Experimental Analysis and Performance Investigation of Immiscible Super-Critical CO₂ Flooding Processes in Tight Oil Reservoir

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ABSTRACT

CO₂ 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 CO₂ is tested in laboratory under immiscible flooding. The results show that: Supercritical CO₂ improves oil recovery, by virtue of its low viscosity, high diffusivity, and easy dissolution. With the same pore volume (PV), supercritical CO₂ flooding significantly boosted the oil recovery factor. The factor reached the maximum, when almost 1.5PV of CO₂ was injected. As CO₂ 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 CO₂ than supercritical flooding. Light hydrocarbon components (C₁-C₃) in crude oil were gradually extracted before CO₂ breakthrough, while heavy hydrocarbon components (C₄+) were extracted mainly after CO₂ breakthrough. In addition, supercritical CO₂ flooding extracted more intermediate hydrocarbons than critical CO₂ flooding. To sum up, supercritical flooding outperforms non-supercritical flooding in injection performance, oil displacement efficiency, and oil exchange rate.

1. INTRODUCTION

CO₂ 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]. CO₂ is mutually soluble with crude oil; the light hydrocarbons from the oil can dissolve in CO₂, and the gas can dissolve in the oil. As a result, the injection of CO₂ can significantly reduce the viscosity of crude oil [3, 4]. Injecting CO₂ 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, CO₂ 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 CO₂ flooding [7], i.e., dissolving a large amount of CO₂ in crude oil. The first step of miscible CO₂ 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.

CO₂-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 CO₂ 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 CO₂ core flooding experiments under different pressures (immiscible, near-miscible, and miscible conditions), and analysed the physiochemical characterization of produced oils and gases. The results show that the produced oil becomes heavier with the growing pore volume (PV) of injected CO₂ at low injection pressure. The opposite trend was observed at a high injection pressure. With the rise of injection pressure, CO₂ 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 CO₂, the phase state of CO₂ in the process of miscible 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. CO₂ becomes a supercritical fluid, when the pressure and temperature surpass the critical level of 7.39 MPa and 31.05°C, respectively. Supercritical CO₂ has a similar density as fluid, which is about one hundred times denser than gas. Meanwhile, the viscosity of supercritical CO₂ is like that...
of gas and two orders of magnitude smaller than that of fluid. Supercritical CO₂ boasts good properties in mass transfer and dissolution. The solubility of supercritical CO₂ is very high, about 100 times that of liquid. In addition, supercritical CO₂ can propagate easily in porous media, because its surface tension is zero. Furthermore, the high temperature and pressure sensitivity of supercritical CO₂ enable flexible control of the temperature and pressure in the production process. Einstein et al. [17] observed that supercritical CO₂ flooding in condensate reservoirs could increase the condensate oil recovery factor to above 65%, and realize a high content of C₃ hydrocarbons in the produced components. Al-Abri and Amin [18] injected supercritical CO₂ and methane separately into condensate oil, and compared the oil recovery factors of the two approaches. The comparison shows that supercritical CO₂ flooding delays the breakthrough of gas injection, and pushes up the recovery factor. Moreover, the high solute solubility of supercritical CO₂ 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 CO₂ on oil displacement, which hinders pressure optimization under immiscible flooding.

Through experiments, this study explores the CO₂ flooding features under the condition of immiscible flooding. Five groups of core displacement experiments were carried out, with CO₂ 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 CO₂ immiscible flooding.

2. EXPERIMENTS

2.1 Materials

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 m³/t. At the saturation pressure and temperature T=43.75 °C, the density and viscosity of the live oil sample were measured to be ρoil=804.9 kg/m³, and μoil=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 CO₂ used has a minimum purity of 99.998 mol%. The properties of CO₂ 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

<table>
<thead>
<tr>
<th>Composition</th>
<th>Na⁺</th>
<th>SO₄²⁻</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>HCO₃⁻</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mg/L)</td>
<td>25,315</td>
<td>122</td>
<td>4,906</td>
<td>496</td>
<td>48,839</td>
<td>385</td>
<td>80,063</td>
</tr>
</tbody>
</table>

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 CO₂ core flooding experiments

Figure 2 is the sketch map of the high-pressure CO₂ core flooding apparatus. The experimental process can be briefly described as follows:

![Figure 2. High-pressure CO₂ core flooding apparatus](image)

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°C) for 48h. Table 2 shows the saturation of the connate water and initial oil. Before injecting CO₂, 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 CO₂ was injected until no more oil was produced, or the GOR reached 10,000. During CO₂ 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

<table>
<thead>
<tr>
<th>Test number</th>
<th>$P_{inj}$ (MPa)</th>
<th>$P_{out}$ (MPa)</th>
<th>Permeability (mD)</th>
<th>Porosity (%)</th>
<th>Pore volume (mL)</th>
<th>$S_{wi}$ (%)</th>
<th>$S_{oc}$ (%)</th>
<th>CO$_2$ BT</th>
<th>Oil RF at CO$_2$ BT</th>
<th>CO$_2$ RF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7</td>
<td>6</td>
<td>1.54</td>
<td>11.72</td>
<td>17.28</td>
<td>59.70</td>
<td>40.30</td>
<td>0.187</td>
<td>11.73</td>
<td>42.81</td>
</tr>
<tr>
<td>2</td>
<td>7.3</td>
<td>6.3</td>
<td>1.65</td>
<td>11.94</td>
<td>17.37</td>
<td>59.22</td>
<td>40.78</td>
<td>0.122</td>
<td>14.80</td>
<td>44.75</td>
</tr>
<tr>
<td>3</td>
<td>7.8</td>
<td>6.8</td>
<td>0.94</td>
<td>9.87</td>
<td>14.53</td>
<td>61.94</td>
<td>38.06</td>
<td>0.102</td>
<td>20.35</td>
<td>47.69</td>
</tr>
<tr>
<td>4</td>
<td>8.5</td>
<td>7.5</td>
<td>1.98</td>
<td>12.31</td>
<td>18.04</td>
<td>62.28</td>
<td>37.72</td>
<td>0.256</td>
<td>26.22</td>
<td>50.86</td>
</tr>
<tr>
<td>5</td>
<td>8.8</td>
<td>7.8</td>
<td>1.27</td>
<td>11.2</td>
<td>16.45</td>
<td>61.75</td>
<td>38.25</td>
<td>0.287</td>
<td>27.52</td>
<td>51.94</td>
</tr>
</tbody>
</table>

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 4 shows the total oil recovery factor and oil recovery factor at CO$_2$ breakthrough under different injection pressures.

Figure 4. Total oil recovery factor and oil recovery factor at CO$_2$ breakthrough under different injection pressures

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 0.1 PV. 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 0.15 PV, 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 0.65 PV, 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—0.187 PV. 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.

![Figure 6](image-url)

**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$_{10+}$) 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


