Experimental Analysis and Performance Investigation of Immiscible Super-Critical CO_2 Flooding Processes in Tight Oil Reservoir

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ABSTRACT

CO_2 flooding, a promising technique of enhanced oil recovery, is widely used for its capability of boosting oil recovery, and reducing greenhouse gas emissions. In this study, the oil displacement performance of supercritical CO_2 is tested in laboratory under immiscible flooding. The results show that: Supercritical CO_2 improves oil recovery, by virtue of its low viscosity, high diffusivity, and easy dissolution. With the same pore volume (PV), supercritical CO_2 flooding significantly boosted the oil recovery factor. The factor reached the maximum, when almost 1.5PV of CO_2 was injected. As CO_2 moved from the gas phase to the supercritical state, the oil displacement efficiency increased by 10%. To obtain the same oil recovery factor, non-supercritical flooding needed to inject more CO_2 than supercritical flooding. Light hydrocarbon components (C_{1-7}) in crude oil were gradually extracted before CO_2 breakthrough, while heavy hydrocarbon components (C_{7+}) were extracted mainly after CO_2 breakthrough. In addition, supercritical CO_2 flooding extracted more intermediate hydrocarbons than critical CO_2 flooding. To sum up, supercritical flooding outperforms non-supercritical flooding in injection performance, oil displacement efficiency, and oil exchange rate.

1. INTRODUCTION

CO_2 flooding, a promising technique of enhanced oil recovery, is widely used for its capability of boosting oil recovery, and reducing greenhouse gas emissions [1, 2]. CO_2 is mutually soluble with crude oil: the light hydrocarbons from the oil can dissolve in CO_2, and the gas can dissolve in the oil. As a result, the injection of CO_2 can significantly reduce the viscosity of crude oil [3, 4]. Injecting CO_2 into the reservoir can greatly expand the volume of crude oil by 10% to 100% [5]. The volume expansion increases the elastic energy of the formation, and makes the oil movable. The rise of movability boosts the efficiency of oil displacement, thereby improving the final recovery of the reservoir [6]. Under a certain pressure, CO_2 can vaporize and extract various light hydrocarbons from the crude oil. Then, the crude oil will have a lower relative density, which contributes to oil recovery [7]. The light hydrocarbons are extracted and vaporized earlier than the heavy hydrocarbons up to the range C30. Extraction and vaporization are important to miscible CO_2 flooding [7], i.e., dissolving a large amount of CO_2 in crude oil. The first step of miscible CO_2 flooding is to dissolve the gas in water, forming carbonated water [8, 9]. The carbonated water is 20% more viscous than the original water. The high viscosity reduces the mobility of the water, improves the oil-water mobility ratio, and expands the sweeping volume [10]. Carbonated water can also improve the permeability of the reservoir.

CO_2-based enhanced oil recovery is affected by pressure, temperature, oil composition, water saturation, permeability, and reservoir properties [9-14]. In a specific reservoir, injection pressure directly bears on the effect of oil displacement. Contraposing immiscible CO_2 flooding, Nobakht et al. [15] found that the ultimate efficiency of enhanced oil recovery is almost independent of the injection pressure, if the injection pressure is higher than a threshold. Cao and Gu [7] conducted a series of CO_2 core flooding experiments under different pressures (immiscible, near-miscible, and miscible conditions), and analysed the physicochemical characterization of produced oils and gases. The results show that the produced oil becomes heavier with the growing pore volume (PV) of injected CO_2 at low injection pressure. The opposite trend was observed at a high injection pressure. With the rise of injection pressure, CO_2 could extract some intermediate hydrocarbons. Overall, the existing studies concentrate on the difference between miscible flooding and immiscible flooding [16].

Owing to the physiochemical properties of CO_2, the phase state of CO_2 in the process of immiscible flooding can be divided into supercritical state and non-supercritical state. Supercritical state, a special state between water and gas phases, has many special properties in density, viscosity, and diffusivity. CO_2 becomes a supercritical fluid, when the pressure and temperature surpass the critical level of 7.39 MPa and 31.05°C, respectively. Supercritical CO_2 has a similar density as fluid, which is about one hundred times denser than gas. Meanwhile, the viscosity of supercritical CO_2 is like that

of gas and two orders of magnitude smaller than that of fluid. Supercritical CO_2 boasts good properties in mass transfer and dissolution. The solubility of supercritical CO_2 is very high, about 100 times that of liquid. In addition, supercritical CO_2 can propagate easily in porous media, because its surface tension is zero. Furthermore, the high temperature and pressure sensitivity of supercritical CO_2 enable flexible control of the temperature and pressure in the production process. Einstein et al. [17] observed that supercritical CO_2 flooding in condensate reservoirs could increase the condensate oil recovery factor to above 65%, and realize a high content of C_{5+} hydrocarbons in the produced components. Al-Abri and Amin [18] injected supercritical CO_2 and methane separately into condensate oi, and compared the oil recovery factors of the two approaches. The comparison shows that supercritical CO_2 flooding delays the breakthrough of gas injection, and pushes up the recovery factor. Moreover, the high solute solubility of supercritical CO_2 boosts the total mass transfer rate, as well as the internal diffusion and external diffusion in porous media [19-22]. In general, there are not many studies on the impact of supercritical and non-supercritical CO_2 on oil displacement, which hinders pressure optimization under immiscible flooding.

Through experiments, this study explores the CO_2 flooding features under the condition of immiscible flooding. Five groups of core displacement experiments were carried out, with CO_2 in non-supercritical, near-supercritical, and supercritical states. Meanwhile, the physicochemical features of the produced oil and gas were analysed during core flooding experiments, laying an experimental basis for future research on CO_2 immiscible flooding.

2. EXPERIMENTS

2.1 Materials
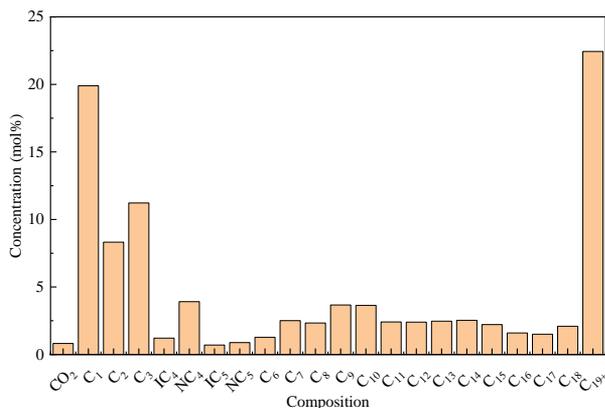
Figure 1. Concentration of components in reservoir fluid

The reservoir fluid (live oil) was reconstituted at a relevant saturation pressure to approximate the current reservoir saturation pressure of 7.45 MPa and gas-to-oil ratio (GOR) of 67.2 m^3/t. At the saturation pressure and temperature T= 43.75℃, the density and viscosity of the live oil sample were measured to be ρ_{oil}=804.9 kg/m^3, and μ_{oil}=2.6 mPa·s, respectively. Through slim-tube experiments, the minimum miscible pressure was measured as 22.15MPa. Then, the synthetic brine was prepared according to the ion compositional of the brine water in the formation (Table 1). The CO_2 used has a minimum purity of 99.998 mol%. The

properties of CO_2 at different pressures and T =43.75 °C were calculated using CMG WinProp (version: 2017.10) (Computer Modelling Group Ltd., Canada), using the Peng-Robinson equation of state [23]. Several tight nature sandstones were drilled from the reservoir core plugs. Figure 1 shows the concentration of components in the reservoir fluid.

Table 1. Ion composition of formation brine water

Composition	Na^+	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	Total
Concentration (mg/L)	25,315	122	4,906	496	48,839	385	80,063

2.2 Gas chromatography (GC) analysis on original oil, produced oil, and produced gas

The composition of the original oil, the produced oil, and the produced gas were analysed through gas chromatography (GC), using the SCION 436-GC system (Techcomp Instruments, United States). The analysis accuracy varies with the mole percentage of each component in the sample. The overall mole percentage of the gaseous HCs in the produced gas was measured using the GC system.

2.3 CO_2 core flooding experiments

Figure 2 is the sketch map of the high-pressure CO_2 core flooding apparatus. The experimental process can be briefly described as follows:
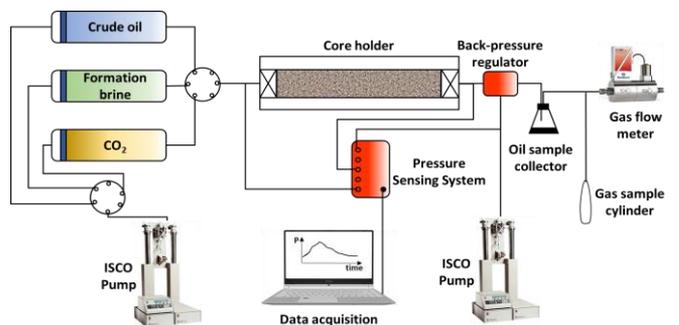
Figure 2. High-pressure CO_2 core flooding apparatus

The sandstone core was cleaned and dried, before being placed into a core holder and vacuumed for 12h. Then, the formation brine was injected to measure the porosity of the core, and injected at different flow rates (0.05-1 mL/min) to measure the permeability of the core. As shown in Table 2, the measured porosity and permeability fell in the range of ϕ=9.87–12.31%, and k=0.94-1.98 mD, respectively. Afterwards, the reservoir live oil was injected through the initially brine-saturated core at a constant flow rate (0.1mL/min) until no more water was produced, i.e., the initial oil and connate water were saturated. Next, a series back-pressure regulator (BPR) (Core Laboratories, The Netherlands) was set above bubble pressure (8MPa) for the saturated oil, to prevent oil and gas separation. In addition, to simulate the wettability of the reservoir condition, the core after the saturated oil was aged at the reservoir temperature (43.75℃) for 48h. Table 2 shows the saturation of the connate water and initial oil. Before injecting CO_2, the BPR was set at a constant pressure according to the scheme in Table 2. The gas was injected at a constant pressure above the BPR 1 MPa. A total of 2PV CO_2 was injected until no more oil was produced, or the GOR reached 10,000. During CO_2 core

flooding experiments, the produced oil samples and gas samples at different PVs of injected CO_2 were collected to measure the gas content.

Table 2. Physical properties of cores, experimental conditions, and results of five core flooding experiments

Test number	P_{inj} (MPa)	P_{out} (MPa)	Permeability (mD)	Porosity (%)	Pore volume (mL)	S_{oi} (%)	S_{wc} (%)	CO_2 BT (PV)	Oil RF at CO_2 BT	CO_2 RF
1	7	6	1.54	11.72	17.28	59.70	40.30	0.187	11.73	42.81
2	7.3	6.3	1.65	11.94	17.37	59.22	40.78	0.122	14.80	44.75
3	7.8	6.8	0.94	9.87	14.53	61.94	38.06	0.102	20.35	47.69
4	8.5	7.5	1.98	12.31	18.04	62.28	37.72	0.256	26.22	50.86
5	8.8	7.8	1.27	11.2	16.45	61.75	38.25	0.287	27.52	51.94

Note: BT and RF are short for breakthrough and recovery factor, respectively.

3. RESULTS AND DISCUSSION

3.1 CO_2 oil recovery factor

The CO_2 core flooding experiments were carried out in series at five different injection pressures, under the non-supercritical, near-supercritical, and supercritical conditions. The physical properties of cores, experimental conditions, and results of five core flooding experiments are summed up in Table 2. The injection pressure of the five experiments were set in the range of 7-8.8MPa. Specifically, Tests 1 and 2 are non-supercritical CO_2 flooding processes (CO_2 belonging to the gas phase), Tests 3 is a near-supercritical CO_2 flooding process, and Test 4 and 5 are supercritical CO_2 flooding processes.

Figure 3 shows the variation of oil recovery factor at different injection pressures. As expected, with the growing PV of injected CO_2, the oil recovery factor increased gradually, and reached the peak, when almost 1.5PV of CO_2 was injected. When the injected CO_2 was 0-0.2 PV, the injection pressure did not significantly affect oil recovery. Compared with supercritical and non-supercritical conditions, after the PV of injected CO_2 surpassed 0.2PV, supercritical flooding greatly increased the oil recovery factor at the same injection PV. The maximum increase was observed at the injection volume of about 1.5PV. To obtain the same oil recovery factor, non-supercritical flooding needed to inject more CO_2 than supercritical flooding. The increase of the oil recovery factor is attributed to the increased mass transfer and dissolution of supercritical CO_2 in the crude oil [7]. The oil recovery factor difference between Tests 4 and 5 was 1.08%, indicating that the small pressure variation has a limited impact on oil recovery in supercritical CO_2 flooding.
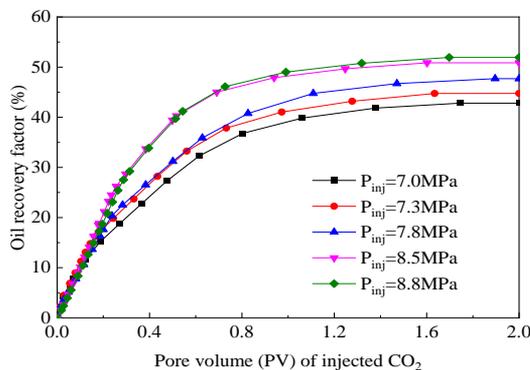
Figure 3. Variation of oil recovery factor at different injection pressures
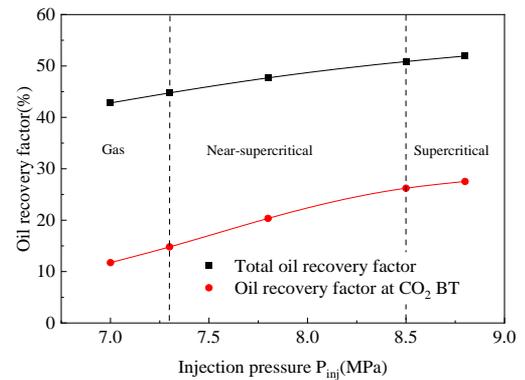
Figure 4. Total oil recovery factor and oil recovery factor at CO_2 breakthrough under different injection pressures

Figure 4 shows the total oil recovery factor and oil recovery factor at CO_2 breakthrough under different injection pressures. As CO_2 changed from gas phase to supercritical state, the total oil recovery factor and oil recovery factor at CO_2 breakthrough both increased. The supercritical state had a greater difference between the total oil recovery factor and the oil recovery factor at CO_2 breakthrough than the gas phase, and a better displacement efficiency of 10%OOIP (original oil in place) than non-supercritical state.

3.2 Produced GOR
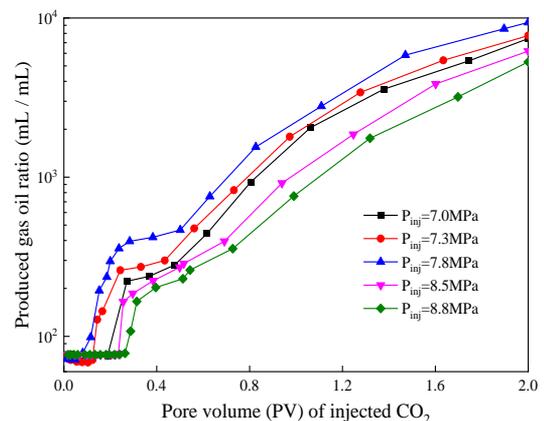
Figure 5. Variation of produced GOR at different injection pressures

The produced GOR variation and test phenomena show that supercritical CO_2 flooding and non-supercritical CO_2 flooding have similar GOR curves. Hence, CO_2 flooding was divided

into three stages: a gas free stage (before CO_2 breakthrough), a gas-oil co-production stage (after CO_2 breakthrough), and stable gas channelling stage (after CO_2 breakthrough).

Figure 5 shows the variation of produced GOR at different injection pressures. It can be observed that, the GOR was extremely low before CO_2 breakthrough, as the injected CO_2 PV was approximately 0.1PV. In this stage, the oil acts like a piston to reach the core outlet, and no CO_2 is produced [24, 25]. As the injected CO_2 PV increased to 0.15PV, CO_2 breakthrough began, and the GOR increased significantly. In this stage, the CO_2 and oil are produced simultaneously, yet contributing mostly to oil recovery. During gas-oil co-production stage, mass transfer and dissolution of CO_2 in oil may occur. This would be discussed in light of the physicochemical features of the produced fluids in the next section. After the injected CO_2 PV moved up to 0.65PV, the GOR increased up to 1,000 mL/mL, entering the stable gas channelling stage (after CO_2 breakthrough), and the oil recovery factor rose slightly.

The PV of CO_2 breakthrough is available in Figure 5 and Table 2. The PV of CO_2 breakthrough in non-supercritical displacement was 0.102~0.187PV. The breakthrough was delayed greatly, as the injection pressure moved up to supercritical pressure. In supercritical displacement, CO_2 breakthrough took place at 0.256-0.287 PV, mainly because the gas is denser and more viscous in the supercritical state than in the gas phase. This weakens the override effect. In addition, the CO_2 solubility in oil in the supercritical state is much greater than that in the gas phase. Mass transfer and dissolution in oil happen to lots of CO_2, making it less likely to realize CO_2 breakthrough.

3.3 Oil sample composition

The original oil sample and the produced oil sample were subjected to composition analysis in the CO_2 flooding process. The components of the original oil changed significantly through the experiments, due to the interaction between supercritical CO_2 and original oil. The component concentrations of the original oil sample and the produced oil sample were obtained through GC analysis.

Comparing the components of the oil samples produced before and after CO_2 breakthrough under different displacement pressure, it can be found that the light HCs (C_{1-7}) were significantly different before and after CO_2 breakthrough. As shown in Figure 6(a), during non-supercritical flooding, near-supercritical flooding, and supercritical flooding, the light HCs (C_{1-7}) was significantly reduced after CO_2 breakthrough, all of which are gradually extracted from the original oil before CO_2 breakthrough. Meanwhile, the concentration of middle HCs (C_{8-10}) and heavy HCs (C_{10+}) increased obviously. As shown in Figures 6(b) and 6(c), the proportion of middle HCs (C_{8-10}) components gradually increased, while that of heavy HCs (C_{10+}) slowly declined. Therefore, the mass transfer and dissolution of CO_2 in oil mainly occur during the gas-oil co-production stage after the CO_2 breakthrough. Supercritical CO_2 mainly extracts the middle HCs (C_{8-10}) from the original oil, and extracts a very small amount of heavy HCs (C_{10+}). The density of supercritical CO_2 is different from that of conventional CO_2. This difference alters the mass transfer effect between original oil and supercritical CO_2, and enhances the dissolvability of supercritical CO_2, making it possible to dissolve more original oil components.

(a)

(b)

(c)
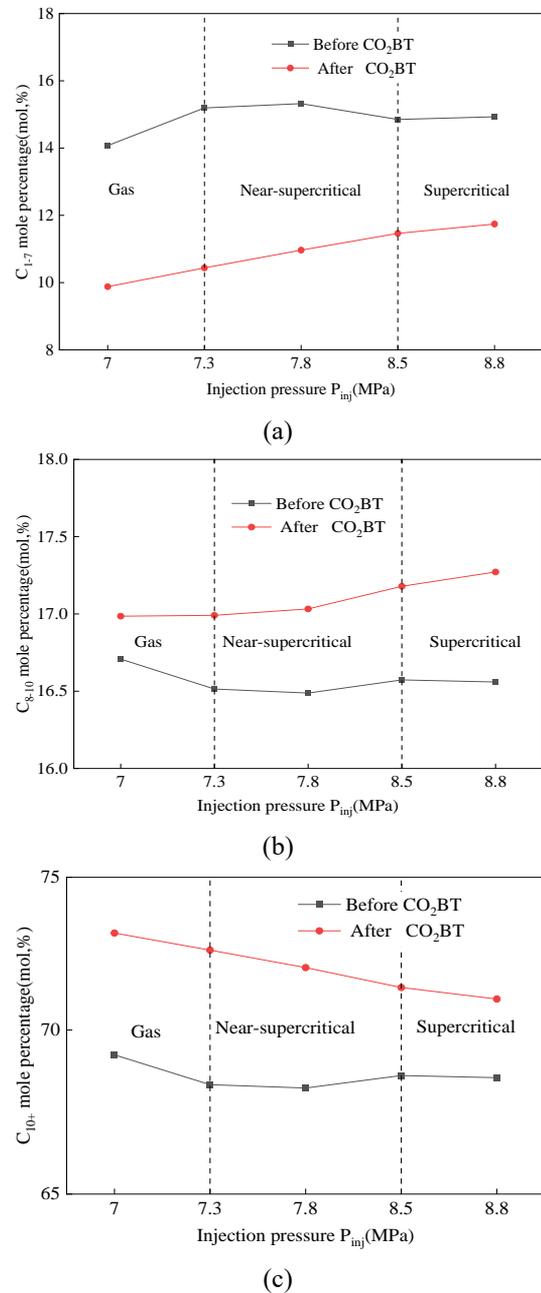
Figure 6. Component concentrations (a) C_{1-7}, (b)C_{8-10} and (c)C_{10+} of produced oil before and after CO_2 breakthrough at different injection pressures

4. CONCLUSIONS

(1) Supercritical state, a special state between water and gas phases, has many special properties in density, viscosity, and diffusivity. Supercritical CO_2 has good properties in mass transfer and dissolution.

(2) As CO_2 changes from gas phase to supercritical state, the oil displacement efficiency increases by 10% OOIP.

(3) Light HCs (C_{1-7}) are gradually extracted from the original crude oil before CO_2 breakthrough, while the heavy HCs (C_{8-10}) are extracted after CO_2 breakthrough.

(4) Supercritical CO_2 is a good choice for enhanced oil recovery, owing to its good properties in mass transfer and dissolution. Relatively more middle HCs(C_{8-10}) are extracted in super-critical CO_2 flooding.

REFERENCES

[1] Ampomah, W., Balch, R.S., Grigg, R.B., McPherson, B., Will, R.A., Lee, S.Y., Pan, F. (2017). Co-optimization of CO2-EOR and storage processes in mature oil reservoirs. Greenhouse Gases: Science and Technology, 7(1): 128-142. https://doi.org/10.1002/ghg.1618

[2] Godin, J., Liu, W., Ren, S., Xu, C.C. (2021). Advances in recovery and utilization of carbon dioxide: A brief review. Journal of Environmental Chemical Engineering, 9(4): 105644. https://doi.org/10.1016/j.jece.2021.105644

[3] Li, L., Su, Y., Hao, Y., Zhan, S., Lv, Y., Zhao, Q., Wang, H. (2019). A comparative study of CO_2 and N_2 huff-n-puff EOR performance in shale oil production. Journal of Petroleum Science and Engineering, 181: 106174. https://doi.org/10.1016/j.petrol.2019.06.038

[4] Rezk, M.G., Foroozesh, J., Zivar, D., Mumtaz, M. (2019). CO_2 storage potential during CO_2 enhanced oil recovery in sandstone reservoirs. Journal of Natural Gas Science and Engineering, 66: 233-243. https://doi.org/10.1016/j.jngse.2019.04.002

[5] Li, L., Wang, C., Li, D., Fu, J., Su, Y., Lv, Y. (2019). Experimental investigation of shale oil recovery from Qianjiang core samples by the CO_2 huff-n-puff EOR method. RSC Advances, 9(49): 28857-28869.

[6] Lashkarbolooki, M., Vaezian, A., Hezave, A.Z., Ayatollahi, S., Riazi, M. (2016). Experimental investigation of the influence of supercritical carbon dioxide and supercritical nitrogen injection on tertiary live-oil recovery. The Journal of Supercritical Fluids, 117: 260-269. https://doi.org/10.1016/j.supflu.2016.07.004

[7] Cao, M., Gu, Y. (2013). Physicochemical characterization of produced oils and gases in immiscible and miscible CO_2 flooding processes. Energy & Fuels, 27(1): 440-453. https://doi.org/10.1021/ef301407k

[8] Gong, Y., Gu, Y. (2015). Miscible CO_2 simultaneous water-and-gas (CO_2-SWAG) injection in the Bakken formation. In SPE/CSUR Unconventional Resources Conference, OnePetro. https://doi.org/10.2118/175976-MS

[9] Gong, Y., Gu, Y. (2015). Experimental study of water and CO_2 flooding in the tight main pay zone and vuggy residual oil zone of a carbonate reservoir. Energy & Fuels, 29(10): 6213-6223. https://doi.org/10.1021/acs.energyfuels.5b01185

[10] Kong, D., Gao, Y., Sarma, H., Li, Y., Guo, H., Zhu, W. (2021). Experimental investigation of immiscible water-alternating-gas injection in ultra-high water-cut stage reservoir. Advances in Geo-Energy Research, 5(2): 139-152. https://doi.org/10.46690/ager.2021.02.04

[11] Li, B.H., Li, Y.Q., Kong, D.B., Chen, Y.H., Fei, C.G., He, Y.F. (2016). Research on influence factors and screening method of tight sandstone oil reservoir CO_2 huff and puff based on multi-index. Chemical Engineering Transactions, 55: 343-348. https://doi.org/10.3303/CET1655058

[12] Lashkarbolooki, M., Eftekhari, M.J., Najimi, S., Ayatollahi, S. (2017). Minimum miscibility pressure of CO_2 and crude oil during CO_2 injection in the reservoir. The Journal of Supercritical Fluids, 127: 121-128.

https://doi.org/10.1016/j.supflu.2017.04.005

[13] Kong, D., Lian, P., Zhu, W., Li, Y. (2020). Pore-scale investigation of immiscible gas-assisted gravity drainage. Physics of Fluids, 32(12): 122004. https://doi.org/10.1063/5.0033027

[14] Singh, H. (2018). Impact of four different CO_2 injection schemes on extent of reservoir pressure and saturation. Advances in Geo-Energy Research, 2(3): 305-318. https://doi.org/10.26804/ager.2018.03.08

[15] Nobakht, M., Moghadam, S., Gu, Y. (2008). Mutual interactions between crude oil and CO_2 under different pressures. Fluid Phase Equilibria, 265(1-2): 94-103. https://doi.org/10.1016/j.fluid.2007.12.009

[16] Zekri, A.Y., Almehaideb, R.A., Shedid, S.A. (2006). Displacement efficiency of supercritical CO_2 flooding in tight carbonate rocks under immiscible conditions. In SPE Europec/EAGE Annual Conference and Exhibition. OnePetro. https://doi.org/10.2118/98911-MS

[17] Einstein, M.A., Gerder Castillo, Y.C., Gil, J.C. (2007). A novel improved condensate-recovery method by cyclic supercritical CO_2 injection. In Latin American & Caribbean Petroleum Engineering Conference, OnePetro. https://doi.org/10.2118/107283-MS

[18] Al-Abri, A.S., Amin, R. (2009). Enhanced natural gas and condensate recovery by injection of pure $SCCO_2$, pure CH_4 and their mixtures: experimental investigation. In SPE Annual Technical Conference and Exhibition, OnePetro. https://doi.org/10.2118/124145-MS

[19] Chen, X., Li, Y., Tang, X., Qi, H., Sun, X., & Luo, J. (2021). Effect of gravity segregation on CO2 flooding under various pressure conditions: Application to CO2 sequestration and oil production. Energy, 226, 120294. https://doi.org/10.1016/j.energy.2021.120294

[20] Zekri, A.Y., Almehaideb, R.A., Shedid, S.A. (2006). Displacement efficiency of supercritical CO_2 flooding in tight carbonate rocks under immiscible conditions. In SPE Europec/EAGE Annual Conference and Exhibition, OnePetro. https://doi.org/10.2118/98911-MS

[21] Wang, S., Liu, K., Han, J., Ling, K., Wang, H., & Jia, B. (2019). Investigation of properties alternation during super-critical CO_2 injection in shale. Applied Sciences, 9(8): 1686. https://doi.org/10.3390/app9081686

[22] Zekri, A.Y., Shedid, S.A., Almehaideb, R.A. (2007). Possible alteration of tight limestone rocks properties and the effect of watershelding on the performance of SC CO_2 flooding for carbonate formation. In SPE Middle East Oil and Gas Show and Conference, OnePetro. https://doi.org/10.2118/104630-MS

[23] Peng, D.Y., Robinson, D.B. (1976). A new two-constant equation of state. Industrial & Engineering Chemistry Fundamentals, 15(1): 59-64. https://doi.org/10.1021/i160057a011

[24] Duan, X., Hou, J., Zhao, F., Ma, Y., Zhang, Z. (2016). Determination and controlling of gas channel in CO_2 immiscible flooding. Journal of the Energy Institute, 89(1): 12-20. https://doi.org/10.1016/j.joei.2015.01.014

[25] Song, Z., Hou, J., Liu, X., Wei, Q., Hao, H., Zhang, L. (2018). Conformance control for CO_2-EOR in naturally fractured low permeability oil reservoirs. Journal of Petroleum Science and Engineering, 166: 225-234. https://doi.org/10.1016/j.petrol.2018.03.030