30 µm to 261 262 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 263 injected to create connate water saturation. The core saturation procedure was made in a self-264 265 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 266 drainage tests, the cores are also prepared with the intention of restoring the connate water 267 268 saturation and the wettability of the core (aging process) to their reservoir conditions 269 (Zendehboudi et al., 2011). After that, the saturated oil-wet cores were centered vertically in the 270 middle of a core holder. The system was obtained to the desired temperature, and then gas thickener or CO₂ was inserted into the 0.42 cm wide annulus, to simulate the fractures between 271 the core samples and core holder. The system was pressurised by gas thickener or CO₂ injection 272 273 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 274 experimentally (Schechter et al., 1996; Pooladi-Darvish et al., 2000; Babadagli et al., 2003). It 275 276 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 277 drainage process in the gas invaded zone, gas thickener or CO₂ was injected from the top of the 278 column at a constant frontal advance rate. At the same time, the capillary number was controlled 279 to be lower than its critical value (less than 10^{-5}) to establish the capillary force dominating the 280 flow process (Babadagli et al., 2003; Firoozabadi et al., 1990, 1994; Saidi 1991). Two different 281 scenarios, including CO₂/PFA and pure CO₂ injection, were considered to study the impact of 282 gas thickener on oil recovery in the gas invaded zone. In addition, the oil recovery factors were 283 measured based on the original oil in place. 284

285

Figure 2

286

Table 2

287 **Results and discussion**

This study investigates the effect of CO₂-philic polymeric thickener (PFA) on the gravity 288 drainage mechanism in the gas invaded zone during CO₂ injection through the synergy of the 289 interfacial mechanisms. First, the dissolution of PFA in CO₂ was conducted for different PFA 290 291 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-292 thickened carbon dioxide on IFT measurements was estimated at various temperatures. After 293 that, the CO₂ diffusion coefficients in porous and non-porous media were calculated during pure 294 CO₂ and PFA-CO₂ scenarios. Finally, the oil recovery was illustrated through a gravity drainage 295 mechanism during CO_2 thickener injection in the gas invaded zone under reservoir conditions 296 (i.e. $T_{res} = 100$ °C and $P_{res} = 3000$ psi). These results have been presented as follows. 297

298

301

• The dissolution of gas thickener in CO₂

The dissolution of PFA in CO₂ was examined by calculating cloud point pressures. The cloud 302 point appears as the pressure at which the single-phase solutions were achieved at favourable 303 304 temperature and pressure. After that, the resulting single-phase mixtures were used for all other 305 tests in the gas invaded zone. The cloud point pressures of CO₂/PFA solutions with four different 306 PFA concentrations, 5000, 10000, 20000, and 30000 ppm, for temperatures of 40, 70, and 100 °C 307 were reported in Figure 3. The cloud point pressure measurements were 2250 to nearly 3100 psi. 308 These results show that increasing temperature and PFA concentration generally raise the cloud 309 point pressures. These were 2260, 2420, and 2680 psi at different temperatures of 40, 70, and 310 100 °C, 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 100 311 312 °C. The results highlighted that the lower temperatures provided higher thickeners solubility in 313 CO₂. Moreover, the high concentrations of PFA (30000 ppm) increased the cloud point pressures to 3100 psi at 100 °C. In addition, Figure 4 illustrates the effect of PFA concentrations on the 314 cloud point pressure at 40, 70, and 100 °C. From this result, it increases approximately linearly 315 with increasing in PFA concentrations. Also, it showed that the cloud point pressure was higher 316 317 than it by increasing the temperature at the same PFA concentration. It is known as the entropy 318 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, 319 the density difference widens and the entropy of mixing decreases, causing the temperature to 320 321 behave inversely during the thickened gas phase (Azizkhani and Gandomkar 2019). Enick et al. (2018) showed that the PFA is remarkably soluble in CO₂, requiring only about 1450 psi to 322

dissolve 30000 ppm of PFA in CO₂ 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 CO₂ 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.

330

Figure 3

331

Figure 4

332

• The effect of gas thickener on IFT

Karimaie et al. (2010) investigated the gravity drainage mechanism in fractured carbonate rock 333 during gas injection in low IFT. They reported that the gas-oil gravity drainage at low IFT is an 334 efficient oil recovery technique at secondary and tertiary injection in the gas invaded zone. 335 Therefore, in this study, the CO₂/PFA solutions were considered to examine the performance of 336 gas thickeners on gravity drainage by IFT reduction. The impact of PFA thickener on oil and 337 CO₂ interfacial tension was measured at reservoir pressure (3000 psi). Also, the cloud point 338 pressure for 30000 ppm PFA at 100 °C was higher than reservoir pressure (3100 psi). Therefore, 339 340 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 341 (Table 3) displays that the high molecular weight of PFA can meaningfully decrease the IFT. For 342 343 example, the IFT between the pure CO₂ and reservoir fluid was 56 dyne/cm, and it was lowered to 24 dyne/cm for 20000 ppm CO₂/PFA scenario at reservoir conditions. Also, the IFTs were 344

345	increased by increasing temperature, but while PFA dissolved to the CO ₂ , it was increased lower
346	than that compared to pure CO_2 scenarios. Moreover, Figure 5 illustrates the effect of PFA
347	concentrations on IFTs between CO ₂ /PFA and reservoir crude oil at the reservoir conditions. The
348	findings indicated that the IFTs were reduced by increasing PFA concentrations. It could be
349	considered as a rise in gas density in the attendance of thickeners (Harrison et al., 1996). Figure 6
350	shows the MMPs of crude oil and CO2/thickener estimated using the vanishing interfacial
351	tension (VIT) approach using interfacial tension data (Ghorbani et al. 2019 and 2020;
352	Gandomkar et al., 2020b). The MMPs were 3510 and 3320 psi for pure CO ₂ and 20000 ppm
353	PFA, respectively, at reservoir temperature. The results show that the CO ₂ thickener could
354	meaningfully decrease the minimum miscibility pressure. Consequently, the MMP for pure
355	carbon dioxide and PFA-thickened CO ₂ (20000 ppm) were more than the reservoir pressure
356	$(P_{res}=3000 \text{ psi})$. So the immiscible injection will happen under reservoir conditions during the
357	gravity drainage and gas diffusion coefficient experiments.

Table 3

359

360

Figure 6

Figure 5

• Gas diffusion in matrix block during CO₂/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 CO₂/PFA scenarios. Table 4 shows the gas diffusion coefficients for the CO₂–oil and CO₂/PFA–oil systems in porous media and bulk oil 368 phase scenarios. At reservoir conditions, the pure CO_2 diffusion coefficients in the bulk oil phase and porous media were 11.8 and $0.24 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, respectively. Results showed that the pure 369 CO₂ diffusion coefficient in the bulk oil phase was higher than that in porous media. In other 370 371 words, the CO₂ pressure drop in the bulk oil phase system was more significant than that in porous media, demonstrating a higher volume of CO₂ was dissolved. The enlargement of the 372 contact area between oil and CO₂ in bulk oil phase system compared to porous media system 373 significantly improved the gas diffusivity coefficient. Therefore, mass transfer between fracture-374 matrix decreases, resulting in low CO_2 reaching inside the porous media compared to the oil 375 phase system. In the porous media case, the mass transfer was decreased due to heterogeneity 376 377 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 378 379 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 380 media would take the longest, corresponding to the pressure decrease in the system (Zhang et al., 381 382 2000; Chai et al., 2019). Based on Figure 7, the CO₂ diffusion coefficients were increased during PFA/CO₂ injection in both scenarios. For example, these were 33.8 and 0.56 * 10^{-9} m².s⁻¹ for 383 384 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 385 on both solvent and solute viscosity (oil and CO₂ respectively), that highlights the impact of 386 temperature, pressure and fluid composition. Therefore, it can be rationalised by bearing in mind 387 two distinctive phenomena from the aspect of the gas thickener enhanced oil recovery technique; 388 1) a reduction in oil viscosity due to CO₂ diffusion, and 2) increasing gas viscosity due to 389 polymer thickener dissolution in CO₂. Additionally, these two phenomena may improve the CO₂ 390

diffusion coefficient during CO₂/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 CO₂ 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):

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

397 Where:

398	*	D _{eff} : gas diffusion coefficient in porous media;
399	*	D _{bulk} : gas diffusion coefficient in the bulk oil phase;
400	*	φ : porosity;
401	*	τ : touristy of the porous media;
402		Table 4

403

Figure 7

• Enhanced oil recovery in gas invaded zone during CO₂/thickener injection

Gravity drainage is one of the most critical mechanisms in gas invaded zone, and it plays a 405 significant impact on oil recovery during gas-based methods. Moreover, the synergy of the 406 aforementioned mechanisms on oil recovery was investigated by two different sets of gravity 407 drainage scenarios: pure CO₂ and PFA/CO₂ (20000 ppm) injection. Figure 8 illustrates the 408 ultimate oil recovery factor based on the gravity drainage process in the gas-vented zone at 409 reservoir conditions. The pure CO₂ and PFA/CO₂ scenarios indicated that about 36 and 52 410 percent oil recovery factor was produced in the gas invaded zone during the gravity drainage 411 412 process. Therefore, an incremental oil recovery of 16 percent was achieved during PFA/CO₂ compared to pure CO₂ injection in the gas invaded zone. The lower oil recovery achieved in the 413

414 pure CO_2 scenario is due to a high capillary hold-up zone. The density difference and low 415 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 416 417 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 418 matrix capillary pressure is the density difference between pure CO₂ or CO₂/PFA in the fracture 419 420 and the oil in the matrix. Furthermore, the interfacial tension between oil and CO₂/PFA lowers, resulting in a decrease in capillary hold-up. The remaining oil saturation above the new hold up 421 422 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 423 CO₂ solubility in the oil phase increases the oil density, the higher density leads to unavoidable 424 natural convection and, consequently, higher oil recovery. Accordingly, the high CO₂ mass 425 transfer and IFT reduction during the gas thickener injection compared to pure CO₂ scenario can 426 improve the oil recovery in gas invaded zone. This is consistent with the findings of other 427 researchers (Pedrera et al., 2002; Shahidzadeh et al., 2003). 428

429

Figure 8

- 430 Conclusion
- Lower temperatures provided higher PFA solubility in CO₂. Also, the high concentration
 of PFA (30000 ppm) increased the cloud point pressure to 3100 psi at 100 °C.
- The high molecular weight of PFA thickener could enhance the oil recovery in gas
 invaded zone due to a decrease in the IFTs.
- The CO₂ thickener could significantly reduce the minimum miscibility pressure and may
 be improved oil recovery during the gravity drainage process.

437	•	The CO_2 pressure drop in the bulk oil phase system was more significant than that in
438		porous media, indicating a higher amount of CO ₂ diffusion coefficient.
439	•	The mass transfer was decreased due to heterogeneity compared to the bulk oil phase
440		during the CO ₂ diffusion tests.
441	•	The CO ₂ diffusion coefficients were increased during PFA/CO ₂ injection in both
442		scenarios at reservoir conditions.
443	•	An incremental oil recovery of 16 percent was achieved during PFA/CO ₂ compared to
444		pure CO ₂ injection in the gas invaded zone.
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460 Nomenclature

461	API	American Petroleum Institute
462	EOR	Enhanced Oil Recovery
463	HPHT	High Pressure-High Temperature
464	HPLC	High Pressure Liquid Chromatography
465	IFT	Interfacial Tension
466	MMP	Minimum Miscibility Pressure
467	PAA	poly(acrylic acid)
468	PDMS	poly(dimethyl siloxane)
469	PEO	poly(ethylene oxide)
470	PFA	poly(fluoroacrylate)
471	PHAA	poly(hydroxy alkanoates)
472	PIB	poly(isobutylene)
473	PPO	poly(phenylene oxide)
474	Pres	Reservoir Pressure
475	PS	poly(styrene)
476	PVAC	poly(vinyl acetate)
477	PVOH	poly(vinyl alcohol)
478	rpm	Revolutions Per Minute
479	T _{res}	Reservoir Temperature
480	VIT	Vanishing Interfacial Tension
481	XRD	X-Ray Diffraction

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661 temperatures

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- 663 systems in different PFA concentrations at reservoir conditions

Table 1

For	mation 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	
\mathbf{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

Carbonata aaroo	Length	D	PV	Porosity	Permeability	Swc
Carbonate cores	(cm)	(in)	(cc)	(%)	(md)	(%)
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 CO₂ diffusion coefficients tests in porous media

Table 3

Injustion Gas	PFA (ppm)	IFT (dyn/cm)		
Injection Gas		40 °C	70 °C	100 °C
CO ₂	0	30.0	42.0	56.0
	5000	23.0	31.0	41.0
	10000	14.0	26.0	33.0
CO2/PFA	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 °C)
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	

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- 826 CO₂/PFA (20000 ppm); 5: CO₂/PFA (30000 ppm)
- 827 **Figure 8**: The ultimate oil recovery factor during gravity drainage process in gas invaded zone
- for pure CO₂ and PFA/CO₂ (20000 ppm) scenarios

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■ T=40 oC ■ T=70 oC ■ 100 oC

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Figure 7





Declaration of interests

 \boxtimes 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,