CO₂ Enhanced Oil Recovery in Unconventional Liquid Reservoirs

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Objectives of NETL

- Increase domestic energy production (Improve U.S. energy security, decrease dependence on foreign oil)
- Reduce environmental impact of fossil fuels
Despite Shale Revolution, much work to be done!

- EOR in unconventionals is needed: recovery after hydraulic fracturing + primary production = 4-6% (Bakken)
- Permeabilities are 1,000 to 10,000 times lower in than in conventional reservoirs
- Low permeabilities are caused by low porosity, small pore sizes, oil-wetness
Mechanism of CO\textsubscript{2} oil recovery in conventional reservoirs

- Conventional and unconventional mechanisms are very different due to the low permeability shale matrix
- CO\textsubscript{2} EOR in conventional: CO\textsubscript{2} easily flows through pores
- Heavy and light hydrocarbons are both produced, no soak time needed
Mechanism of CO₂ Enhanced Oil Recovery in Fractured Shale Reservoirs

• Diffusion is a key mechanism: long soak times improve recovery, lighter hydrocarbons produced preferentially

Unconventional reservoirs

Step 1: Injection
CO₂ flows through fractures, driven by high injection pressures

Step 2: Early Soaking Period
Some CO₂ enters pores, driven by high injection pressures

Step 3: Late Soaking Period
Injection pressure equilibrates and CO₂ enters pores by diffusion

Step 4: Production
Oil and CO₂ in fractures move to production well
Implications of diffusion mechanism

Diffusion mechanism of CO₂ EOR in ULRs

- Long soak times improve oil recovery
- High exposed shale surface area improves recovery
- Lighter hydrocarbons are produced preferentially
- High injection pressures beyond MMP improve oil recovery

CO₂ EOR in ULRs
### Fluids being considered for EOR in Fractured Shale Reservoirs

<table>
<thead>
<tr>
<th>Attribute</th>
<th>CO₂</th>
<th>Ethane</th>
<th>Methane</th>
<th>Nitrogen</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic diameter (nm)</td>
<td>0.33</td>
<td>0.44</td>
<td>0.38</td>
<td>0.36</td>
<td>0.27</td>
</tr>
<tr>
<td>Critical temperature, °C</td>
<td>31</td>
<td>32</td>
<td>-83</td>
<td>-147</td>
<td>374</td>
</tr>
<tr>
<td>Critical pressure, Mpa</td>
<td>7.4</td>
<td>4.9</td>
<td>4.6</td>
<td>3.4</td>
<td>22.1</td>
</tr>
<tr>
<td>Critical Density (g/cm³)</td>
<td>0.47</td>
<td>0.21</td>
<td>0.12</td>
<td>0.31</td>
<td>0.32</td>
</tr>
<tr>
<td>Viscosity (cP), 100 °C, 20.7 MPa</td>
<td>0.039</td>
<td>0.038</td>
<td>0.018</td>
<td>0.025</td>
<td>0.29</td>
</tr>
<tr>
<td>MMP, Bakken oil (MPa), 110 °C</td>
<td>17.4</td>
<td>9.3</td>
<td>31.1</td>
<td>101.4</td>
<td>-</td>
</tr>
<tr>
<td>Swells oil?</td>
<td>Significant</td>
<td>Significant</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Reduces oil viscosity?</td>
<td>Significant</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Contaminant if present in produced oil/gas?</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Forms acid in water?</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

- **Advantageous for oil recovery**
- **Moderate effect on oil recovery**
- **Disadvantageous for oil recovery**
CO₂ and Nat. Gas are both viable gases for EOR in Shale

Rich natural gas (~15% C₂+) and CO₂ yield similar oil recovery in lab-scale huff ‘n puff experiments

11 mm diameter rods from Middle Bakken, 110 °C, 5000 psi, Hawthorne et. al., 2017
CO₂ and Nat. Gas are both viable gases for EOR in Shale

<table>
<thead>
<tr>
<th>Eagle Ford Formation</th>
<th>Bakken</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Injectivity</strong></td>
<td>Good</td>
</tr>
<tr>
<td><strong>EOR Results</strong></td>
<td>Natural gas injection increased production*</td>
</tr>
<tr>
<td><strong>Problems</strong></td>
<td>Conformance control issues, early breakthrough, influence of nearby wells unknown</td>
</tr>
</tbody>
</table>

*No comparison to CO₂ reported.

Pilot tests do not clearly show which high-pressure gas is better for oil recovery.
Lab tests are overly optimistic

Surface area to volume ratio in laboratory is high, does not correspond to field

Core Volume / Surface Area Exposed to CO₂ (cm)

CO₂ is allowed to surround entire core

Confined Core Huff n’ Puff

1. 2. Soak

Confined cores to better model field conditions

NETL Pittsburgh: CO₂  Morgantown: natural gas

At-depth cores from Eagleford
Surfactants are commonly used in waterflooding (conventionals) and fracturing fluid (Unconventionals).

Surfactants improve hydrocarbon recovery by:

1. Decreasing interfacial tension (IFT) between oil and water
2. Changing surface from oil-wet to water-wet
CO₂-soluble surfactants for CO₂ EOR

- CO₂-soluble surfactants have already been studied for CO₂ foams
- Nonionic surfactants are inexpensive and commercially available
- Combine the advantages of low viscosity CO₂ with the IFT and wettability-altering capabilities of surfactants
Our experimental plans: CO$_2$ EOR using shale cores

- Pump, transfer vessel and soaking vessel are in place, setup completed
- Shake down with Berea in decane completed
- Experimental procedures: Huff n’ Puff with confining pressure-setup in progress
- Oil analysis: Filtering the Eagle Ford oil, SARA analysis
Conclusions

- Natural Gas and CO₂ are both viable fluids for EOR in Unconventionals
- Use of CO₂ or natural gas largely depends on cost and availability
- Laboratory core floods for EOR in Unconventionals are more optimistic than field results
- We are using confined, “at-depth” cores for CO₂ EOR experiments
- Will combine the benefits of CO₂ with wettability-altering surfactants