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Abstract

Carbon capture aims to mitigate the emission of CO₂ by capturing it at the point of combustion then storing it in geological reservoirs or applied through enhanced oil recovery (EOR) in a technology known as miscible flooding, so reduce CO₂ atmospheric emissions. Miscible CO₂-EOR employs supercritical CO₂ to displace oil from a depleted oil reservoir. CO₂ improve oil recovery by dissolving in, swelling, and reducing the oil viscosity. Hydrocarbon gases (natural gas and flue gas) used for miscible oil displacement in some large reservoirs. These displacements may simply amount to “pressure maintenance” in the reservoir. In such flooding techniques, the minimum miscibility pressure determined through multiple contact experiments and swelling test to determine the optimum injection conditions.

Keywords: miscible flooding, enhanced oil recovery, swelling test, minimum miscibility pressure

1. Background

CO₂ concentration in atmosphere increases due to the industrial revolution that attributed to the combustion of fossil fuels [1]. CO₂ is responsible of 64% of environmental pollution [1], so there is a dire need to mitigate its concentration to avoid global warming emissions. CO₂ miscible flooding in crude oil reservoirs is a currently successful technique to reduce its amount in the atmosphere, in addition to increasing the mobility of the oil and, consequently, increase the reservoir productivity [2]. It is preferred other than hydrocarbon gases since it does not only increase oil recovery but also causes a reduction of greenhouse gas emissions [3]. Moreover, it is a cheap technology as an ultimate long-term geologic storage solution for CO₂ owing to its economic productivity from incremental oil production offsetting the cost of carbon sequestration, and exhibit high displacement efficiency and the potential for environmental contamination
decrease through its disposal in the petroleum reservoir [1, 4]. This chapter aims to provide basic technical information concerning enhanced oil recovery by CO₂ flooding.

2. Enhanced oil recovery (EOR) processes

Owing to increased oil demand, improved oil recovery become a challenging task [3], since fossil fuels are the dominant source of the global energy supply [2] and represent about 85% of energy needs. Crude oil production occurs through three distinct phases [5–9]. The first stage is known as primary recovery, in which oil is recovered by natural reservoir energy including expansion of rock, fluid and dissolved gases, gravity drainage, and aquifer influx, or combination of these factors, which drive the hydrocarbon fluids from the reservoir to the wellbores. Primary oil recoveries range between 5 and 20% [10] of the original oil-in-place (OOIP). As reservoir pressure declines with the sustained production process, so the reservoir pressure must be built-up by injecting either water or natural gas, which drive reservoir fluid to wellbore [11]. This stage is known as secondary oil recovery, in which the recovered oil estimated to be in the range of 20–40% of the OOIP [10]. At the end of secondary recovery, a significant amount of residual oil remains in the reservoir and becomes the target for additional recovery using tertiary recovery or enhanced oil recovery (EOR) methods. EOR refers to the displacement of the remaining oil in the reservoir through injection of materials not normally present in the reservoir [10, 12–17]. Generally, EOR processes comprise the following three categories:

2.1. Thermal EOR

Injection of steam has historically been the most widely applied EOR method. Heat from steam or hot water dramatically reduces heavy oils viscosity, thus improving its flow. The process involves cyclic steam injection (“huff and puff,” where steam is first injected, followed by oil production from the same well); Continuous steam injection (where steam injected into wells drives oil to separate production wells); hot water injection, and steam assisted gravity drainage (SAGD) using horizontal wells. Another set of thermal methods include, in situ combustion or fire flooding are currently implemented [18–20].

2.2. Miscible EOR

Miscible EOR employs supercritical CO₂ to displace oil from a depleted oil reservoir. CO₂ improve oil recovery by dissolving in, swelling, and reducing the viscosity of the oil. CO₂ is a cheap injection source for increasing recovery factor by the rate of 1–2$/Mscf [21]. Most CO₂ flooding processes occur in United States [22]. Hydrocarbon gases (natural gas and flue gas) in addition to compressed nitrogen used for miscible oil displacement in high deep reservoirs. These displacements may simply amount to “pressure maintenance” in the reservoir [23–25].

2.3. Chemical EOR

Chemical flooding was, up to 2000s, a less common EOR method than thermal and gas flooding, but now, huge projects are retrieved. The chemical flooding processes involve the
injection of three kinds of chemicals; alkaline, surfactant and polymer (soluble and cross-linked polymers), in addition to other chemicals such as foaming agents, acids and solvents [26] and/or combination of alkaline-surfactant-polymer flooding (ASP) [27]. In the polymer flooding method, water-soluble polymers aimed to shut-off the high-permeability areas of the reservoir and increase injected water viscosity to increase the swept areas in the reservoir [28, 29] leading to a more efficient displacement of moderately viscous oils. Addition of a surfactant to the polymer formulation may, under very specific circumstances, reduce oil–water interfacial tension (IFT) and hence remobilizing the trapped oil [30], changing surface wettability, so enhance the oil production. For some oils, alkaline may convert some naphthenic acids within the oil to surfactants that increase oil recovery. The alkaline may also play a beneficial role in reducing surfactant retention in the rock [31–34].

3. Fundamentals and mechanism of CO\textsubscript{2} flooding

Improvement of oil recovery occurs through different techniques, one of which is CO\textsubscript{2} flooding in low permeable and light-oil reservoirs [35, 36], as it can increase recovery factor from 10 to 20% [37]. Moreover, it reduces atmospheric gas emissions through CO\textsubscript{2} storage [38]. Gas miscible flooding implies that the displacing gas is miscible with reservoir oil either at first contact or after multiple contacts, which in turn improve the volumetric sweeping and displacement efficiencies (\(E_v\) and \(E_d\)) respectively [39, 40]. A transition zone will develop between the reservoir oil and displacing gas, where the miscibility of the injected gas depend on reservoir pressure, temperature, and oil properties [41, 42]. CO\textsubscript{2} miscible flooding comprises two mechanisms.

3.1. Miscible flooding

Miscible flooding depends on mobilizing the oil light components, reduction of oil viscosity, the vaporization and swelling of the oil, and the lowering of interfacial tension [41]. The injected CO\textsubscript{2} completely dissolve through crude oil at the minimum miscibility pressure (MMP) which determined experimentally through slim-tube tests or by mathematical correlations [3, 43, 44] and defined as, the pressure at which more than 80% of original oil-in-place (OOIP) is recovered at CO\textsubscript{2} breakthrough [45]. However, on an industrial scale, an oil recovery of at least 90% at 1.2 pore volume of CO\textsubscript{2} injected is used as a rule-of-thumb for estimating MMP [46, 47]. When the reservoir pressure is above the MMP, miscibility between CO\textsubscript{2} and reservoir oil is achieved through multiple-contact or dynamic miscibility, where the intermediate and higher molecular weight hydrocarbons from the reservoir oil vaporize into the CO\textsubscript{2} (vaporized gas-drive process) and part of the injected CO\textsubscript{2} dissolves into the oil (condensed gas-drive process) [48]. This mass transfer between the oil and CO\textsubscript{2} allows the two phases to become completely miscible without any interface and helps to develop a transition zone [49] that is miscible with oil and CO\textsubscript{2}. CO\textsubscript{2} miscible flooding comprises; 1 first contact; vaporizing gas drive; and condensing gas drive [10].

A. First contact: in which miscible solvents mix with reservoir oil in all proportions and the mixture remains in one phase. Either through single or multiple contacts, and resulting in much improved oil recovery [50].
B. The vaporizing gas-drive process (high-pressure gas drive): achieves dynamic miscibility by in situ vaporization of the intermediate-molecular-weight hydrocarbons from the reservoir oil through injection of lean gases or CO_2 [51].

C. The condensing gas-drive process (enriched gas drive): achieves dynamic miscibility by in situ transfer of intermediate molecular weight hydrocarbons from rich solvent to lean reservoir oil through condensation process [52].

3.2. Immiscible flooding

Immiscible flooding depends on oil viscosity reduction, oil phase swelling, the extraction of lighter components, and the fluid drive [53]. When the reservoir pressure is below the MMP or the reservoir oil composition is not favorable, the CO_2 and oil will not form a single phase (i.e., immiscible). However, CO_2 will dissolve in the oil causing oil swelling, viscosity reduction and solution gas derive which in turn improve sweeping efficiency and facilitate further oil recovery [54]. Like hydrocarbon gases, CO_2 miscibility through crude oil increases with pressure and decreases with temperature [55, 56].

4. Properties of CO_2

In order to fully understand CO_2-EOR flooding, it is important to look at the properties of CO_2 and the fundamentals of the CO_2-EOR process. Under ambient conditions, CO_2 is a colorless, odorless gas and about 1.5 times heavier than air. CO_2 is (2–10 times) more soluble in oil than in the water. CO_2 increases the water viscosity and forms carbonate acid, which has a beneficial effect on shale and carbonate rocks [57]. Its properties under standard and critical conditions are summarized in Table 1. Above critical pressures and temperatures, CO_2 is in the supercritical state and forms a phase whose density is close to that of a liquid, even though its viscosity

<table>
<thead>
<tr>
<th>Properties at standard conditions (14.7 psia, 0 °C)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>44.010 g/mol</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.529</td>
</tr>
<tr>
<td>Density</td>
<td>1.95 kg/m³</td>
</tr>
<tr>
<td>Viscosity</td>
<td>0.0137 mPa/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Critical properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical pressure (P_c)</td>
<td>1070.6 psia</td>
</tr>
<tr>
<td>Critical temperature (T_c)</td>
<td>87.98 °F</td>
</tr>
<tr>
<td>Critical volume (V_c)</td>
<td>94 cm³/mol</td>
</tr>
<tr>
<td>Critical viscosity (μ_c)</td>
<td>0.0335 cp</td>
</tr>
</tbody>
</table>

Table 1. Properties of CO_2 under standard and critical conditions.
remains quite low (0.05–0.08 cp). This dense CO₂ phase can extract hydrocarbon components from oil more easily than gaseous CO₂ [49].

5. CO₂ flooding and injection designs

Depending on the reservoir geology, fluid and rock properties, the CO₂ flooding involves the following:

5.1. Continuous CO₂ injection

This process requires continuous CO₂ injection with no other fluid. Sometimes a lighter gas, such as nitrogen, follows CO₂ injection to maximize gravity segregation.

5.2. Continuous CO₂ injection followed with water

This process is the same as the continuous CO₂ injection process except for chase water that follows the total injected CO₂ slug volume.

5.3. Conventional water-alternating-gas (WAG) followed with water

In this process, a predetermined volume of CO₂ is injected in cycles alternating with equal volumes of water. The water alternating with CO₂ injection helps overcome the gas override and reduces the CO₂ channeling consequently, improving overall CO₂ sweep efficiency.

5.4. Tapered WAG

This design is similar in concept to the conventional WAG but with a gradual reduction in the injected CO₂ volume relative to the water volume.

5.5. WAG followed with gas

This process is a conventional WAG process followed by a chase of less expensive gas (e.g., air or nitrogen) after the full CO₂ slug volume has been injected.

6. CO₂-EOR flooding projects and case studies

Several literatures stated about implementation of CO₂ and carbonated water to improve oil recovery since 1951 [45, 54, 58, 59], owing to its availability in adequate amounts from both natural and industrial sources [60]. The first field-wide application occurred in 1972 at the SACROC (Scurry Area Canyon Reef Operators Committee) unit in the Permian Basin, where the CO₂ was transported via a 200-mile-long pipeline from the Delaware-Val Verde Basin.
Hashemi and Pouranfard [1] reported about the investigation of immiscible miscible CO₂ injection southwest of Iranian oil field, which has two reservoirs: Gurpi and a shallower Asmari reservoir. Main reservoir in this field is the Asmari formation with Oligocene and Miocene ages, which is divided into seven zones. Therefore, only the Asmari formation has been producing oil at commercial scale. The Asmari formation in this field consists of fractured carbonates with a low permeability matrix. The matrix has a porosity and permeability of about 0.088% and 3.4 md, respectively [1]. They concluded that the minimum miscibility pressure (MMP) was 4630 psia, The optimum injection rates for immiscible and miscible CO₂ injection scenarios were 17,000 and 30,000 Mscf/day, respectively and oil recovery factor reach 36.59% [1]. Al-Aryani and others [61] have reported on the first CO₂-EOR pilot test in the Middle East where pulsed neutron logging was used to monitor the performance of a CO₂ flood in one of the largest oil fields in Abu Dhabi, United Arab Emirates. The results of this test will be viewed with great interest based on the fact that it will have a significant impact on the application of CO₂-EOR in many oil-rich countries in the Middle East with the potential for very large additional oil recoveries. In India, a CO₂-EOR feasibility study was implemented in an oil field on the west coast, but the results are not yet publically available [62]. In China, there is ongoing research and pilot testing of CO₂-EOR and carbon sequestration in the Jilin oil field with plans to expand to other fields [63]. As of 2012, there were 15 CO₂-EOR projects outside of the United States—six in Canada, three in Brazil, five in Trinidad, and one in Turkey [64]. Of the six CO₂-EOR miscible projects in Canada, the Weyburn project is the most significant because it was the first project with the primary objective of injecting CO₂ for additional oil recovery as well as for carbon sequestration to help mitigate climate change. In recent years, there have been some serious efforts by Scottish Carbon Capture & Storage (SCCS), the Scottish Government, and other companies to investigate the possible application of CO₂-EOR in the North Sea. This interest is based on the potential for additional oil recovery from depleted oil fields using CO₂ captured from power plants and industry [10]. The objective is to gain a better understanding of the use of CO₂ in EOR operations with the goal of extending the producing life of North Sea oil fields using CO₂ captured from large emitters, such as power plants and industrial facilities, and permanently store the greenhouse gas in offshore oil reservoirs. It is estimated that there is the potential to recover 24 billion barrels of additional oil in the North Sea using the CO₂-EOR process. About 60 active miscible CO₂ projects were in operation in the United States in 1996, whereas in Canada, hydrocarbon miscible floods reach nearly ~40 active projects [35, 65]. Most CO₂-flooding projects carried out in the United States in Colorado, Louisiana, Mississippi, New Mexico, Michigan, Oklahoma, Texas, Utah, and Wyoming. During 2014, about 22 companies implemented CO₂ flooding projects; where 128 projects contributed about 126 million tons of oil [66], applied through carbonate and sandstone reservoirs with a percentage of 55 and 37% respectively, while the other 6% were implemented in tripolite reservoirs [67]. The range of porosity is from 4 to 29.5% with a permeability of 100 mD. The main operators and their productions reported in Table 2. The increased implementation of CO₂ flooding projects resort to its availability from natural and industrial sources in addition to its relatively low cost as a displacing agent compared to other alternatives [68]. It is observed that the outcome of these projects summarized in Table 2, where the recovery factor ranged from 0.15 to 36.37%. The reservoirs properties are summarized in Table 3.
Screening criteria for CO₂ flooding comprise reservoir depth, pressure and temperature, minimum miscibility pressure (MMP), residual oil saturation, net pay thickness, crude oil gravity, and viscosity in addition to permeability, porosity, and reservoir heterogeneity [40].

<table>
<thead>
<tr>
<th>Operator</th>
<th>No. of projects</th>
<th>Improved production (× 10⁴ tons)</th>
<th>Recovered oil (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Occidental</td>
<td>33</td>
<td>459.63</td>
<td>36.37</td>
</tr>
<tr>
<td>Kinder Morgan</td>
<td>3</td>
<td>138.34</td>
<td>10.94</td>
</tr>
<tr>
<td>Chevron</td>
<td>7</td>
<td>126.30</td>
<td>9.99</td>
</tr>
<tr>
<td>Hess</td>
<td>4</td>
<td>106.89</td>
<td>8.46</td>
</tr>
<tr>
<td>Denbury Resources</td>
<td>18</td>
<td>86.82</td>
<td>6.87</td>
</tr>
<tr>
<td>Merit Energy</td>
<td>7</td>
<td>71.12</td>
<td>5.63</td>
</tr>
<tr>
<td>Anadarko</td>
<td>6</td>
<td>55.79</td>
<td>4.41</td>
</tr>
<tr>
<td>ExxonMobil</td>
<td>1</td>
<td>45.36</td>
<td>3.59</td>
</tr>
<tr>
<td>Breitburn Energy</td>
<td>5</td>
<td>36.87</td>
<td>2.92</td>
</tr>
<tr>
<td>ConocoPhillips</td>
<td>2</td>
<td>28.42</td>
<td>2.25</td>
</tr>
<tr>
<td>Whiting Petroleum</td>
<td>1</td>
<td>24.51</td>
<td>1.94</td>
</tr>
<tr>
<td>Apache</td>
<td>5</td>
<td>23.88</td>
<td>1.89</td>
</tr>
<tr>
<td>XTO Energy Inc.</td>
<td>4</td>
<td>13.43</td>
<td>1.06</td>
</tr>
<tr>
<td>Chaparral Energy</td>
<td>8</td>
<td>9.18</td>
<td>0.73</td>
</tr>
<tr>
<td>Fasken</td>
<td>5</td>
<td>4.30</td>
<td>0.34</td>
</tr>
<tr>
<td>Core Energy</td>
<td>9</td>
<td>1.90</td>
<td>0.15</td>
</tr>
<tr>
<td>Others</td>
<td>12</td>
<td>31.19</td>
<td>2.47</td>
</tr>
</tbody>
</table>

Table 2. CO₂ miscible flooding operator and production dataset [66, 69, 70].

<table>
<thead>
<tr>
<th>Property</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Median</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>4</td>
<td>29.5</td>
<td>12</td>
<td>14.25</td>
</tr>
<tr>
<td>Permeability, mD</td>
<td>2</td>
<td>700</td>
<td>14</td>
<td>44.35</td>
</tr>
<tr>
<td>API gravity</td>
<td>27</td>
<td>45</td>
<td>38</td>
<td>37</td>
</tr>
<tr>
<td>Viscosity, cp</td>
<td>0.4</td>
<td>6</td>
<td>1.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Temperature, °F</td>
<td>83</td>
<td>260</td>
<td>108.5</td>
<td>133.9</td>
</tr>
<tr>
<td>Depth, ft</td>
<td>1150</td>
<td>11,950</td>
<td>5500</td>
<td>6107.3</td>
</tr>
<tr>
<td>Oil saturation (% PV)</td>
<td>26.3</td>
<td>89</td>
<td>46</td>
<td>49.6</td>
</tr>
<tr>
<td>Net thickness, ft</td>
<td>15</td>
<td>268</td>
<td>90</td>
<td>110</td>
</tr>
<tr>
<td>Minimum miscibility pressure (MMP), psia</td>
<td>1020</td>
<td>3452</td>
<td>1987.5</td>
<td>2058.4</td>
</tr>
</tbody>
</table>

Table 3. Properties of reservoirs subjected to CO₂ flooding.

7. Screening criteria for CO₂ flooding

Screening criteria for miscible CO₂ flooding comprise reservoir depth, pressure and temperature, minimum miscibility pressure (MMP), residual oil saturation, net pay thickness, crude oil gravity, and viscosity in addition to permeability, porosity, and reservoir heterogeneity [40]. In
preliminary screening, according to National Petroleum Council, the optimum reservoir criteria for CO$_2$ miscible flooding [64, 71] are summarized in Table 4. Any deviation from these criteria would depend on the size of the reservoir and potential hydrocarbon recovery. For example when reservoir temperatures are greater than 120°F, additional pressure ranges from 200 to 500 psi is required to achieve miscibility. The density of CO$_2$ depends on the injection depth, which controls the ambient temperature and pressure and range from 0.6–0.8 g/cc [72]. The CO$_2$ should be injected at depth greater than 800 m, where it is in a dense phase (either liquid or supercritical) [2]. High saline reservoirs are more susceptible to CO$_2$ storage than low salinity reservoirs.

All reservoir lithology, including carbonate and siliciclastic are appropriate for CO$_2$-EOR flooding as long as they have interconnected pore space for fluid accumulation and flow. Proper reservoir characterization leads to accurate estimates of OOIP and a convenient evaluation of reservoir behavior. The OOIP calculated volumetrically, by the following equation;

$$OOIP = \frac{(7758 \times A \times H \times \Phi \times S_{oi})}{B_{oi}}$$  (1)

7758, multiplying factor, (barrels/acre-feet); $A$, reservoir area,(acres);h; average net reservoir thickness, (feet); $\Phi$; average porosity of formation; $S_{oi}$, initial oil saturation in pore space; $B_{oi}$, oil formation volume factor at initial reservoir pressure (bbl/STB).

8. CO$_2$-miscible flooding performance and simulation

Before conducting a CO$_2$-flooding, its miscibility with the reservoir is determined through measurement of MMP. After that, a pilot test is conducted to check the success of the CO$_2$-EOR process on a small scale in the field. If all results are positive, reservoir simulation is
carried out to (a) scale-up the EOR process to an entire oil field and (b) define the optimum design of the WAG ratio and hydrocarbon pore volume injection volumes for maximum oil recovery [75]. The performance of a flooding process evaluated by exploring the slug of CO$_2$ and water, the performance of oil-production wells, gas-oil ratio and water cut, and the injection wells for fluid distribution among various reservoir layers, since these parameters greatly effect on the recovery factor [76].

9. Operational aspect

In order to implement a successful CO$_2$-miscible flooding several parameters are considered;

9.1. CO$_2$ source

There are three possible sources of CO$_2$: (1) natural hydrocarbon gas reservoirs containing CO$_2$ as an impurity (generally less than 25%), (2) industrial or anthropogenic sources with wide variation of CO$_2$ percentage in the effluent like power plants and so on [2], and (3) natural CO$_2$ reservoirs [49].

9.2. Surface facilities

The facility requirements for CO$_2$-EOR include the following items.

i. CO$_2$ extraction: it is extracted from the separator gas, which begins to show increasing quantities of CO$_2$ after its breakthrough in producing wells [77].

ii. CO$_2$ processing: it is purified to specification after its extraction from the separator gas and is dehydrated before compression [78].

iii. CO$_2$ compression: it is compressed to raise its pressure for injection [79].

9.3. Technological challenges

Technical challenges of CO$_2$ flooding can be summarized in the following [80].

1. Increasing CO$_2$ injection volumes,

2. Optimizing flood design and well placement for extracting more of the residual oil,

3. Improving the mobility ratio by increasing the viscosity of water by use of polymers, and

4. Extending miscibility by reducing the miscibility pressure through the use of liquefied petroleum gas (LPG).

10. Conclusion

The primary and secondary oil recovery produces about 20–40% of the OOIP [48]. Consequently, there is a huge amount of potentially unrecovered oil left in the reservoir, which becomes the
target for suitable EOR processes. One of the widely implemented EOR processes is CO$_2$-miscible flooding which recovers high amounts of crude oil and reduces environmental pollution results from gas emissions. CO$_2$ can be injected either as a continuous stream, water-alternating gas (WAG). Implementation of successful CO$_2$ miscible flooding require an accurate investigation of reservoir screening criteria comprising reservoir porosity and permeability, API gravity, oil viscosity, reservoir temperature, depth, oil saturation, and net pay thickness.

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