Characterizing CO$_2$ as a Recovery Agent to Mobilize Hydrocarbons from Shale

U.S. Department of Energy
National Energy Technology Laboratory
Oil & Natural Gas
2020 Integrated Review Webinar
Characterizing Application of CO$_2$ as a Recovery Agent to Mobilize Hydrocarbons from Shale

- **Objective:**
  - Determine viability of CO$_2$ as an enhanced recovery agent for unconventional oil

- **Challenges:**
  - Primary oil recovery from fractured unconventional formations is typically less than 10% - EOR is highly desired by industry
  - However, EOR in shale is far more challenging than conventional formations due to their extreme low permeability and mixed wettability

- **Approach:**
  - Determine how CO$_2$ and in surfactants dissolved in CO$_2$ can be used to increase EOR by simulating subsurface EOR conditions in the laboratory
    - Surfactants – identify CO$_2$-soluble surfactants to change wetting properties
    - Contact angle – observe change from oil-wet to water-wet
    - Confined Huff n’ Puff core floods – relate to field tests

- **Value:**
  - Successful EOR in shales would lead to tremendous increases in domestic oil production
Characterizing Application of CO₂ as a Recovery Agent to Mobilize Hydrocarbons from Shale

Analysis of prior efforts for enhanced oil recovery from shales
• Critical review developed from literature study which defined laboratory R&D needs for EOR
Laboratory-based confined huff n’ puff tests to relate to the field and are a primary focus of this project moving forward.

Findings:
• CO₂ and natural gas are promising fluids for huff ‘n puff EOR
• CO₂ EOR shale is a complex process that involves many mechanisms, especially miscibility and diffusion
• High pressure CO₂ and natural gas will recover much more oil than water. However, interest persists in the lower cost, water-based EOR
• CO₂ EOR reduces the carbon intensity of the oil produced by associated CO₂ storage
• Field cores “from depth” and reservoir crude oil (rather than outcrop cores and synthetic crude oil) are needed to improve the reliability of laboratory-scale results

“A Literature Review of CO₂, Natural Gas, and Water-Based Fluids for Enhanced Oil Recovery in Unconventional Reservoirs”
Energy & Fuels 2020 34 (5), 5331-5380
DOI: 10.1021/acs.energyfuels.9b03658

Experimental approach: CO₂ EOR using shale cores

**Oil-saturated cores**
- Taken from oil-producing shales, at depth. Weigh cores, no cleaning

**Extraction experiments**
- Monitor weight of hydrocarbons extracted
- Extract oil with methylene chloride/acetone

**Grind core to powder**

**Experimental conditions:**
- Confined huff n’ puff
- Bathing huff ‘n puff
- HPHT Contact angle measurements

**Shale samples:**
- Eagle Ford, Mancos, Bakken, Wolfcamp

**Oil:**
- Eagle Ford, Bakken, Wolfcamp Live Oil

**Partner for samples:**
- HFTS Project (Wolfcamp)

**Confined cores to better model field conditions using NETL’s core flow apparatus**

- CO₂ Flow
- Injection pump
- Mancos Core (A1)
- Injection pump
- CO₂ Flow

**Milestone:**
- Milestone 9D. 06/2019 Obtain shale samples for future CO₂ hydrocarbon extraction tests
- Milestone 9F. 12/2019 Quantify hydrocarbon oil from shale
CO₂ huff ‘n puff for EOR in unconventional formations

Oil Recovery Mechanisms

- CO₂ extraction of oil
- CO₂ diffusion into oil
- Oil diffusion into CO₂
- Oil swelling
- Oil viscosity reduction
- Solution gas drive

New mechanism
Wettability alteration during soaking due to the dissolution of nonionic surfactants in the CO₂
Why nonionic surfactants in CO$_2$

- CO$_2$ is a **solvent** for nonionic surfactants
- Objective of this study in unconventional formations
- Long-term application in conventional formations
- In-situ generation of CO$_2$-in-water mobility control foam as the surfactant partitions into the in-situ brine to improve sweep efficiency
- Wettability alteration toward more oil-phobic and CO$_2$-philic

- To combine the advantages of low viscosity CO$_2$ with the IFT and wettability-altering capabilities of surfactants in a single phase
- Inexpensive and commercially available
- Many options, can be oil-soluble or water-soluble
- Even low surfactant solubility (0.1-1.0 wt.%) in high pressure CO$_2$ may be more than enough for EOR
Surfactants added to CO₂
Potential wettability alteration during CO₂ fracturing and CO₂-EOR

- Oil-wet pore: 90° < θ < 180°; P_c is negative; oil is trapped.
- CO₂-wet pore: 0° < θ < 90°; P_c is positive; oil is recovered by spontaneous imbibition.

Wettability alteration due to adsorption of CO₂-soluble surfactant.

**Large positive P_c**
Surfactant needs to make the surface as CO₂-wet as possible while reducing the IFT by as little as possible.

**Risk**
With ultralow IFT, wettability alteration may not have a significant effect on improving the displacement of oil.

Desired wettability for shale:
- Strongly oil-wet
- Oil-wet
- Intermediate-wet/neutral wet
- CO₂-wet
- Strongly CO₂-wet
Identification of CO$_2$-Soluble Surfactants

Two water-soluble, nonionic ethoxylated alcohols were selected for this study. Huntsman N100, a branched nonylphenol ethoxylate with an average of 10 EO groups (left, average x = 10) and Huntsman TDA 9, a branched ethoxylated tridecylalcohol with an average of 9 EO groups (right, average x = 9).

Example: At 58°C, ~4000 psi is required to dissolve 0.5wt% N 100 in CO$_2$.

- **Huntsman N100**
  - 25°C
  - 58°C
  - 77°C

- **Huntsman TDA 9**
  - 25°C
  - 58°C
  - 100°C
  - 77°C

✓ Milestone 9I. 03/2020 Generate surfactant solubility in CO$_2$ data for one surfactant at a low temperature and compare with literature data.
Contact angle measurements (Wettability)

Eagle Ford Shale

Huntsman N100

- No change* in wettability due to exposure to pure CO₂

- Before treatment: Oil-wet
- Treated with CO₂: Treated with CO₂-surfactant at 25 °C
- Treated with CO₂-surfactant at 80 °C

- Before treatment: Water-wet
- Treated with CO₂: Treated with CO₂-surfactant at 80 °C

Huntsman TDA 9

- No change* in wettability due to exposure to pure CO₂

- Before treatment: Oil-wet
- Treated with CO₂: Treated with CO₂-surfactant 80 °C
- Treated with CO₂-surfactant 80 °C

Huff n’ Puff Experiments with CO₂

8 Huff n’ Puff Cycles: 79% recovery with pure CO₂

Core | Length | Diameter | Bulk Volume | Pore Volume | Porosity | Permeability | Dry Weight | Soaked Weight | oil in place |
-----|--------|----------|-------------|-------------|----------|--------------|------------|---------------|--------------|
CO₂ run 1 | Eagleford | 5.076   | 2.552       | 25.95       | 1.96     | 7.55         | 56.45      | 58.78         | 2.33         |
CO₂ run 2 | Eagleford | 5.022   | 2.555       | 25.74       | 1.69     | 6.56         | 56.12      | 58.26         | 2.15         |

Milestone 9.C 06/2020 Complete shakedown of continuous core flooding apparatus, in preparation for hydrocarbon extraction from tight and shale cores using supercritical CO₂
Huff n’ Puff Experiments with CO₂ and Surfactant

8 Huff n’ Puff Cycles:
- 79% recovery with pure CO₂
- 85% recovery with surfactant (TDA9) dissolved in CO₂
- 75% recovery with surfactant (N100) dissolved in CO₂

<table>
<thead>
<tr>
<th>Core</th>
<th>Length (cm)</th>
<th>Diameter (cm)</th>
<th>Bulk Volume (cc)</th>
<th>Pore Volume (cc)</th>
<th>Porosity (%)</th>
<th>Permeability (μD)</th>
<th>Dry Weight (g)</th>
<th>Soaked Weight (g)</th>
<th>Oil in Place (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ run 2</td>
<td>Eagleford</td>
<td>5.022</td>
<td>2.555</td>
<td>25.74</td>
<td>1.69</td>
<td>6.56</td>
<td>56.12</td>
<td>58.26</td>
<td>2.15</td>
</tr>
<tr>
<td>0.1% TDA9 in CO₂</td>
<td>Eagleford</td>
<td>4.523</td>
<td>2.556</td>
<td>23.20</td>
<td>1.80</td>
<td>7.78</td>
<td>50.33</td>
<td>52.30</td>
<td>1.97</td>
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<tr>
<td>0.01% TDA9 in CO₂</td>
<td>Eagleford</td>
<td>4.719</td>
<td>2.556</td>
<td>24.20</td>
<td>1.81</td>
<td>7.48</td>
<td>52.49</td>
<td>54.56</td>
<td>2.07</td>
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<tr>
<td>0.1% N100 in CO₂</td>
<td>Eagleford</td>
<td>5.032</td>
<td>2.553</td>
<td>25.75</td>
<td>1.86</td>
<td>7.22</td>
<td>55.99</td>
<td>58.24</td>
<td>2.24</td>
</tr>
</tbody>
</table>

Milestone 9.J 06/2020  Perform core flooding experiments for one type of shale using CO₂ and using CO₂-surfactant solutions
Physical and chemical alterations of Eagle Ford and Barnett Shale after hydrocarbon extraction with CO$_2$.

- **Milestone 9G. 03/2020** Identify key physical and chemical alterations for Eagle Ford and Barnett Shales after hydrocarbon extraction with CO$_2$.

**Eagle Ford**
- **FTIR:** In situ characterization
- **SEM:** Visualization of shale matrix alterations
- **BET:** Pore size distribution changes

**Barnett**
- **FTIR:** In situ characterization
- **SEM:** Visualization of shale matrix alterations
- **BET:** Pore size distribution changes
Physical and chemical alterations of Eagle Ford and Barnett Shale after hydrocarbon extraction with CO₂

Milestone 9G. 03/2020 Identify key physical and chemical alterations for Eagle Ford and Barnett Shales after hydrocarbon extraction with CO₂.

- **BET**: Pore size distribution changes
- **SEM**: Visualization of shale matrix alterations
- **FTIR**: In situ characterization

**Gypsum Formation**
- CO₂-Saturated Fluid Exposed
- Gypsum Flowers

**Barnite Formation**
- HFF Exposed
- Barnite

**HFF-Exposed**
- Frack Fluid pH = 1.4
- Frack Fluid reacts with shale matrix
- Sample submerged in synthetic frack fluid
- N₂ introduced to the system (10.3 MPa)

**HFF-Unexposed**
- Millipore water pH = 7
- CO₂ dissolved into water to form carbonic acid and react with shale matrix
- Sample submerged in Millipore water
- CO₂ introduced to the system (10.3 MPa)

**Barite Formation**
- HFF Exposed
- Barite

**CO₂-Saturated Fluid Exposed**
- Organics Matrix
- Gypsum Flowers
**Published Papers**

**A Literature Review of CO₂, Natural Gas, and Water-Based Fluids for Enhanced Oil Recovery in Unconventional Reservoirs**
Lauren C. Burrows, Foad Haeri, Patricia Cvetic, Sean Sanguinito, Fan Shi, Deepak Tapriyal, Angela Goodman, and Robert M. Enick
*Energy & Fuels* 2020 34 (5), 5331-5380
DOI: 10.1021/acs.energyfuels.9b03658

**2019: Filed patent application 62/931,653 “Method of Oil Recovery Using Compositions of Carbon Dioxide and Compounds to Increase Water Wettability of Formations.” Developed and submitted critical literature review to Energy and Fuels.**

**URTeC: 2774**
*Improving CO₂-EOR in Shale Reservoirs using Dilute Concentrations of Wettability-Altering CO₂-Soluble Nonionic Surfactants*

**Accepted abstracts**

We are determining how CO\(_2\) and CO\(_2\)/surfactant can be used to increase EOR by simulating subsurface EOR conditions in the laboratory by changing wetting.

Successful EOR in shales would lead to tremendous increases in domestic oil production.

Examples of simulated laboratory EOR techniques we are performing include:

- Confined huff n’ puff and Bathing huff n’ puff

In progress:
- Currently soaking Wolfcamp in live oil
- Preparing for Huff n’ Puff (confined and bathing)
- Comparing oil recovery with CO\(_2\) and CO\(_2\) and surfactants (URTEC)
- Soaking cores in fracture fluid or brine prior to oil recovery
- Trying a new surfactant - Surfonic L12-6
- High pressure contact angle experiments with CO2 and oil in contact with oil-wet shale.
- High pressure IFT experiments to determine the degree of IFT reduction.