

http://pubs.acs.org/journal/acsodf

Stimulation and Sequestration Mechanism of CO₂ Waterless Fracturing for Continental Tight Oil Reservoirs

Jiaping Tao, Siwei Meng, Xu Jin, Jianguo Xu, Qinghai Yang, Xiaoqi Wang, He Liu,* and Bo Peng*

Cite This: ACS Omega 2021, 6, 20758–20767		Read Online		
ACCESS	Jul Metrics & More		E Article Recommendations	

ABSTRACT: CO_2 fracturing is a promising technology for oil field development in tight, continental deposits, with potential advantages of enhanced oil recovery (EOR), CO_2 sequestration, and water conservation. Compared with CO_2 -EOR techniques, such as CO_2 huff and puff and CO_2 flooding, CO_2 can interact with reservoir rock and fluid under higher pressure conditions during fracturing, resulting in CO_2 stimulation and sequestration effects that differ from those that occur during conventional CO_2 -EOR. In this paper, the CO_2 interactions between CO_2 and reservoirs in continental tight oil reservoirs under fracturing conditions are systematically studied through laboratory experiments. The results show that under high pressure, CO_2 effectively changes the pore structure through the extraction of hydrocarbons, dissolution of the



rock matrix, and migration of minerals. CO_2 dissolution of the rock matrix can significantly increase the number and complexity of fractures. Furthermore, CO_2 has a higher solubility in formation fluid under high-pressure conditions. Given the higher pressures, CO_2 forms a miscible phase with crude oil, diffuses more deeply into the formation, and reacts fully with the reservoir minerals and fluid during CO_2 fracturing. Accordingly, CO_2 can improve the permeability of the reservoir and flowability of crude oil significantly. Hence, CO_2 fracturing can enhance oil recovery and CO_2 sequestration more effectively. Core displacement experiments indicate that oil recovery of CO_2 soaking process after CO_2 fracturing is 36%, which is 12% and 9% higher than those of CO_2 huff and puff and CO_2 flooding with 5 pore volume, respectively. Field tests show that average oil production after CO_2 fracturing is 1.42 times higher than that after CO_2 flooding, which further validates the advantage of CO_2 fracturing and demonstrates its huge application potential.

1. INTRODUCTION

Tight oil refers to the accumulation of crude oil that occurs in source rocks, tight sand, or carbonate interbeds, in a free or trapped form, without long-distance movement.^{1,2} As an important supplement to China's oil production growth, tight oil is regarded as a major strategic alternative resource. Due to the low-porosity and low-permeability reservoir characteristics, the development of tight oil resources requires fracturing technology to enhance oil production.

 $\rm CO_2$ fracturing is a novel fracturing technology, in which $\rm CO_2$ is used as the fracturing fluid to replace water.^{3–5} The process of $\rm CO_2$ fracturing can be divided into two stages: fracturing stage (typically lasting for 2 h) and soaking stage (typically lasting for 3–14 days). $\rm CO_2$ fracturing can result in a series of physical and chemical reactions with the reservoir rock and formation fluid, respectively. These reactions can increase the porosity and permeability of reservoirs and improve crude oil flowability. As a result, $\rm CO_2$ fracturing could significantly enhance oil recovery and $\rm CO_2$ sequestration.^{6–11} Although the interaction mechanism and sequestration effect of $\rm CO_2$ -enhanced oil recovery ($\rm CO_2$ -EOR) under relatively low pressure and injection rates have been quite widely investigated,^{12–16} the stimulation and sequestration mechanisms of CO_2 fracturing under higher pressure and injection rates have not been widely reported.¹⁷ Some researchers investigated the effect of CO_2 –rock interactions on porosity, permeability, and mechanical properties for the Lujiaping and Longmaxi formations of the marine sedimentary Sichuan Basin during the CO_2 fracturing treatment.¹⁸ However, tight oil resources in China are mainly in continental deposits, in which formation minerals, pore structures, and reservoir fluid characteristics are different from those of marine tight reservoirs.^{19,20} Therefore, the interaction mechanism during CO_2 fracturing under high pressure in

Received:February 26, 2021Accepted:July 13, 2021Published:August 4, 2021





© 2021 The Authors. Published by American Chemical Society



Figure 1. Bottom-hole temperature and pressure curve for CO₂ fracturing.

continental tight oil reservoirs needs further investigation and clarification.

A series of experiments were carried out in this paper to systematically investigate the interaction mechanisms of CO₂rock and CO₂-oil during CO₂ fracturing in continental tight oil reservoirs under high-pressure conditions. First, scanning electron microscopy (SEM) imaging, nitrogen adsorption testing, and computed tomography (CT) scanning were carried out to investigate the interaction between CO₂ and the reservoir rock. Subsequently, the interactions between CO₂ and oil were investigated by slim tube testing and CO₂ dissolution experiments. Core displacement experiments were carried out to compare the EOR effect between CO₂ flooding and CO₂ fracturing. All of the laboratory experiments were carried out under high-pressure conditions. Finally, field tests were carried out to verify the effect of CO₂ fracturing. This paper presents the CO2 stimulation and sequestration mechanisms that occur during fracturing in continental tight oil reservoirs and provides a theoretical framework for the technical adaptability evaluation of the development model and engineering design for CO₂ fracturing.

2. METHODOLOGY

2.1. Determination of Relevant Experimental Conditions. During fracturing, CO_2 undergoes complex phase changes under the influence of external temperature and pressure changes, which will change the physical properties of CO_2 and affect the stimulation and CO_2 sequestration effect.^{21,22} Therefore, the investigation of CO_2 phase evolution in the fracturing process forms the first step in studying the stimulation and CO_2 sequestration mechanisms. Accordingly, a pilot field test of fracturing was carried out in the H 87 tight oil block of the Jilin Oilfield, and sensors were set at the bottom of the well to collect bottom-hole temperature and pressure data during and after fracturing. The results are shown in Figure 1.

Before fracturing, the bottom-hole temperature was stable at 103 °C and the pressure was 20 MPa. After fracturing started, with the injection of low-temperature CO_2 (the injection rate being 5 m³/min), the bottom-hole temperature gradually decreased to 24 °C; meanwhile, the pressure rapidly increased to 41 MPa, at which time, the CO₂ was in the liquid state. After injection and entering the reservoir fractures, liquid CO₂ rapidly

exchanged heat with the reservoir and achieved a supercritical state. The soaking stage began after the completion of the active fracturing treatment. In this part of the process, the bottom-hole temperature gradually rose to the original formation temperature and the bottom-hole pressure slowly dropped. As the formation temperature and pressure of CO₂ were much higher than the critical temperature and pressure, the CO₂ remained in the supercritical state. In this state, the density of CO₂ is close to that of liquid and its migration capacity is similar to that of gas, which makes it easy for the CO₂ to diffuse into the reservoir.²³

2.2. Experimental Investigation on the Interaction between Supercritical CO₂ and Rock. To study the impact of supercritical CO₂ on reservoir rock properties, the drill cores from the H 87 block of the Jilin Oilfield were soaked in supercritical CO₂ for the periods of 2 h, 1 day, 3 days, 7 days, and 14 days, after which they were subjected to SEM imaging (using a Thermo Scientific Apreo SEM), nitrogen adsorption testing (using a Microtrac BELSORP MAX II surface area and size distribution analyzer), and CT scanning (using an Xradia 510 Versa submicron imaging system) to analyze the change in pore and fracture structures. The main mineral compositions of the core included quartz (31.8%), clay (25.4%), albite (21.8%), biotite (4.9%), potash feldspar (3.4%), calcite (3.0%), and other minerals (9.7%). In accordance with the downhole condition during CO₂ fracturing, soaking temperature and pressure were set at 103 °C and 30 MPa, respectively.

2.3. Experimental Investigation on the Minimum Miscibility Pressure and CO₂ Solubility. The minimum miscibility pressure (MMP) of the oil in block H 87 was determined by the slim tube test. The average formation temperature (103 °C) of this block was used as the test temperature. Under this condition, the viscosity of the oil in block H 87 is 5.76 mPa s and its density is 0.82 g/cm^3 . The coiled slim tube used in the test was 20 m in length and 3 mm inner diameter and was filled with fine sand to simulate the porous media of the reservoir rock. The slim tube was washed with petroleum ether and dried with nitrogen first. Then, the slim tube was saturated with oil at the test temperature and pressure. After that, 1.2 pore volume (PV) CO₂ was injected under different pressure conditions to analyze the MMP.

The experimental procedures of miscible process visualization are briefly described as follows. First, crude oil was added into a high-temperature and high-pressure cell, after which CO_2 was injected into the cell with a high-pressure pump. The temperature and pressure in the cell were maintained at the specified conditions. After that, the pressure in the cell was gradually increased from 10 to 28 MPa, and the miscible process between CO_2 and crude oil was observed.

The experimental procedures of the CO₂ dissolution experiment are briefly described as follows. (1) Formation brine or crude was loaded into a high-temperature and highpressure cell, and then, the cell was heated to 103 °C. (2) CO₂ was injected in the cell to a desired pressure until the pressure remained stable. (3) The undissolved CO₂ was released out of the cell, and the gas production was measured through a gas flowmeter to calculate the CO₂ solubility.

2.4. Core Displacement Experiment. The ultimate oil recovery of CO_2 flooding, CO_2 huff and puff, and CO_2 soaking after CO_2 fracturing was compared and analyzed through the core displacement experiments. First, the drill core samples from block H 87 were dried in an oven at 120 °C for 48 h; then, the permeability and porosity were measured, and the results are shown in Table 1. Second, the core samples were split into half

Table 1. Properties of Drill Core Samples

number	length (cm)	diameter (cm)	matrix permeability (mD)	porosity (%)	experiment
1	5.02	2.51	0.04	8.9	flooding
2	5.00	2.52	0.04	8.5	huff and puff
3	5.02	2.50	0.05	9.2	soaking after fracturing

along the axial direction. Epoxy resin was used to pack and fix the quartz sands of different grain sizes on the sections, to simulate artificial fractures. Third, the core samples were saturated with crude oil and the oil amount of each core block was measured. The test temperature was set at 103 $^{\circ}$ C.

The experimental procedures of CO_2 flooding are briefly described as follows. (1) The core was put into a core holder, and the back pressure was set at 15 MPa. (2) The confining pressure was set at 2.0 MPa higher than the injection pressure. (3) CO_2 was injected continuously at 0.5 mL/min until the pressure at the inlet reached 15 MPa. (4) CO_2 was injected continuously at 0.1 mL/min until the injection volume reached 10 PV, and the oil production at the outlet was recorded to evaluate the EOR effect.

The experimental procedures of CO_2 huff and puff are briefly described as follows. (1) The core was put into a core holder, and the back pressure was set at 20 MPa. (2) The confining pressure was set at 2.0 MPa higher than the injection pressure. (3) CO_2 was injected continuously at 0.5 mL/min until the pressure at the inlet reached 20 MPa. (4) The inlet of the core holder was shut down and the pressure was kept stable for 12 h. (5) The inlet of the core holder was recorded.

The experimental procedures of CO_2 soaking after CO_2 fracturing are briefly described as follows. (1) The core was put into a core holder, and the back pressure was set at 30 MPa. (2) The confining pressure was set at 2.0 MPa higher than the injection pressure. (3) CO_2 was injected continuously at 0.5 mL/min until the pressure at the inlet reached 30 MPa. (4) The inlet of the core holder was shut down and the pressure was kept stable for 12 h. (5) The inlet of the core holder.

3. RESULTS AND DISCUSSION

3.1. Study on the Interaction between Supercritical CO_2 and Rock. As mentioned above, CO_2 in the reservoir was maintained at the supercritical state for a long time during the fracturing process. Supercritical CO_2 can diffuse into the fractures, and micro- and nanopores within the tight reservoir exert chemical, thermodynamic, and other effects on reservoir rocks, changing the pore and fracture structures in the reservoir.^{24–26} In this process, the interactions between supercritical CO_2 and rock under high pressure were studied as described below.

3.1.1. Influence of Supercritical CO_2 on Organic Pore Structures of Rock. To evaluate the effect of CO_2 -organic matter interactions on the pore structure, the rock samples before and after soaking were observed in the same field with SEM. The results are shown in Figure 2.

In the original state, after mechanical polishing and argon-ion polishing, the surface of the rock sample was relatively flat, and there were only a few primary organic pores in the organic matter (Figure 2, T = 0 days). After 2 h of soaking in CO₂, many new small organic pores (diameter, $0.5-1 \mu m$) were present due to the dissolution of organic matter, with some mineral migration (Figure 2, T = 2 h). This is an indication that the interaction between CO₂ and the organic matter has already started. After 1 day of soaking, the sizes of these generated organic pores significantly expanded (diameter, $1-3 \mu m$), and a few additional new organic pores were generated (Figure 2, T =1 day). This demonstrates that CO_2 can extract more organic matter with the prolongation of soaking time. After 3 and 7 days of soaking, with the consumption of movable components in the organic matter, there was no further change in the organic pore structure. At the same time, more minerals started migrating and blocked partial pores (Figure 2, T = 3 and 7 days). After 14 days of soaking, a part of the organic matter was stripped, and more organic pores were blocked. In addition, new fractures were observed in the organic matter, and these fractures may have provided more flow channels for crude oil (Figure 2, T = 14days). This indicates that some organic components require a longer time of CO_2 soaking, to be affected.

3.1.2. Influence of Supercritical CO₂ on the Matrix Pore Structure of Rock. To evaluate the effect of CO₂-rock matrix interactions on the pore structure, the rock samples before and after soaking were observed in the same field with SEM, as shown in Figure 3. After mechanical polishing and argon-ion polishing, there were a few primary matrix pores (diameter, 2–4 μ m) (Figure 3, T = 0 days). After 2 h of soaking, the size of these primary pores showed a marked increase (diameter, 5–15 μ m), and several new dissolution pores were generated (diameter, 0.5–3 μ m), indicating that the dissolution effect was very intense (Figure 3, T = 2 h). As the composition of the core used includes albite (21.8%), potash feldspar (3.4%), and calcite (3.0%), the probable interaction mechanism during soaking is shown as follows:

$$NaAlSi_{3}O_{8} + CO_{2} + 5.5H_{2}O$$

$$\rightarrow Na^{+} + HCO_{3}^{-} + 2H_{4}SiO_{4} + 0.5Al_{2}Si_{2}O_{5}(OH)_{4}$$
(1)

$$2\text{KAlSi}_{3}\text{O}_{8} + 2\text{H}^{+} + 9\text{H}_{2}\text{O}$$

$$\rightarrow 2\text{K}^{+} + 4\text{H}_{4}\text{Si}\text{O}_{4} + \text{Al}_{2}\text{Si}_{2}\text{O}_{5}(\text{OH})_{4}$$
(2)



Figure 2. SEM analysis of organic matter after soaking in CO_2 for different lengths of time (with the increase of soaking time, CO_2 could extract more organic matter and lead to more mineral migration).

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^{-}$$
(3)

During the soaking process, the size of these dissolution pores increased constantly, but as time passed, the change ceased because the matrix minerals that can react with CO_2 had been consumed. In addition, only a few additional micropores were generated. At the same time, some minerals were mobilized and blocked partial pores (Figure 3, T = 1, 3, 7, and 14 days). These migrated minerals probably originated from shedding due to dissolution or from precipitation caused by geochemical reactions.

3.1.3. Influence of Supercritical CO_2 on Rock Pore Volume. The N₂ adsorption test was adopted to determine the overall pore volume change in the rock sample. The specific surface area and pore diameter distribution of the rock sample under different soaking times were calculated by the inversion of the adsorption and desorption curve, as shown in Figure 4.

During CO_2 fracturing, the rock pore volume was influenced by the structural change in organic pores and dissolution pores as well as by the mobilization and redeposition of minerals. With increased soaking time, the specific surface area of the rock sample gradually increased. This indicates that CO_2 soaking can increase the effective pore volume of the rock sample and effectively improve the permeability of the sample. The measured specific surface area increased significantly in the first 3 days, indicating a definite increase in pore volume. As shown in Figure 4b, increased soaking time leads to an obvious increase in the mesoporous volume. According to the SEM imaging results, the change in the pore structure appeared to have stopped by T = 3 days. However, the SEM images only show changes on the sample surface. As supercritical CO₂ has strong penetrability and diffusivity, it could easily invade into the core and react with the minerals inside the core, resulting in a continuous increase in pore volume. After 7-14 days of soaking, the increasing speed of the specific surface area detected using N₂ absorption gradually reduced. The reason is that with the increase in the soaking time, reactable mineral components (albite, potash feldspar, and calcite) in the rock matrix and movable components in the organic matter are gradually consumed. Furthermore, due to the migration of some minerals, a portion of the original pores is blocked by redeposited minerals.

It should be noted that the interaction between the supercritical CO_2 and the reservoir rock not only improves the reservoir permeability but also consumes a considerable amount of CO_2 , which is an important mechanism for CO_2 sequestration during fracturing. Compared to those in the conventional CO_2 -EOR technology application, the injection pressure and rate in



Figure 3. SEM test analysis of the rock matrix after CO_2 soaking (with the increase of soaking time, CO_2 could generate more dissolution pores and lead to mineral mobilization. At the same time, the mobilized minerals may plug these new pores).

 CO_2 fracturing are much higher. CO_2 could enter the micro- and nanopores that might not be swept during conventional CO_2 -EOR processes at lower pressures. This could enhance the contact area between CO_2 and the reservoir and enable the CO_2 to interact with the reservoir more efficiently. 3.1.4. Influence of Supercritical CO_2 on Rock Fracture Morphology. To study the influence of supercritical CO_2 on natural and artificial fractures, microscopic image analysis before and after soaking in supercritical CO_2 was carried out by utilizing micro-CT. The results are shown in Figure 5.

Article



Figure 4. N₂ adsorption test analysis of the rock sample during CO₂ soaking: (a) specific surface area and (b) pore diameter distribution.



Figure 5. CT test analysis of core soaked in CO₂ (left: 3D images; right: section images).

Under high-pressure conditions, CO₂ could fully diffuse into the microfractures and micro- and nanopores, dissolving minerals such as albite, calcite, and K-feldspar. Thus, with an increase in the soaking time, the complexity of fractures increases significantly. The generated fractures can be divided into two types: extension of existing fractures and new fractures. Most of the existing fracture extension occurred in the first week of soaking. During this stage, the existing fractures gradually extended, and the width and depth of these fractures also gradually increased. In the second week of soaking, the existing fractures were further extended and branched out. Meanwhile, some new fractures were generated under high-pressure CO₂ due to cracking along structural weakness such as the bedding surfaces and the interlayer surfaces. This resulted in a significant increase in the complexity of the fracture network. Furthermore, these changes in the rock structure may lead to a dramatic decrease in the rock material strength.^{2'}

3.2. Study on the Interaction between Supercritical CO_2 and Formation Fluid. Compared with conventional CO_2 -EOR, the soaking stage after CO_2 fracturing makes it

possible for supercritical CO_2 to give full play to its miscibility and extraction effect on crude oil under high pressure, thereby enhancing oil recovery and CO_2 sequestration of tight oil reservoirs.^{21,22,28} To explore the interaction mechanism of supercritical CO_2 and crude oil under high-pressure conditions, the lab experiments described below were carried out.

3.2.1. Determination of CO_2 -Oil MMP. CO_2 -oil MMP refers to the minimum pressure at which CO_2 and crude oil could form a miscible phase through multistage contact at the reservoir temperature. It is an important parameter for the CO_2 soaking stage. The MMP of the oil in block H 87 was determined by the slim tube test, as described earlier. The results are shown in Figure 6.





With a continued increase in the injection pressure, the oil recovery increased rapidly. When the pressure reached 28 MPa, oil recovery exceeded 95%. Then, the oil recovery tended to stabilize and the miscible process between oil and CO_2 reached a dynamic equilibrium. By fitting the curve, the MMP in this block was found to be 27.45 MPa. During the conventional CO_2 -EOR processes, the pressure is about 18–21 MPa; hence, CO_2 would be unable to dissolve into the reservoir oil to form a miscible phase.

The visualization results of the miscibility process are shown in Figure 7. The interface between the tight oil sample in the



Figure 7. Miscible process of CO₂ and crude oil.

lower layer and the supercritical CO₂ in the upper layer was clear at 10 MPa. As the pressure increased to 20 MPa, the volume of crude oil expanded. At this time, the interaction between CO_2 and crude oil is mainly dissolution, with a few misty areas formed by a small number of light components that are extracted. When the pressure was increased to 25 MPa, large quantities of hydrocarbon components in the crude oil were extracted, forming a hydrocarbon-rich zone.²³ When the pressure reached 27 MPa, the mass transfer of oil-gas at the interface intensified. The interface became increasingly indistinct. Finally, when the pressure was increased to 28 MPa, the oil-CO₂ interface completely disappeared and the CO₂ and crude oil were miscible. CO₂ cannot form a miscible phase with crude oil during the conventional CO₂-EOR process due to the relatively low pressure (18–21 MPa), resulting in a lower oil recovery than what is possible with the higher pressures utilized during miscible CO₂-EOR or used during fracturing with CO₂.

3.2.2. Evaluation of CO_2 Solubility in Formation Fluid for Sequestration. To illustrate the influence of CO_2 solubility, the CO_2 dissolution experiments in crude oil and formation water were carried out. The results are shown in Figure 8. The solubility of CO_2 in oil and water both increased significantly as pressure increased. Under the conventional CO_2 -EOR condition (20 MPa), the CO_2 solubilities in crude oil and formation water were 149.1 and 24.5 m³/m³, respectively. As the recovery of tight oil is typically less than 10%, ¹ a large amount of of CO_2 can be sequestrated in the reservoir through dissolution in the formation fluid. As mentioned above, the injection pressure and rate of CO_2 fracturing are much higher than that of conventional CO_2 -EOR. Under the high-pressure condition (30 MPa), CO_2 can contact the formation fluid more efficiently on a larger scale. This further increases the amount of CO_2 dissolved into the pore fluid, and this should in turn enhance the CO_2 sequestration effect.

3.2.3. Core Displacement Experiment. The core displacement experiment further demonstrates the advantages of CO_2 fracturing. The results are shown in Figure 9. After conventional



Figure 9. Oil recovery of core displacement experiments.

 CO_2 huff and puff, the oil recovery was 24%. After the CO_2 soaking stage of CO_2 fracturing (at higher pressure), the oil recovery was 36%, which was higher than that in CO_2 huff and puff. In the soaking stage of CO_2 fracturing, the pressure was higher than that in CO_2 huff and puff. Under high-pressure conditions, CO_2 could diffuse more deeply into the cores and form a miscible phase with crude oil, making the mixture more mobile, thereby leading to a higher rate of oil recovery. After 10 PV CO_2 flooding, the oil recovery was 38%. However, in practical engineering, the injection volume of CO_2 is generally



Figure 8. CO₂ dissolution experiment (a) with crude oil and (b) with formation water.

limited. The oil recovery after the CO_2 soaking stage of CO_2 fracturing is higher than those of both CO_2 huff and puff and CO_2 flooding with low injection volume. Thus, compared with conventional CO_2 -EOR technology, CO_2 fracturing appears to have technical advantages in enhancing oil recovery.^{29,30}

3.3. Field Tests of CO₂ Fracturing. Field tests were carried out to validate the advantages of CO₂ fracturing. Block H 87 was the main test area for CO₂ fracturing for tight oil, where the fracturing test was conducted seven times. In this block, the porosity is 4.0-12.3% and the permeability is 0.01-6.0 mD. The production data after the CO₂ fracturing treatment were acquired, and the results are shown in Figure 10. For the CO₂



Figure 10. Daily oil production after CO₂ fracturing.

fracturing wells, the average CO_2 injection volume was 632 m³ and the injection pressure was 40–70 MPa. The average daily oil production after fracturing was 1.62 t. In the same area, there are more than 20 wells that were subjected to hydraulic fracturing treatment, and the daily oil production after fracturing was 0.6 t. CO_2 fracturing has apparent advantage in enhancing oil production.

Meanwhile, CO_2 conventional flooding field tests were carried out in the adjacent Block H 79. In this block, the porosity is 4.5– 13.0% and the permeability is 0.02–4.5 mD. In this CO_2 flooding test, the injection rate of CO_2 is about 4.3 t/day. The production data after the CO_2 flooding treatment were acquired, and the results are shown in Figure 11. The average daily oil production per well after CO_2 flooding was 1.14 t, and the daily oil production per well without CO_2 flooding was 0.2 t. CO_2 flooding can enhance oil production significantly.

Although both of the CO₂ flooding and CO₂ fracturing can enhance oil production, the average oil production after CO₂ fracturing is 1.42 times higher than that after CO₂ flooding. During CO₂ flooding, the formation pressure is lower than MMP and CO₂ cannot form a miscible phase with crude oil. Furthermore, under a relatively low pressure, CO₂ does not diffuse as effectively into the reservoir and the swept volume of CO₂ is limited. As a result, the capability of EOR is relatively weak. In summary, the comparison of field tests further validates the advantages and demonstrates the huge application potential of CO₂ fracturing, which merits further investigation and testing.



Figure 11. Daily oil production after CO₂ flooding.

4. CONCLUSIONS

In this paper, the CO_2 -rock and CO_2 -oil interaction mechanisms were systematically analyzed under high-pressure conditions. In combination with field tests, the stimulation and sequestration mechanisms of CO_2 fracturing in continental tight oil reservoirs were comprehensively analyzed. The conclusions are as follows:

- (1) After entering the reservoir, the liquid CO_2 rapidly turns into a supercritical state due to the changes in temperature and pressure, and CO_2 can remain in the supercritical state for an extended period during the entire fracturing process.
- (2) It can be seen that after CO_2 soaking, the surface morphology of reservoir samples has been changed significantly. In this process, supercritical CO_2 can extract the hydrocarbon component of the organic matter and dissolve parts of the rock matrix, causing a significant increase in the diameter and total volume of pores in the rock. At the same time, existing fractures are extended and new fractures are generated. Furthermore, these changes in the matrix structure may lead to a dramatic decrease in the rock material strength.
- (3) Compared with conventional CO_2 -EOR, the pressure during the soaking stage of CO_2 fracturing is much higher. Thus, the CO_2 can form a miscible phase fluid with crude oil and diffuse more deeply into the formation. Furthermore, the CO_2 solubility in crude oil and formation water increases with the increased injection pressure. Therefore, under higher pressure conditions, CO_2 fracturing could enhance oil recovery and CO_2 sequestration more effectively than conventional CO_2 -EOR.
- (4) The core displacement experiments show that after the CO_2 soaking stage of CO_2 fracturing, the oil recovery is 36%, which is higher than those of both CO_2 huff and puff and CO_2 flooding with low injection volume. The field tests show that the average oil production after CO_2 fracturing is 1.62 t/day, which is 1.42 times higher than that after CO_2 flooding. These field tests further validate the advantages and demonstrate the huge application potential of CO_2 fracturing, which merits further investigation and testing.

AUTHOR INFORMATION

Corresponding Authors

- He Liu School of Petroleum Engineering, China University of Petroleum (East China), Qingdao, Shandong 266580, China; PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China; Email: liuhe@ petrochina.com.cn
- **Bo Peng** Beijing Key Laboratory for Greenhouse Gas Storage and CO₂–EOR, China University of Petroleum (Beijing), Beijing 102249, China; Email: cbopeng@cup.edu.cn

Authors

Jiaping Tao – School of Petroleum Engineering, China University of Petroleum (East China), Qingdao, Shandong 266580, China; PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China;
orcid.org/0000-0001-6248-7836

Siwei Meng – PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China

- Xu Jin PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China
- Jianguo Xu PetroChina Jilin Oilfield Company, Songyuan, Jilin 138000, China
- Qinghai Yang PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China
- Xiaoqi Wang PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c01059

Funding

This work was funded by the Program of Basic Science Center of the National Natural Science Foundation of China (No. 72088101), the National Key R&D Program of China (No. 2018YFE0196000), and the Foundation Program for Directly Affiliated Institutions of CNPC (No. 2019D-500808).

Notes

The authors declare no competing financial interest.

REFERENCES

(1) ARI. EIA/ARI World Shale Gas and Shale Oil Resource Assessment -Technically Recoverable Shale Gas and Shale Oil Resources: An Assessment of 137 Shale Formations in 41 Countries Outside the United States; DOE: Washington, DC, 2013.

(2) Zou, C.; Yang, Z.; Cui, J.; Zhu, R.; Hou, L.; Tao, S.; Yuan, X.; Wu, S.; Lin, S.; Wang, L.; Bai, B.; Yao, J. Formation mechanism, geological characteristics and development strategy of nonmarine shale oil in China. *Pet. Explor. Dev.* **2013**, *40*, 15–27.

(3) Liu, H.; Wang, F.; Zhang, J.; Meng, S.; Duan, Y. Fracturing with carbon dioxide: Application status and development trend. *Pet. Explor. Dev.* **2014**, *41*, 513–519.

(4) Middleton, R. S.; Carey, J. W.; Currier, R. P.; Hyman, J. D.; Kang, Q.; Karra, S.; Jiménez-Martínez, J.; Porter, M. L.; Viswanathan, H. S. Shale gas and non-aqueous fracturing fluids: Opportunities and challenges for supercritical CO₂. *Appl. Energy* **2015**, *147*, 500–509.

(5) Kurdi, M.; Veveakis, M.; Poulet, T. Leveraging supercritical CO_2 to rejuvenate hydraulically fractured wells in unconventional reservoirs. Paper presented at the SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition, Dammam, Saudi Arabia, April 2018, SPE-192367-MS.

(6) Pan, Y.; Hui, D.; Luo, P.; Zhang, Y.; Sun, L.; Wang, K. Experimental investigation of the geochemical interactions between supercritical CO_2 and shale: Implications for CO_2 storage in gasbearing shale formations. *Energy Fuels* **2018**, *32*, 1963–1978.

(7) Zhang, L.; Ezekiel, J.; Li, D.; Pei, J.; Ren, S. Potential assessment of CO₂ injection for heat mining and geological storage in geothermal reservoirs of China. *Appl. Energy* **2014**, *122*, 237–246.

(8) Middleton, R.; Viswanathan, H.; Currier, R.; Gupta, R. CO₂ as a fracturing fluid: Potential for commercial-scale shale gas production and CO₂ sequestration. *Energy Procedia* **2014**, *63*, 7780–7784.

(9) Li, S.; Li, Z.; Dong, Q. Diffusion coefficients of supercritical CO_2 in oil-saturated cores under low permeability reservoir conditions. *J.* CO_2 Util. **2016**, 14, 47–60.

(10) Eide, Ø.; Fernø, M. A.; Alcorn, Z.; Graue, A. Visualization of carbon dioxide enhanced oil recovery by diffusion in fractured chalk. *SPE J.* **2016**, *21*, 112–120, *SPE-170920-PA*.

(11) Yang, L.; Ge, H.; Shi, X.; Cheng, Y.; Zhang, K.; Chen, H.; Shen, Y.; Zhang, J.; Qu, X. The effect of microstructure and rock mineralogy on water imbibition characteristics in tight reservoirs. *J. Nat. Gas Sci. Eng.* **2016**, *34*, 1461–1471.

(12) Alam, M. M.; Hjuler, M. L.; Christensen, H. F.; Fabricius, I. L. Petrophysical and rock-mechanics effects of CO_2 injection for enhanced oil recovery: Experimental study on chalk from South Arne Field, North Sea. J. Pet. Sci. Eng. **2014**, 122, 468–487.

(13) Pankaj, P.; Mukisa, H.; Solovyeva, I.; Xue, H. Boosting Oil Recovery in Naturally Fractured Shale Using CO_2 Huff-n-Puff. Paper presented at the SPE Argentina Exploration and Production of Unconventional Resources Symposium, Neuquen, Argentina, August 2018, SPE-191823-MS.

(14) Liu, F.; Lu, P.; Griffith, C.; Hedges, S. W.; Soong, Y.; Hellevang, H.; Zhu, C. CO_2 -brine-caprock interaction: Reactivity experiments on eau claire shale and a review of relevant literature. *Int. J. Greenhouse Gas Control* **2012**, *7*, 153–167.

(15) Seo, Y.-J.; Kim, D.; Koh, D.-Y.; Lee, J. Y.; Ahn, T.; Kim, S.-J.; Lee, J.; Lee, H. Soaking process for the enhanced methane recovery of gas hydrates via CO₂/N₂ gas injection. *Energy Fuels* **2015**, *29*, 8143–8150.

(16) Chen, C.; Gu, M. Investigation of cyclic CO_2 huff-and-puff recovery in shale oil reservoirs using reservoir simulation and sensitivity analysis. *Fuel* **2017**, *188*, 102–111.

(17) Lu, J.; Nicot, J. P.; Mickler, P. J.; Ribeiro, L. H.; Darvari, R. Alteration of bakken reservoir rock during CO_2 -based fracturing-an autoclave reaction experiment. *J. Unconv. Oil Gas Resour.* **2016**, *14*, 72–85.

(18) Zou, Y.; Li, S.; Ma, X.; Zhang, S.; Li, N.; Chen, M. Effects of CO_2 -brine-rock interaction on porosity/permeability and mechanical properties during supercritical- CO_2 fracturing in shale reservoirs. *J. Nat. Gas Sci. Eng.* **2018**, *49*, 157–168.

(19) Jia, C.; Zou, C.; Li, J.; Li, D.; Zheng, M. Assessment criteria, main types, basic features and resource prospects of the tight oil in China. *Acta Petrol. Sin.* **2012**, *33*, 343–350.

(20) Zou, C.; Zhu, R.; Wu, S.; Yang, Z.; Tao, Z.; Yuan, X.; Hou, L.; Yang, H.; Xu, C.; Li, D.; Bai, B.; Wang, L. Types, characteristics, genesis and prospects of conventional and unconventional hydrocarbon accumulations: Taking tight oil and tight gas in China as instance. *Acta Petrol. Sin.* **2012**, *33*, 173–187.

(21) Rudyk, S.; Spirov, P.; Samuel, P.; Joshi, S. J. Vaporization of crude oil by supercritical SC-CO₂ at different temperatures and pressures: Example from Gorm Field in the Danish North Sea. *Energy Fuels* **2017**, *31*, 6274–6283.

(22) Zhang, Y.; Gao, M.; You, Q.; Fan, H.; Li, W.; Liu, Y.; Fang, J.; Zhao, G.; Jin, Z.; Dai, C. Smart mobility control agent for enhanced oil recovery during CO₂ flooding in ultra-low permeability reservoirs. *Fuel* **2019**, *241*, 442–450.

(23) Rudzinski, W. E.; Aminabhavi, T. M. A review on extraction and identification of crude oil and related products using supercritical fluid technology. *Energy Fuels* **2000**, *14*, 464–475.

(24) Kolle, J. J. Coiled-tubing drilling with supercritical carbon dioxide. *Paper presented at the SPE/CIM International Conference on Horizontal Well Technology*, Calgary, Canada, November 2000, SPE-65534-MS.

(25) Ishida, T.; Aoyagi, K.; Niwa, T.; Chen, Y.; Murata, S.; Chen, Q.; Nakayama, Y. Acoustic emission monitoring of hydraulic fracturing laboratory experiment with supercritical and liquid CO₂. *Geophys. Res. Lett.* **2012**, 39, No. 10.1029/2012GL052788.

(26) Al-Yaseri, A.; Zhang, Y.; Ghasemiziarani, M.; Sarmadivaleh, M.; Lebedev, M.; Roshan, H.; Iglauer, S. Permeability evolution in sandstone due to CO₂ injection. *Energy Fuels* **2017**, *31*, 12390–12398.

(27) Meng, S.; Jin, X.; Tao, J.; et al. Evolution Characteristics of Mechanical Properties under Supercritical Carbon Dioxide Treatment in Shale Reservoirs. *ACS Omega* **2021**, *6*, 2813–2823.

(28) Li, Z.; Gu, Y. Soaking effect on miscible CO_2 flooding in a tight sandstone formation. *Fuel* **2014**, *134*, 659–668.

(29) Holm, L. W.; Josendal, V. A. Mechanisms of oil displacement by carbon dioxide. J. Pet. Technol. 1974, 26, 1427–1438, SPE-4736-PA.

(30) Liu, B.; Wang, C.; Zhang, J.; Xiao, S.; Zhang, Z.; Shen, Y.; Sun, B.; He, J. Displacement mechanism of oil in shale inorganic nanopores by supercritical carbon dioxide from molecular dynamics simulations. *Energy Fuels* **201**7, *31*, 738–746.