Lab Comparisons: Methane, Ethane, Propane, CO_2 and Produced Gas for Hydrocarbon Mobilization

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Critical Challenges. **Practical Solutions.**

Today's talk reports results from multiple lab research projects focusing on IOR/EOR in conventional and unconventional reservoirs.

Multiple projects supporting studies on CO_2 storage and utilization. Present project focusing on rich gas EOR for "tight oil."

Bakken Petroleum Optimization Program (BPOP) focusing on rich gas EOR.

PARTNERS IN EERC BAKKEN PROJECTS

Critical Challenges. **Practical Solutions.**

Laboratory experiments were conducted with Bakken crude oil (MMP and "miscible" phase sampling) and rock cores obtained from the North Dakota Geological Survey's Wilson M. Laird Core and Sample Library.

- All experiments were performed at 110 ^{o}C (230 ^{o}F).
- Rock samples were NOT re-saturated. Extracted hydrocarbons were those naturally occurring in the rock.
- Produced gas was assumed to be 70/20/10 methane/ethane/propane.
- The Bakken crude oil was obtained from a test separator.
  - API 41
  - Oil density, 0.82 g/mL
  - Oil viscosity, 2.65 cP

CO_2 and Produced Gas-Oil Fluid Behavior and Rock Extraction Studies

MMP Studies

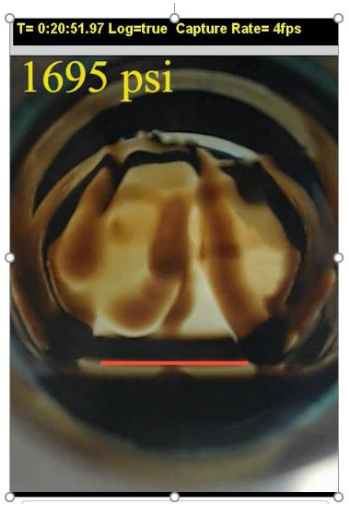
Patent pending

MMP of crude oil with rich gas components and different rich gas mixtures.

- CO_2, methane, ethane, propane, and produced gas.

(Capillary-rise, vanishing interfacial tension measurements of MMP, EERC patent US 9851339)

Miscible Behavior Studies



How well do injected gases mobilize crude oil hydrocarbons into the "miscible" upper phase?

Which injected gases mobilize higher MW hydrocarbons better?

Rock Extraction Studies

Determine ability of rich gas components to mobilize oil from the Bakken matrix.

- CO_2, methane, ethane, propane, and produced gas at reservoir conditions.

EERC

3 basic lab experiments:

- *MMP = multiple contact minimum miscibility pressure by vanishing interfacial tension.*
- *Hydrocarbon compositions in the "miscible" phase.*
- *Crude oil hydrocarbon recovery from Bakken rock samples.*

Definitions of Multiple Contact "Miscibility" (MMP)

To a PVT lab: 90% of the oil in a 50 foot "slim tube" of sand comes out in 1.2 pore volumes (slow and very expensive but has served conventional EOR well).

To a chemist: miscible fluids mix in any ratio without forming two phases.

EERC approach (via Rao, et al.): vanishing interfacial tension. "Miscibility" is defined as no surface tension between the CO_2- and oil-dominated phases.

MMP by vanishing interfacial tension/capillary rise.

1.12, 0.84, 0.68 mm i.d.

Rapid and Simple Capillary-Rise/Vanishing Interfacial Tension Method To Determine Crude Oil Minimum Miscibility Pressure: Pure and Mixed CO_2, Methane, and Ethane

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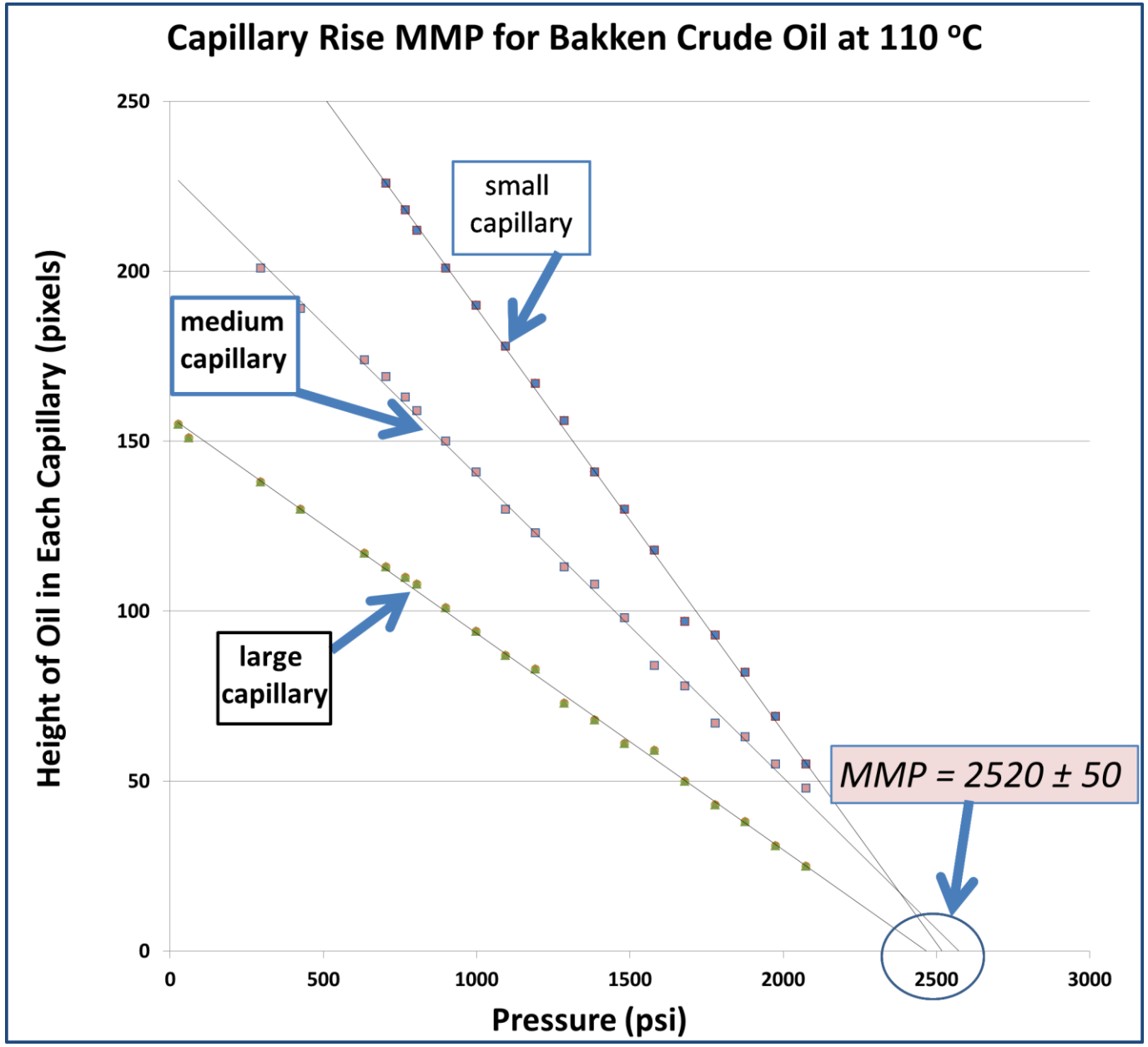
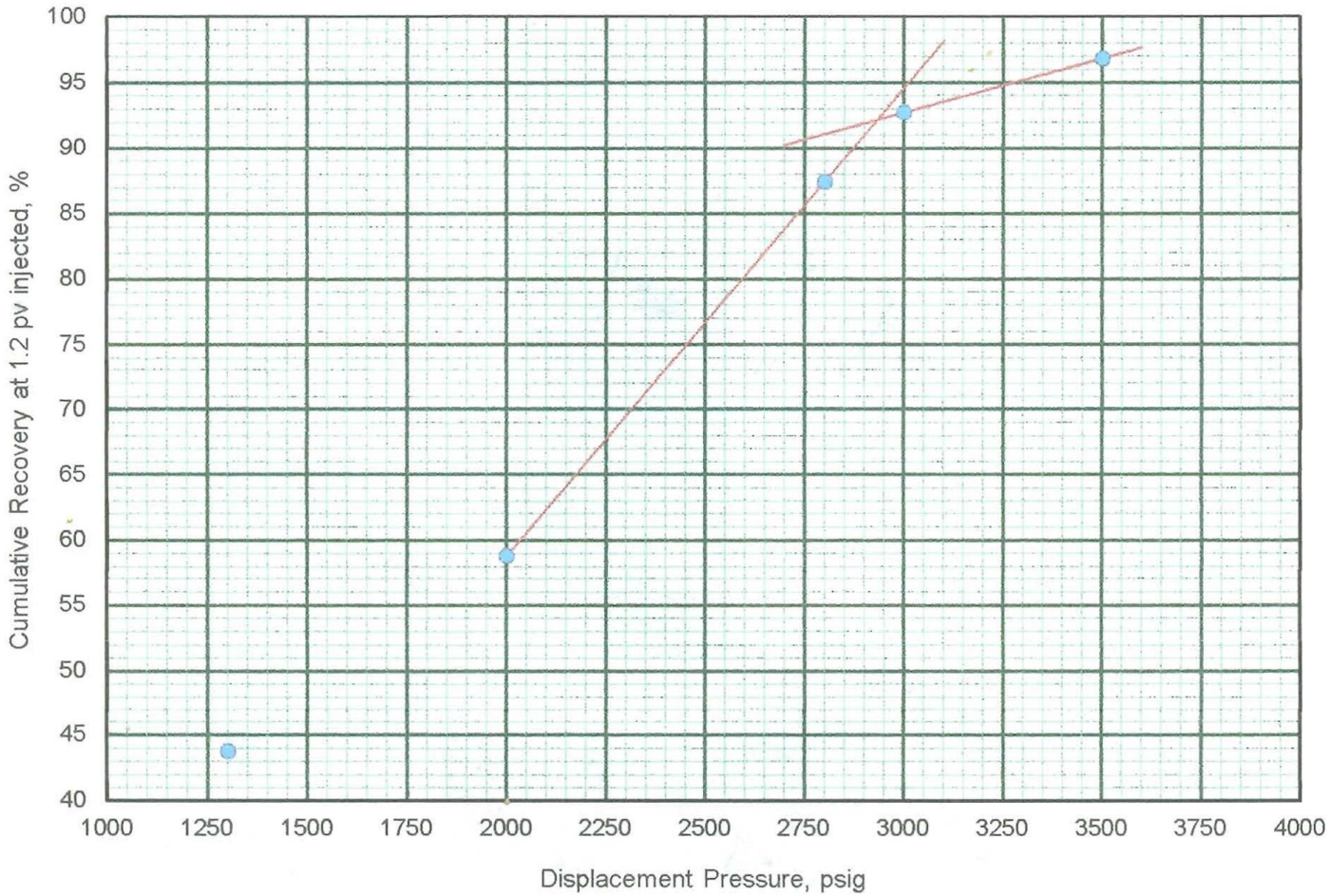
EERC patent US 9851339



EERC patent US 9851339

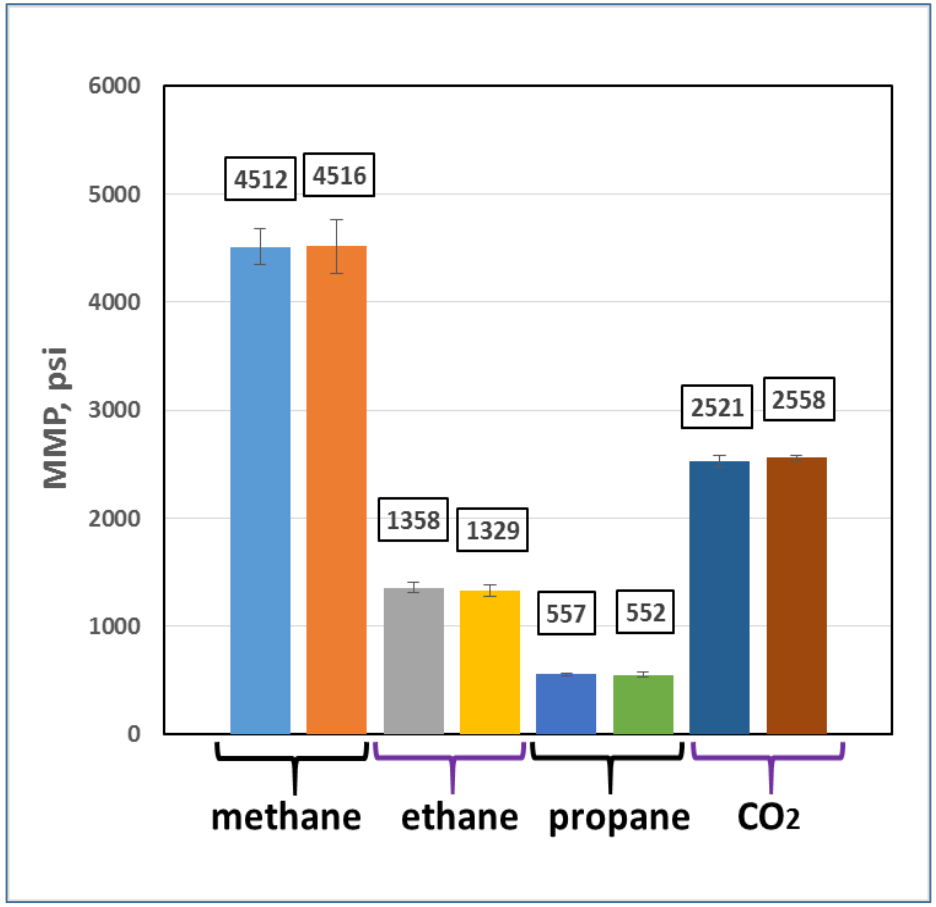
Slim Tube Determination of MMP (>$10,000, 2-4 weeks)



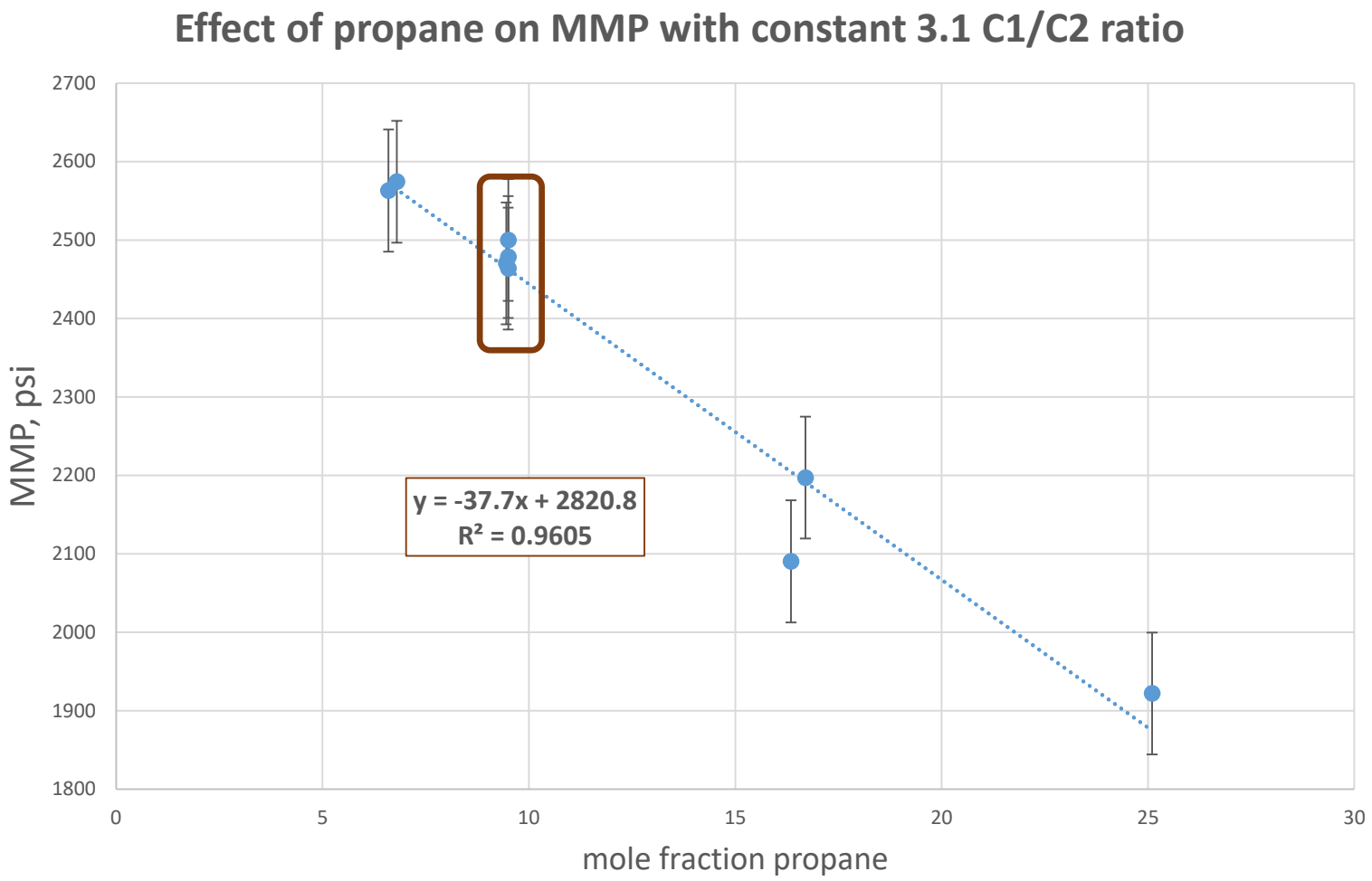
Minimum Miscibility Pressure (MMP) with Methane, Ethane, Propane, and CO_2*

The richer the gas, the lower the MMP !!

Bakken Crude Oil (230 F)

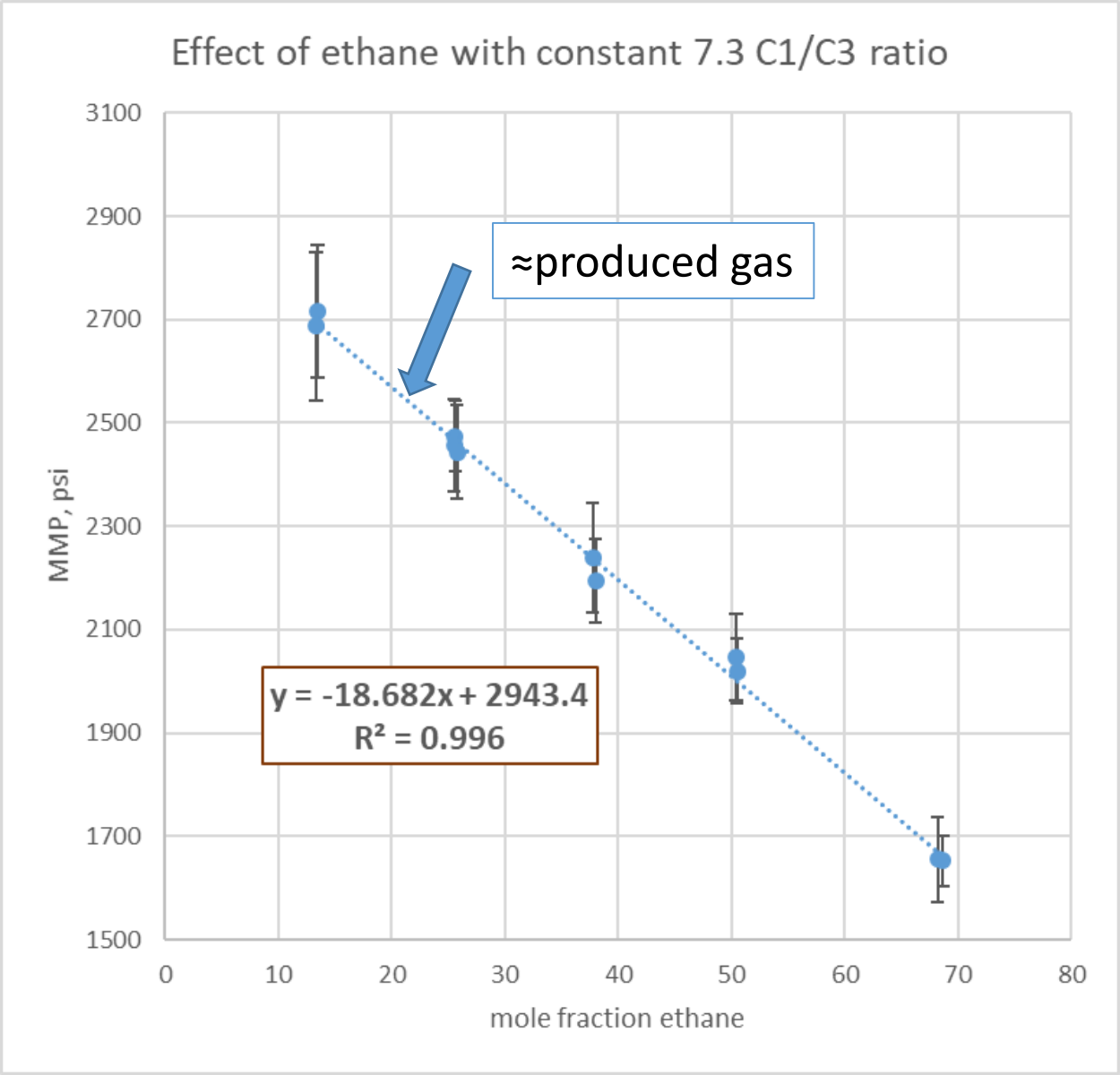


* CO_2 MMPs were determined under separate funding from the US Department of Energy, and are presented only for comparison purposes.



A typical Bakken produced gas is a 70/20/10 ratio of C1/C2/C3. How is MMP affected if we sweeten up the gas with propane?

A linear combination of pure fluid MMPs predicts an MMP about 40% higher than the experimental value.



What is the effect on MMP if we sweeten produced gas with ethane?

Adding ethane lowers MMP in a linear fashion.

What if I have a supply of CO_2, but my reservoir is too shallow to attain MMP?

- *We know that mixing CO_2 with methane raises MMP in proportion to the mole ratio methane.*
- *We also know that mixing CO_2 with ethane lowers MMP (but don't have mole ratio data yet).*
- *We are pretty sure that mixing CO_2 with propane will lower MMP even faster than adding ethane.*

3 basic lab experiments:

- *MMP = multiple contact minimum miscibility pressure by vanishing interfacial tension.*
- *Hydrocarbon compositions in the "miscible" phase.*
- *Crude oil hydrocarbon recovery from Bakken rock samples.*

CO_2/crude oil interactions with increasing and decreasing pressure.

- API gravity 38.7 crude oil
- 1450 MMP (10.0 MPa)
- 42 C
- CO_2 injected into the top

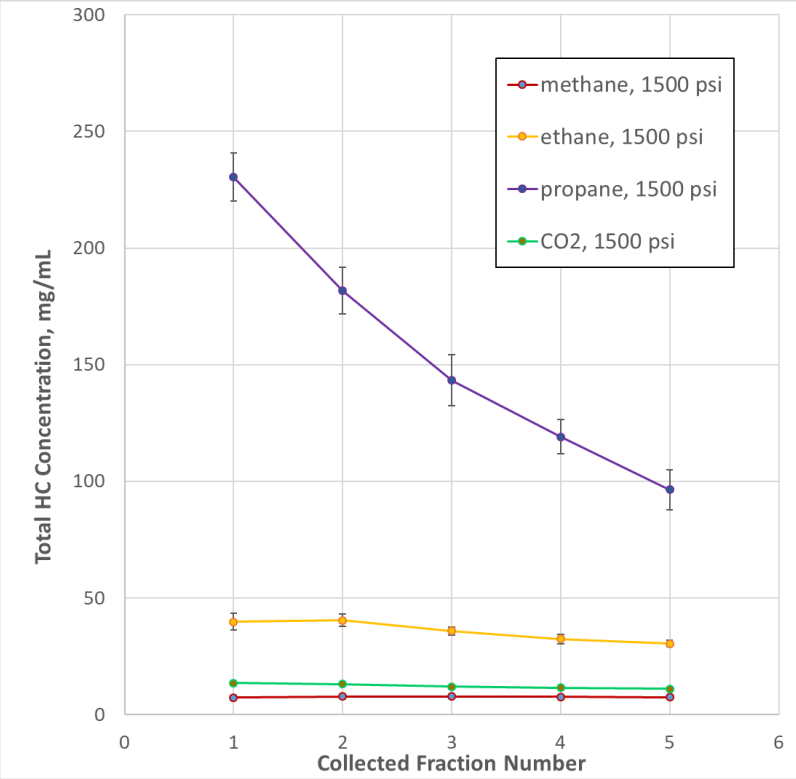
2 min

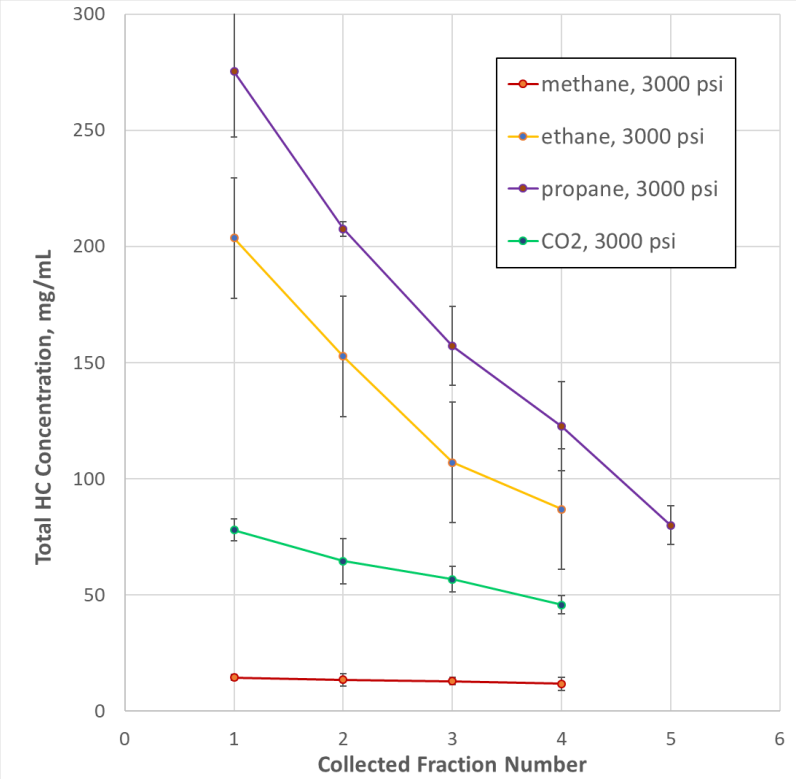
Which crude oil hydrocarbons (and how much) are dissolved into the gas-dominated upper “miscible” phase?

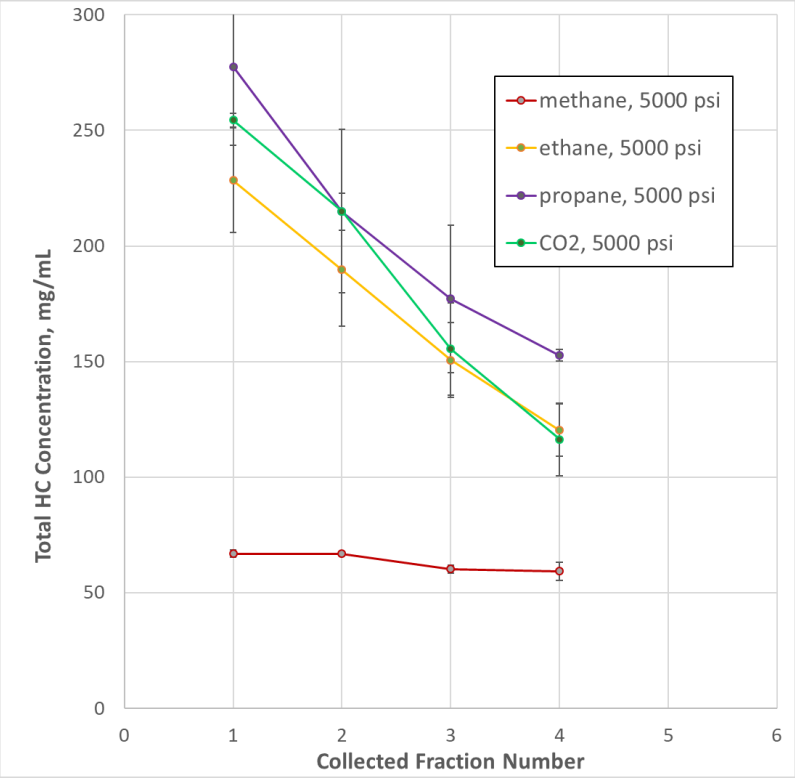
1. The gas is percolated through a 10-mL (8-gram) oil column and equilibrated at reservoir temperature (230 ^{o}F) and pressure (1500-5000 psi).
2. The upper “miscible” phase is sampled while maintaining reservoir T and P.
3. Dissolved HCs are collected and analyzed by GC/FID.

Total Bakken crude oil hydrocarbons mobilized at 230 °F.

Based on mg/mL, propane is effective at all pressures, CO2 and ethane require higher pressures, and methane is least effective at all pressures.



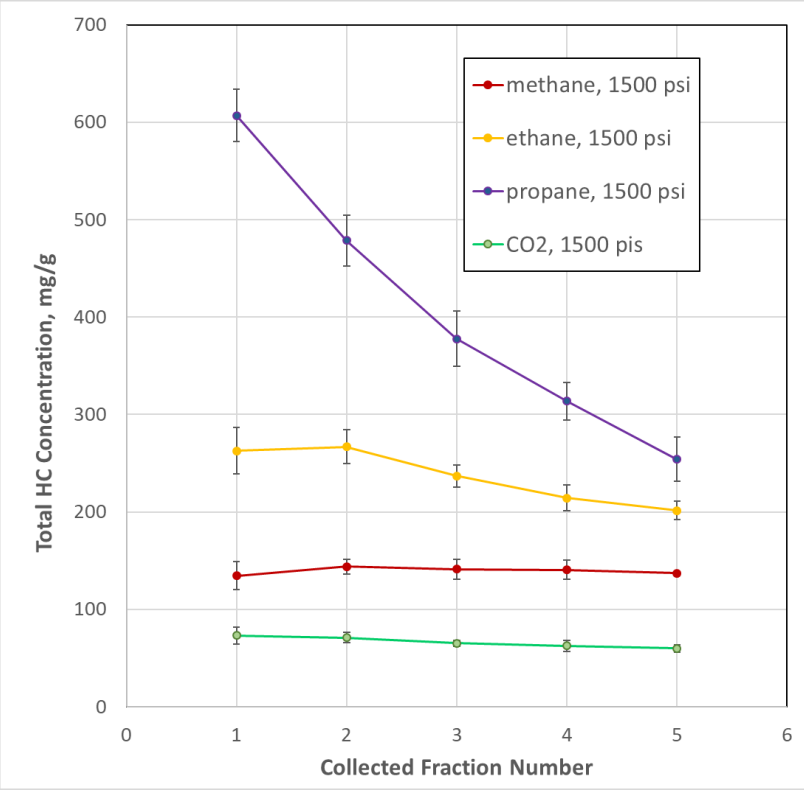


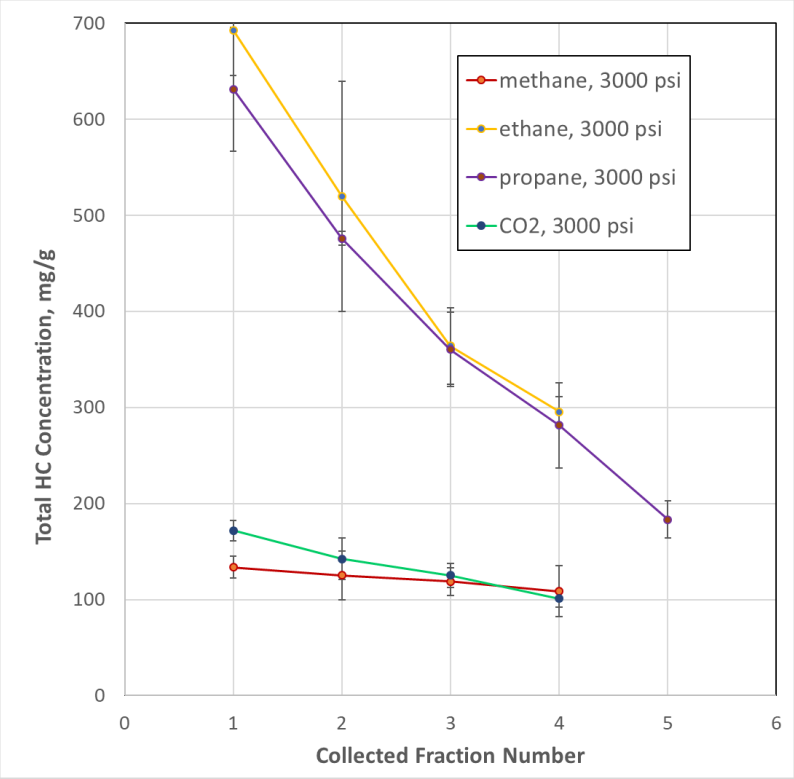


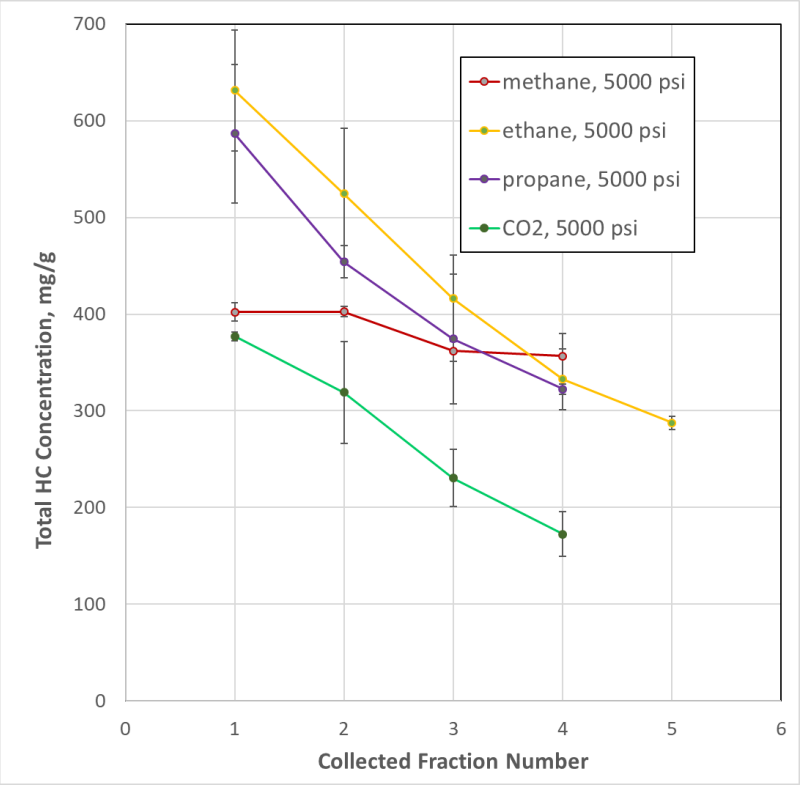
10 mL of crude oil was equilibrated with 10 mL of injected C1, C2, or C3 headspace at reservoir conditions before taking five sequential aliquots at 1-hour intervals. The error bars represent the standard deviation in hydrocarbon concentrations for triplicate experiments at each condition.

Total Bakken crude oil hydrocarbons mobilized at 230 °F.

Based on mg/gram, propane is effective at all pressures, ethane rivals propane at higher pressures, and methane exceeds CO2 at 5000 psi.







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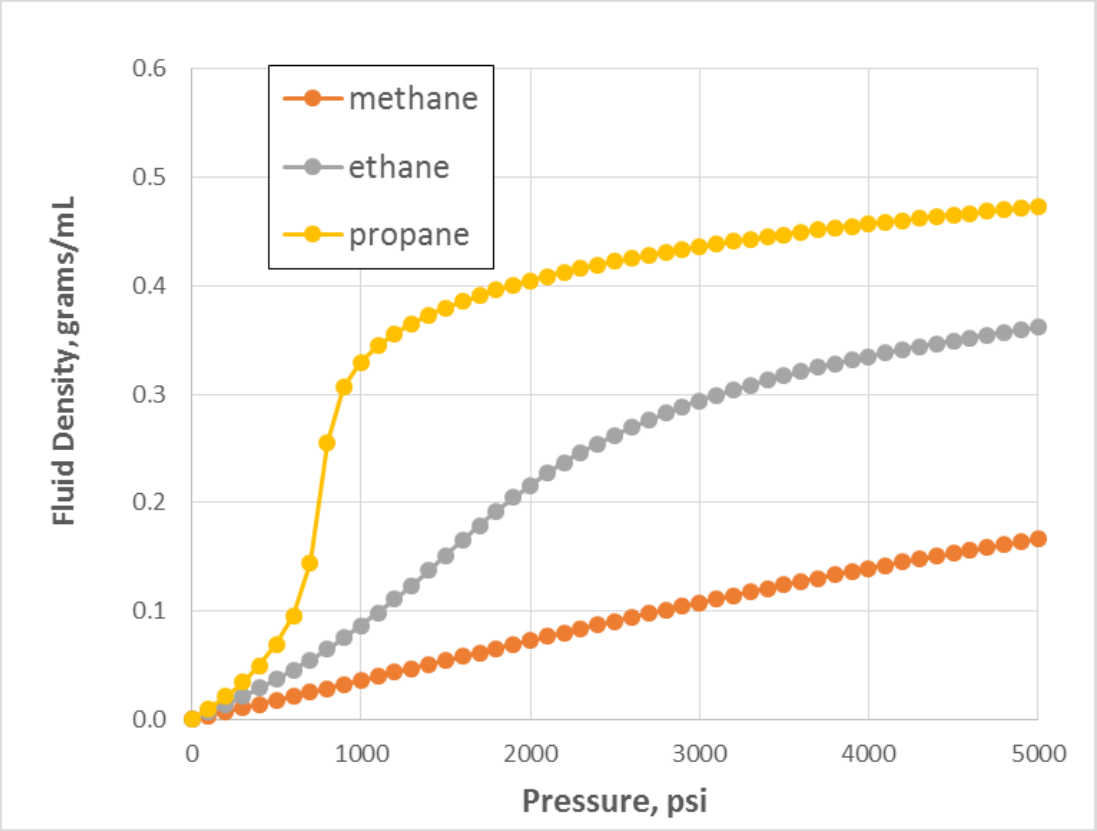
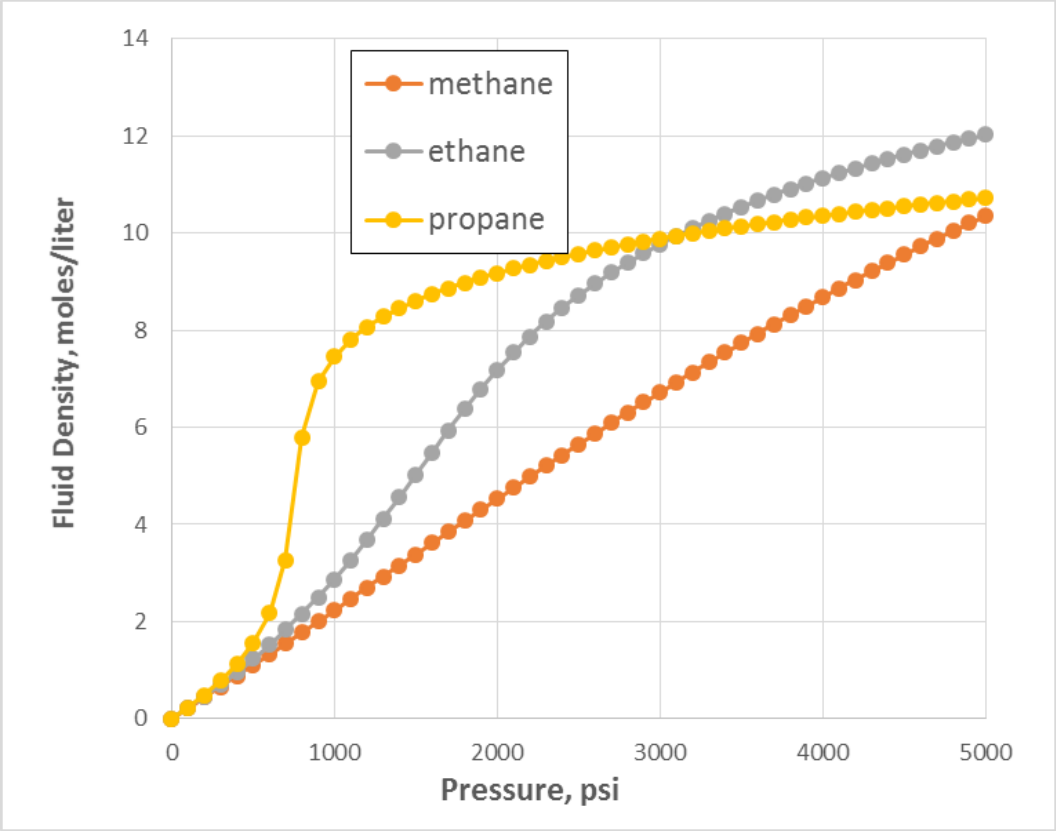
Methane, ethane, and propane mass (g/mL) and molar (moles/L) densities correlate with their general abilities to mobilize crude oil hydrocarbons into the gas-dominated "miscible" phase.

Higher pressure doesn't help propane nearly as much as methane and ethane, since propane's density does not change much above 1000 psi. (all values at 230 ^{o}F)

Molar density describes oil mobilization with HC gases best!

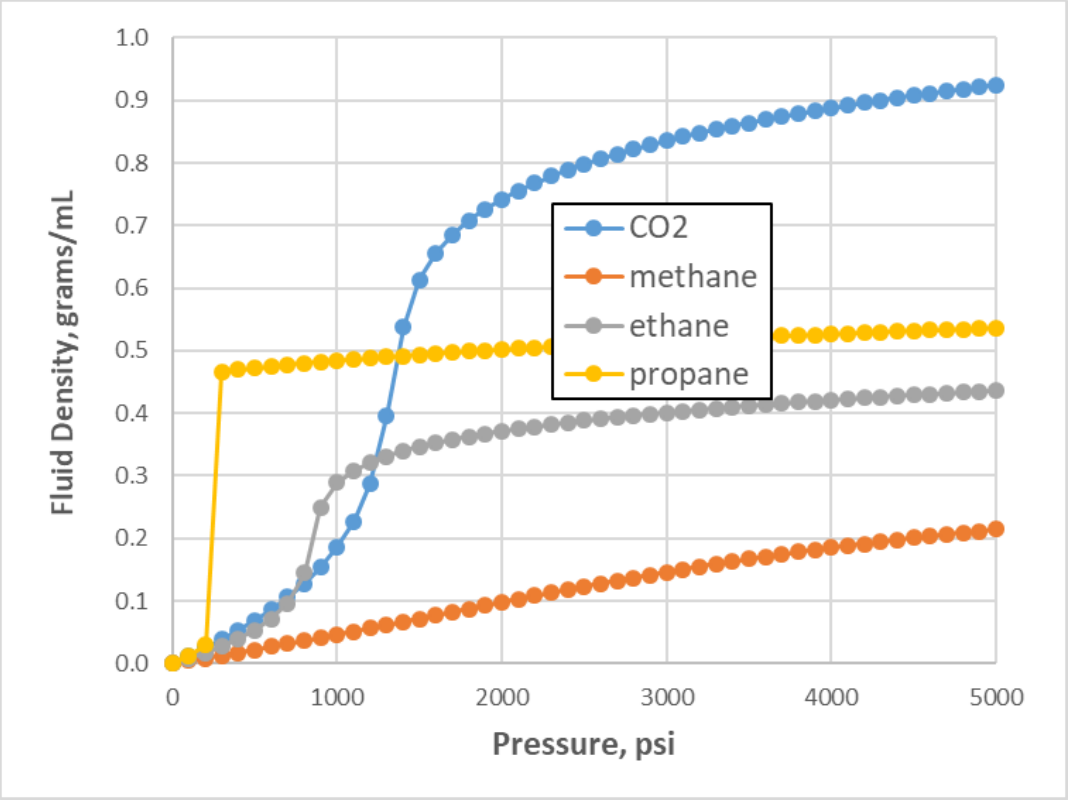


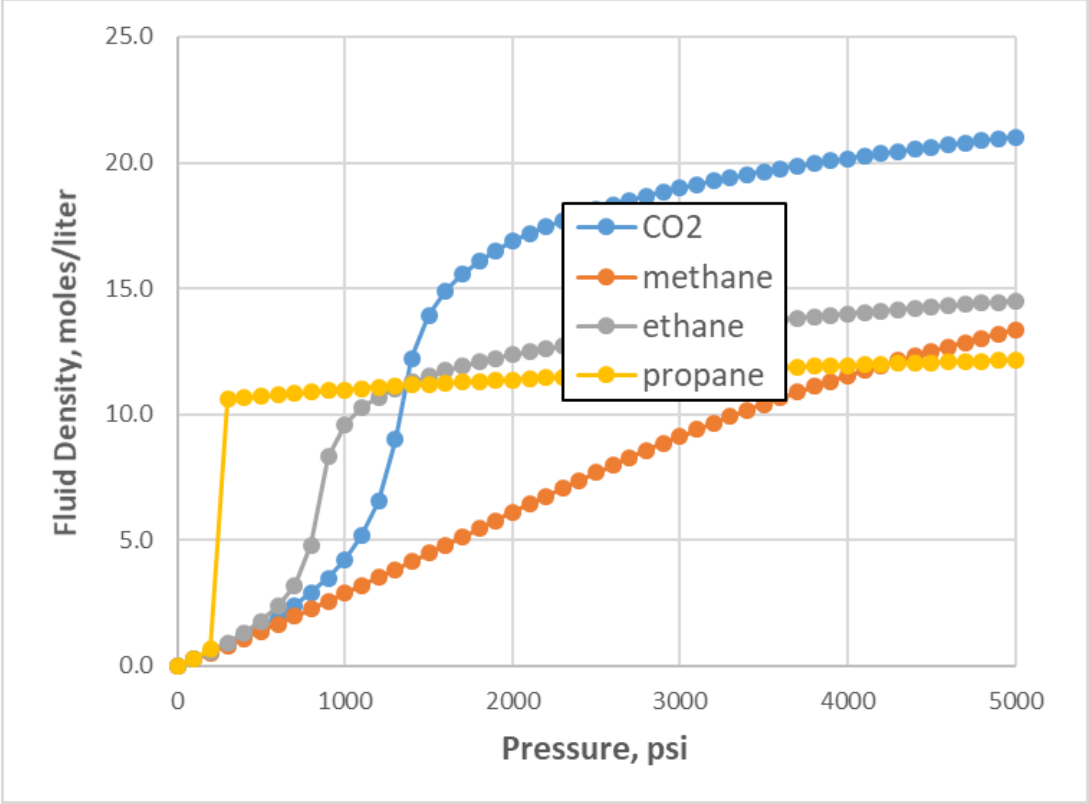


Note that molar density (# of molecules per volume) is similar at 5000 for all three fluids, while mass density is proportionally higher based on their MW.

Methane, ethane, and propane mass (g/mL) and molar (moles/L) densities correlate with their general abilities to mobilize crude oil hydrocarbons into the gas-dominated “miscible” phase.

CO_2 density also matters, but doesn’t fit the HC gas trend well since CO_2 is a different chemical class.

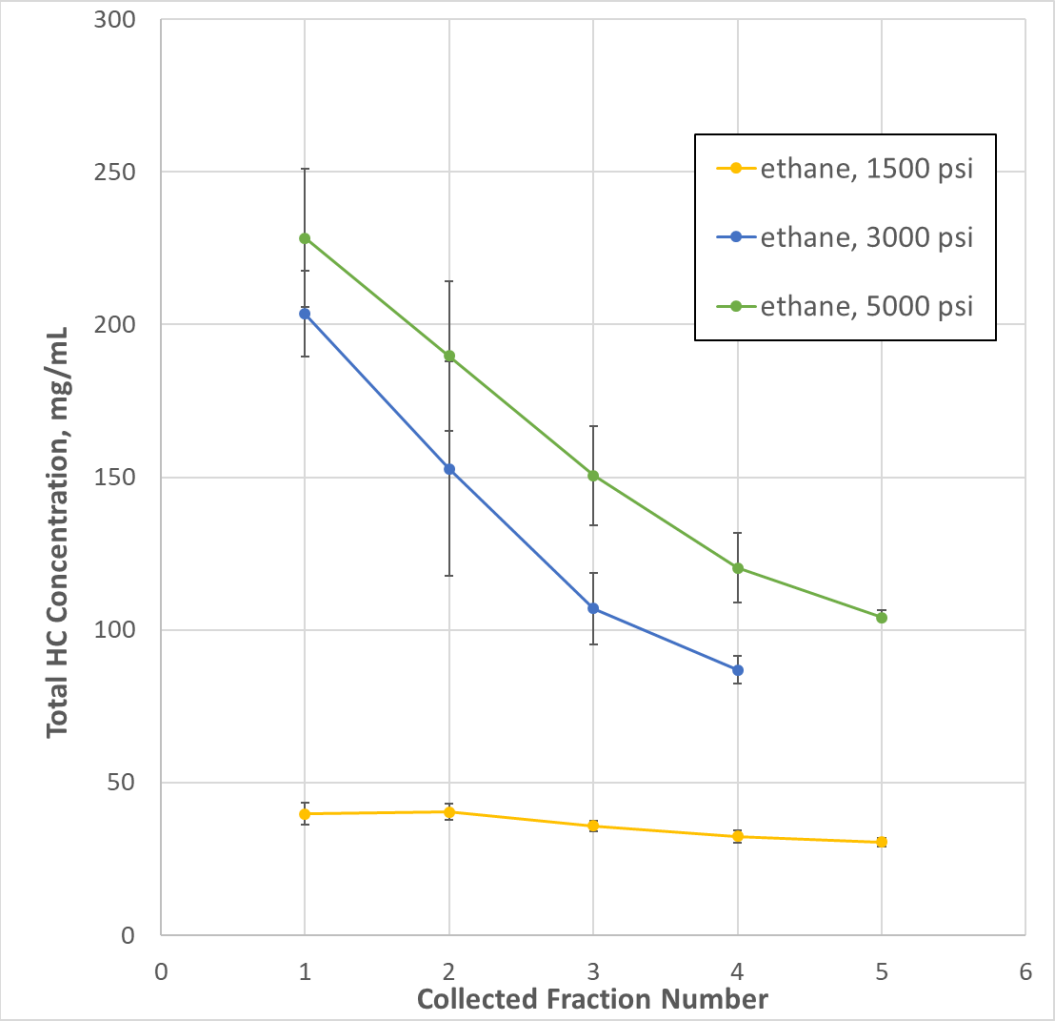


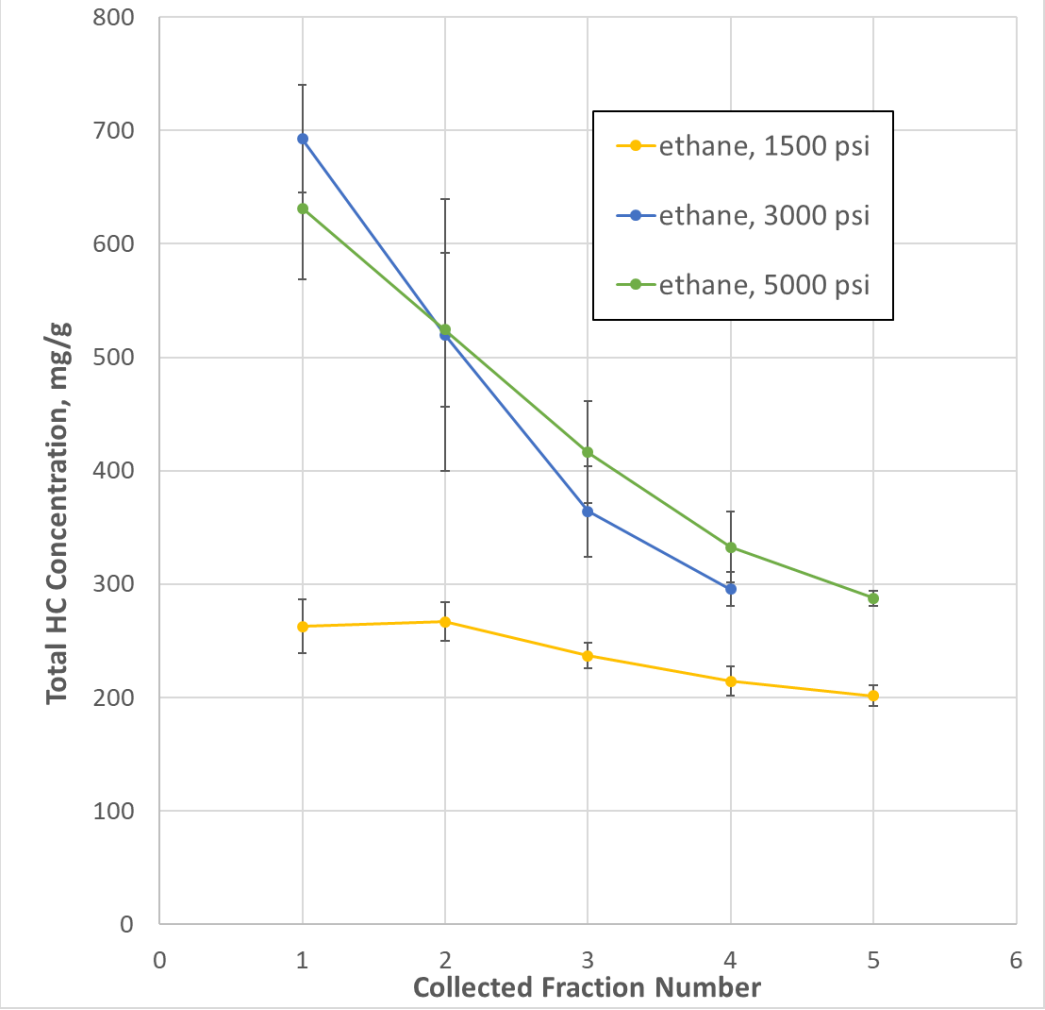


Doesn't MMP control how much oil is mobilized by vaporization/solvation?

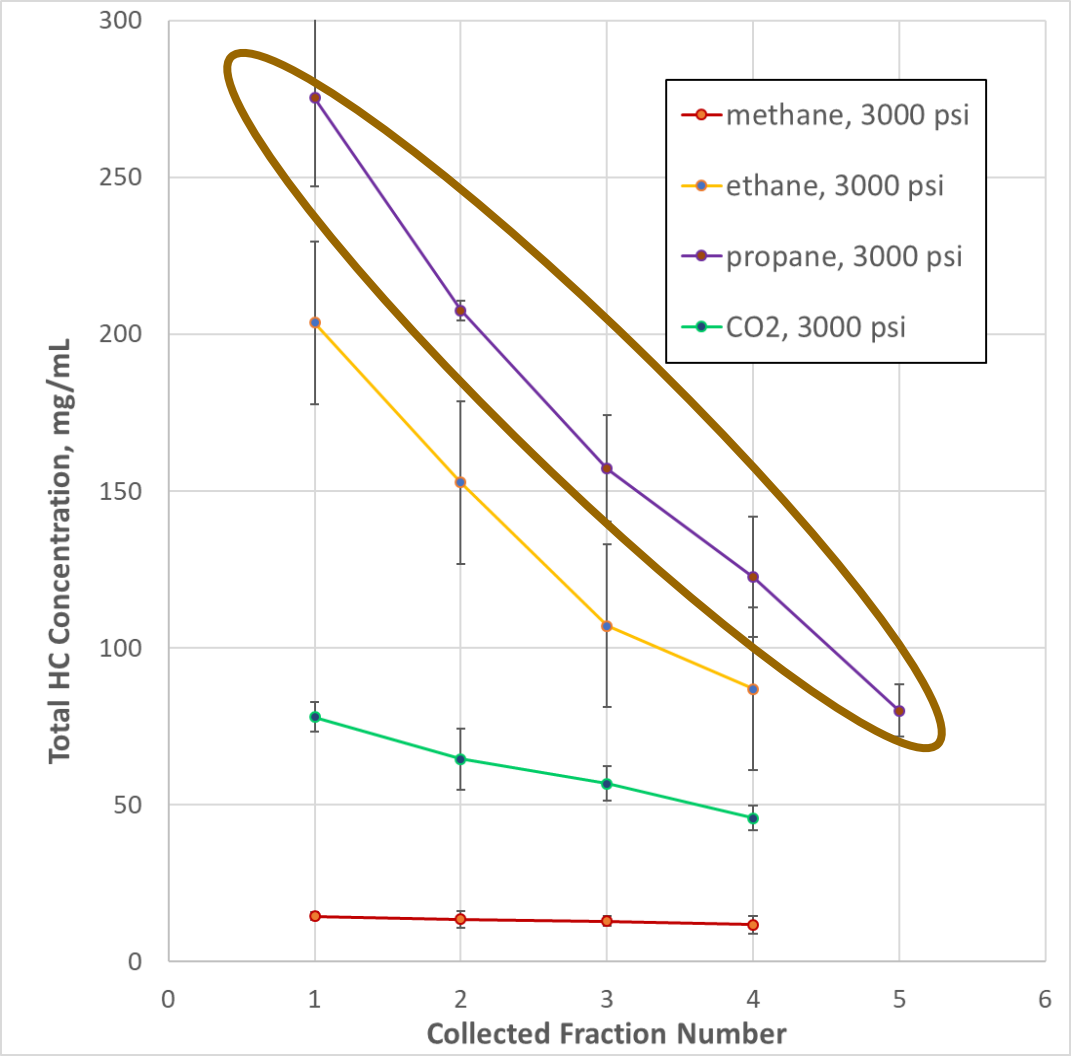
Ethane MMP with this oil is 1345 psi, so all test pressures are above MMP.

Higher pressure mobilizes more oil regardless of MMP !!





Why does the amount of oil decrease with each subsequent exposure to injected EOR gas?



The amount of oil dissolved into the gas is controlled by equilibrium partitioning, NOT by saturation solubility.

- Saturation solubility would yield the same concentration of oil dissolved in each new gas exposure until the oil was gone.
- Equilibrium partitioning (liquid/liquid) dissolves the same fraction of the remaining oil.

For example, propane dissolves ca. 17% of the remaining oil upon each exposure, so the mass of oil dissolved drops from 275 mg/mL to 75 mg/mL with 5 exposures as fits equilibrium partitioning.

If saturation solubility controlled the oil dissolved, propane would dissolve ca. 275 mg/mL with each exposure until the oil was all gone after 7 exposures.

We are not dealing with crude oil/injected gas partitioning.

We are dealing with partitioning between thousands of HCs and the injected gas. The HC composition of both the injectant-dominated phase and bulk crude oil phase is continually changing.

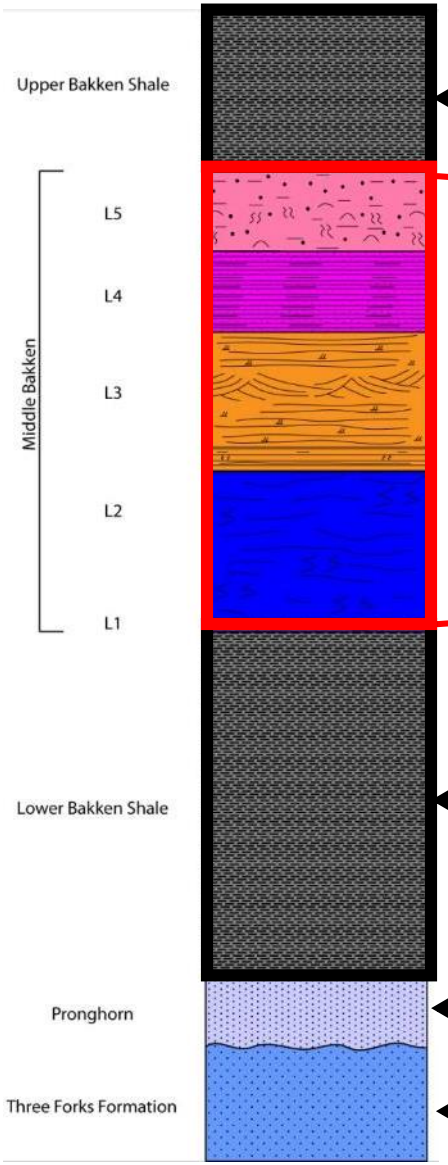
All fluids prefer the lower MW hydrocarbons, regardless if pressures are below or above MMP. *Propane does the best with higher MW HCs, ethane is next best followed by CO_2. Methane can only mobilize the lightest HCs except at very high pressures.*

Residual oils have higher MWs, viscosities, and densities (lower API gravities) after exposure to all fluids, but propane shows the least negative changes.

3 basic lab experiments:

- *MMP = multiple contact minimum miscibility pressure by vanishing interfacial tension.*
- *Hydrocarbon compositions in the "miscible" phase.*
- *Crude oil hydrocarbon recovery from Bakken rock samples.*

Bakken Petroleum System Lithology



Drilling Targets

Drilling Targets

Upper Bakken Shale: Brown to black, organic-rich.

- **Bakken source rock**

Middle Bakken: Variable lithology (up to 9 lithofacies), ranging from silty sands to siltstones and tight carbonates

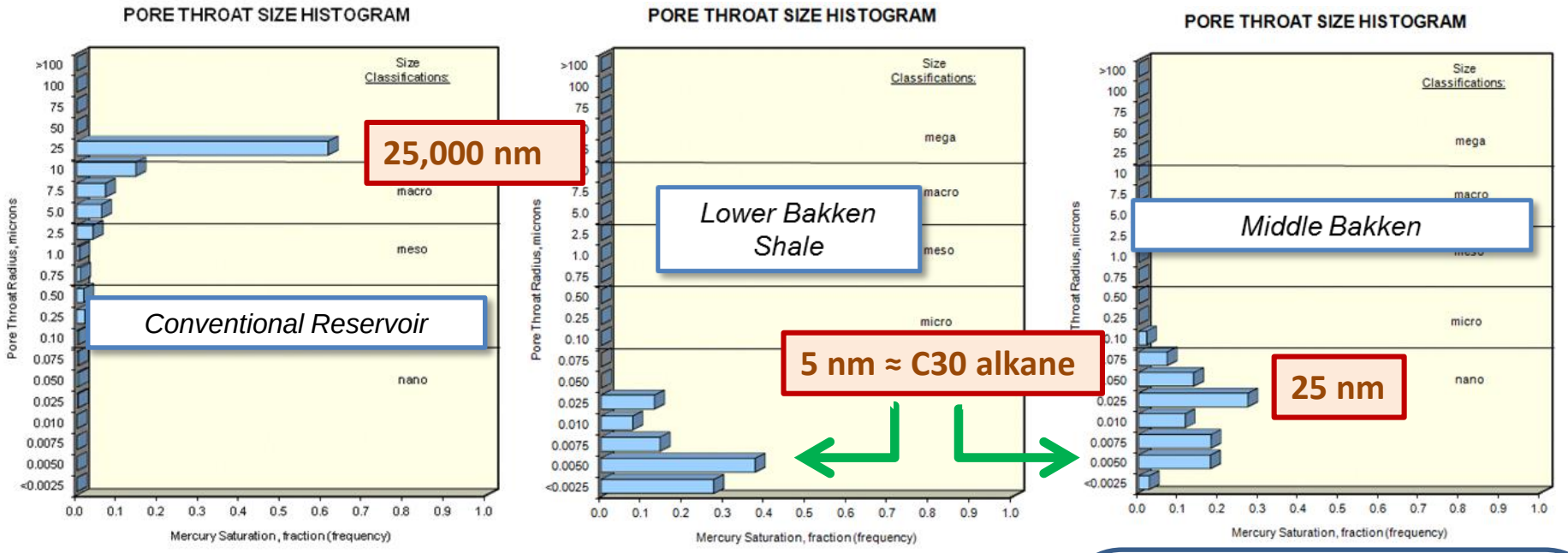
- **Bakken tight reservoir rock (horizontal drilling target)**

Lower Bakken Shale: Brown to black, organic-rich

- **Bakken source rock**

Pronghorn Member: Mixed sandstone, siltstone, dolomite, and shale.

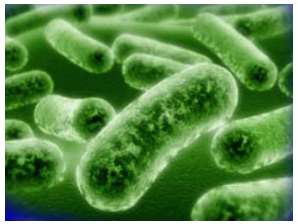
Three Forks Formation: Interbedded dolostone/limestone, siltstone/mudstone, shale, evaporites.



Where do injected fluids have to go to access oil?

- *Enormous holes for conventional reservoirs.*
- *Small holes for unconventional reservoirs.*
- *Itsy-bitsy molecule-sized holes for shales.*

ca. 80,000 nm diameter

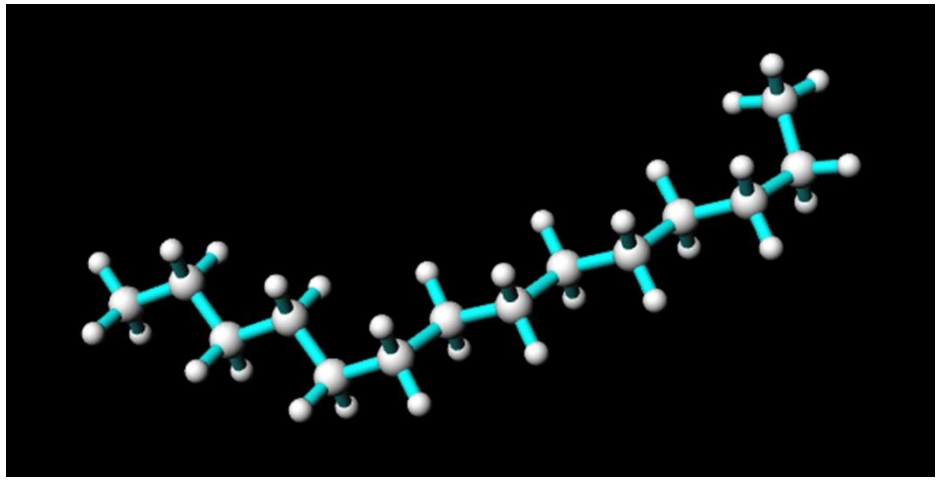


ca. 3000 nm long

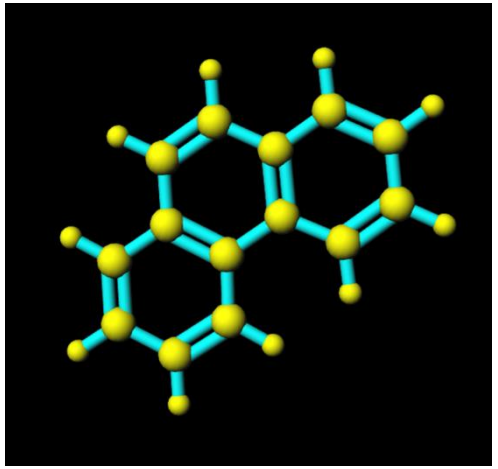
How big is a nanometer?

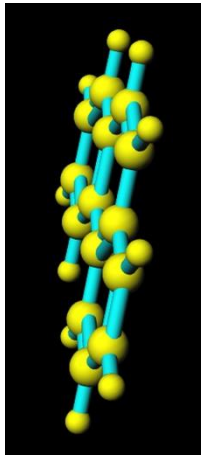
1 nanometer

Tetradecane $C_{14}H_{30}$



Phenanthrene $C_{14}H_{10}$





If you were a C14 oil molecule, in a conventional permeable reservoir your pore throat "doorway" would be a few miles wide.

For the Bakken shales, your pore throat "doorway" would be somewhere around the size of a pet door to a garage door.

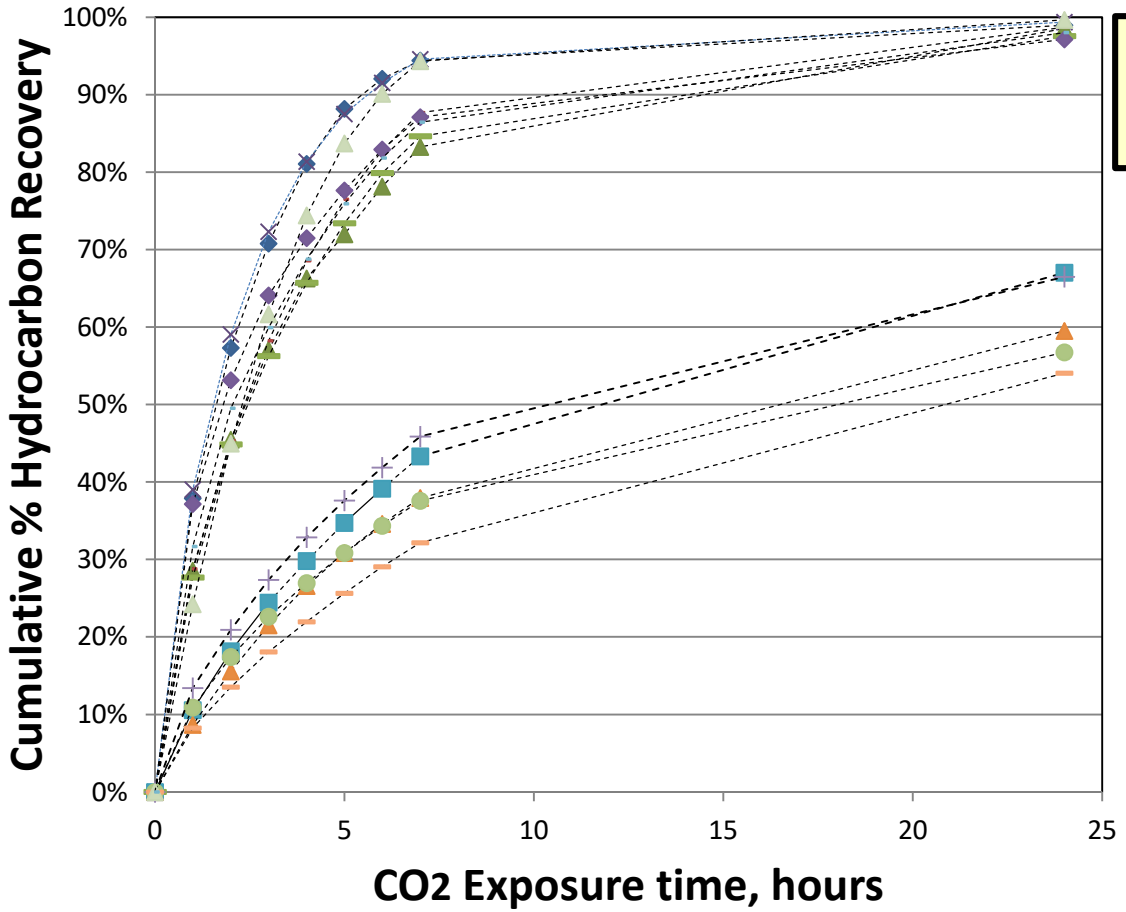
How effective are methane, ethane, and propane at different pressures for recovering hydrocarbons from Middle Bakken and Bakken Shale rock samples?

Laboratory Exposures Include:

>***VERY*** small core samples (11-mm rod for Middle Bakken, 1-3.4 mm crushed rock for Upper and Lower shales).

- Rock is “bathed” in the fluid to mimic fracture flow, not swept with the fluid as would be the case in confined flow-through tests.
- Recovered oil hydrocarbons are collected periodically and analyzed by gas chromatography/flame ionization detection (GC/FID) (kerogen not determined); 100% recovery based on rock crushed and solvent extracted after CO_2 exposure.
- Exposures at 1500 to 5000 psi, 230 ^{o}F.

Previous lab tests with ca. 80 rock core samples from 20 different wells show that CO_2 can recover crude oil from Middle Bakken, Three Forks, and Upper and Lower Shales. (5000 psi, 110 C, 11.2 mm diameter round rods)



Middle Bakken and Three Forks

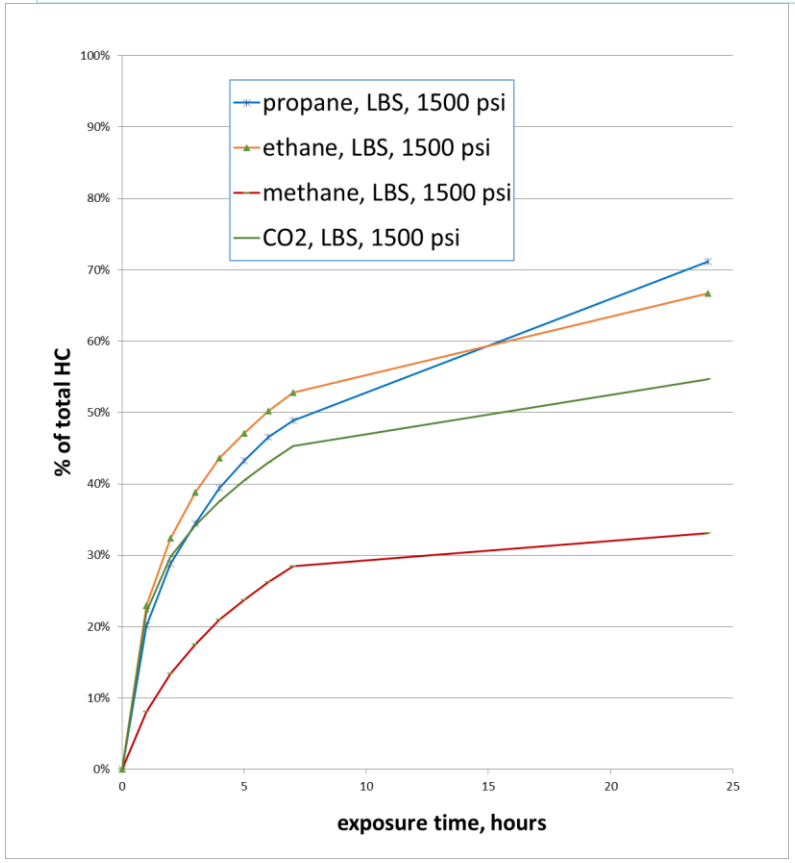
Upper and Lower Bakken Shales

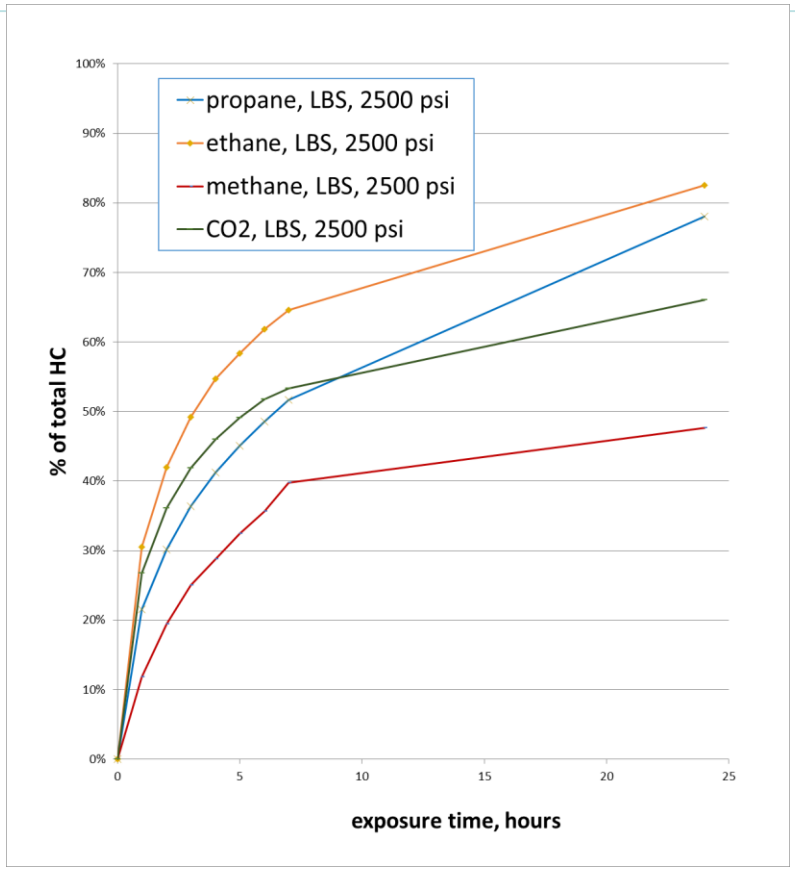
So how do methane, ethane, and propane compare to CO_2?

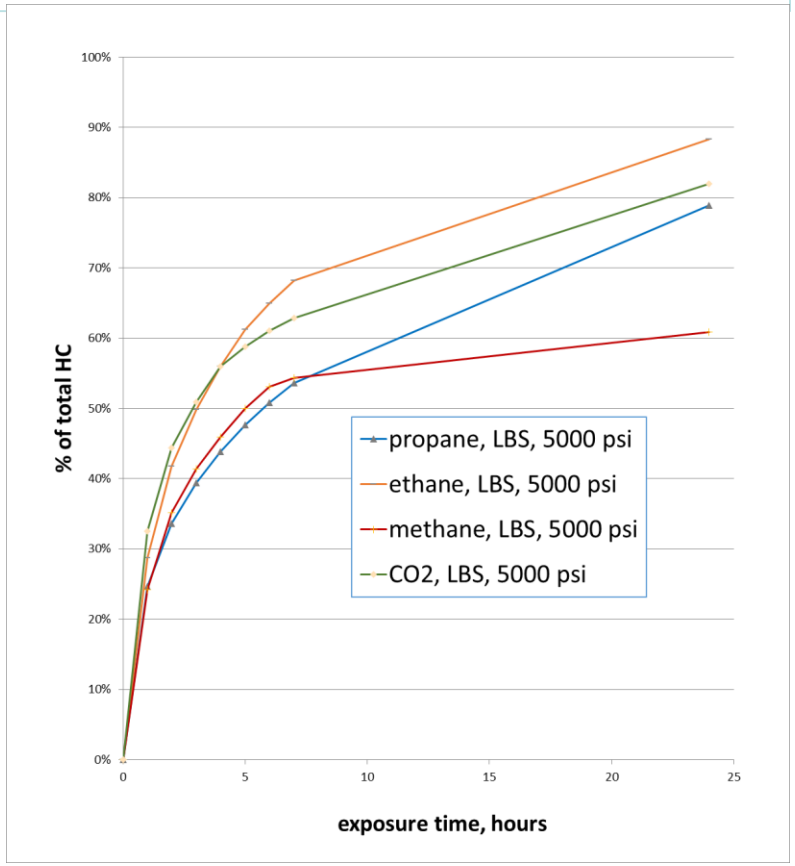
11-mm rods for Middle Bakken, 1-3.4 mm chunks for Upper and Lower Shales.

Comparisons are done with the LBS rock to simplify the data presentation. Middle Bakken recoveries are always faster than the shale.

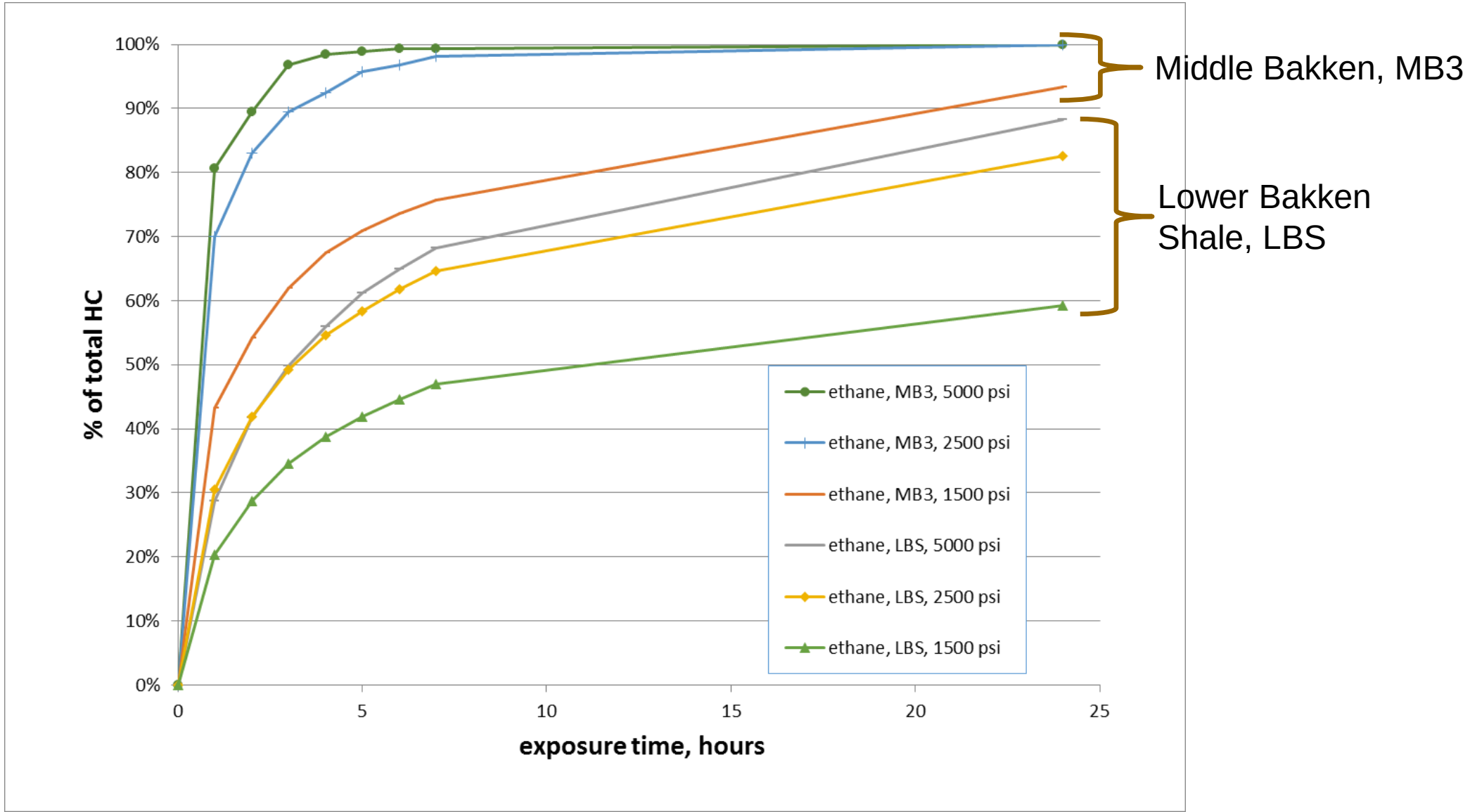
Ethane is equal or better than propane at recovering oil from the tight Bakken shale.
CO_2 and (especially) methane require higher pressures, and at 5000 psi CO_2 exceeds propane.
All fluids prefer lower MW hydrocarbons, but methane is the worst, followed by CO_2, then ethane and propane.



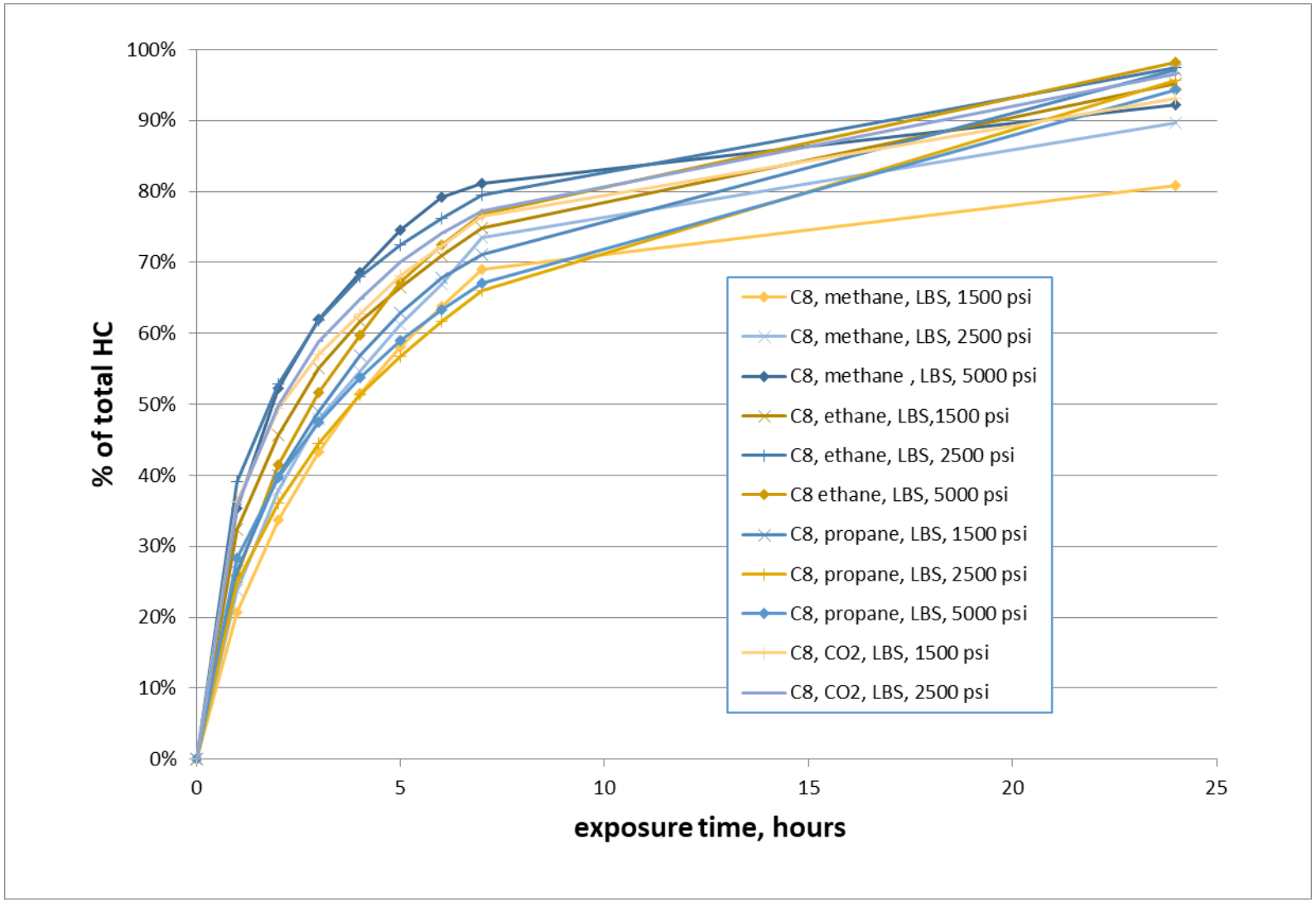




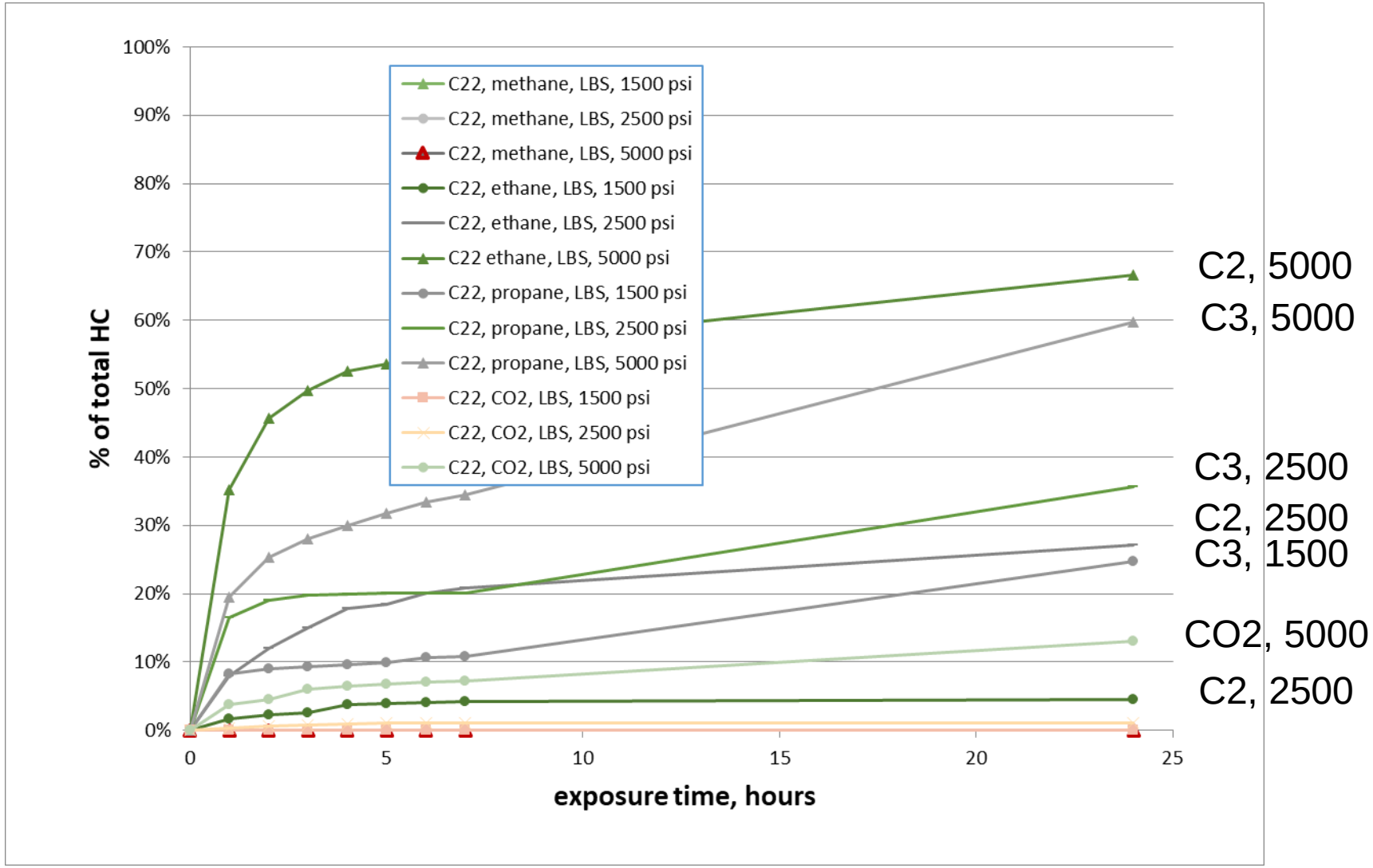
Total HC recovery from Middle Bakken and Lower Bakken Shale is increased with higher ethane pressure, ***regardless of the ethane MMP of 1345*** for this oil. Biggest improvement is between 1500 and 2500 psi.



All fluids at 1500 to 5000 psi can recover the most volatile HCs from the shales (though methane is a little slower). C8 (octane) recovery is driven by vaporization in the 230F reservoir.



But all fluids have trouble recovering mid- and high-MW HCs from the shales (similar to the “miscible” phase compositions). Methane fails at all pressures (even though 5000 psi is above its MMP), CO2 fails at 1500 and 2500 psi.



What lab chemists say to petroleum engineers and geologists: "Fantastic data, game-changer lab tests, chemistry controls everything, these results will greatly improve your field operations….."

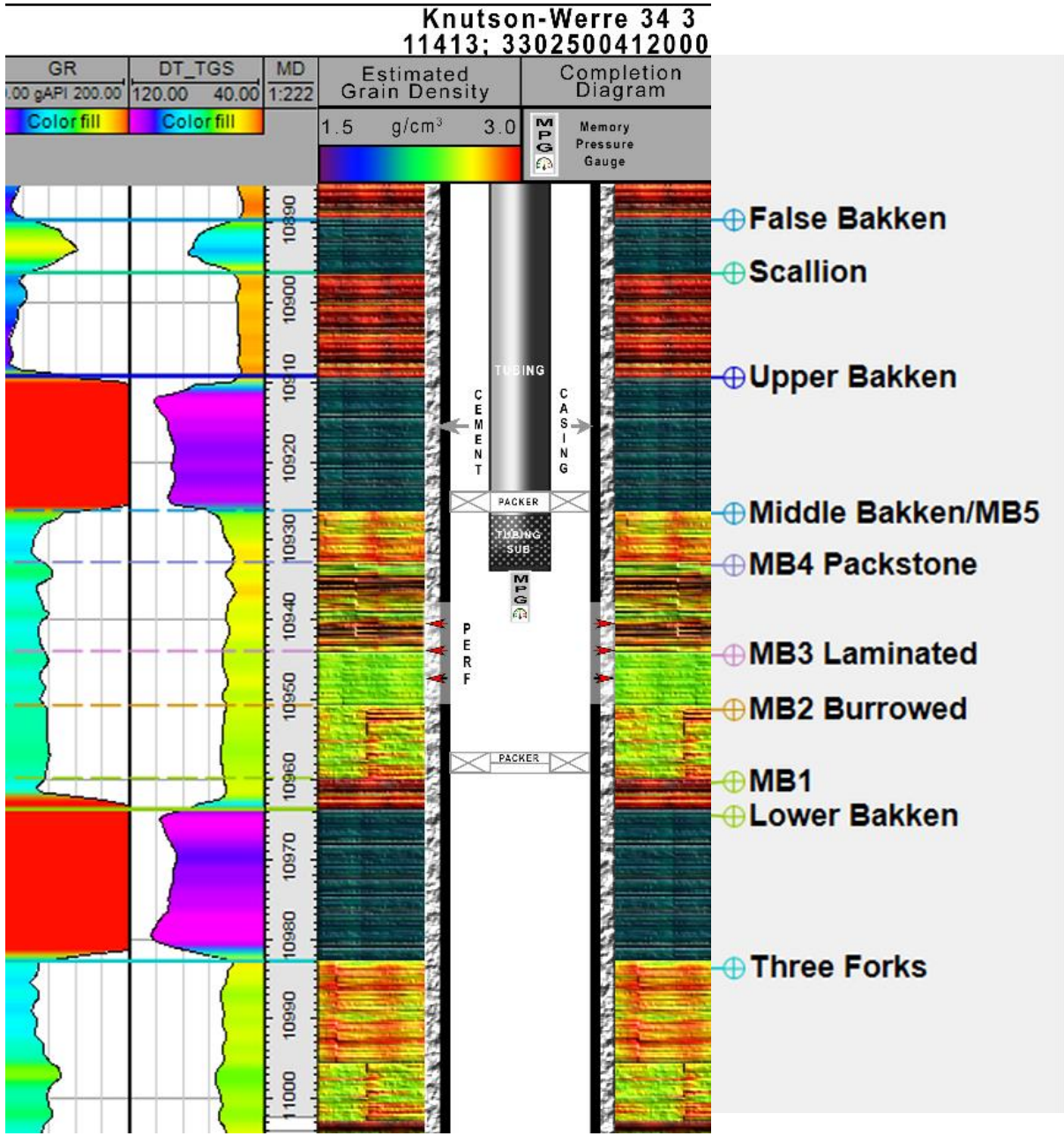
What engineers and geologists hear: Blah, blah, blah, chemistry, blah, blah, blah, lab tests, blah, blah, blah, molecular weight, blah, blah blah no field data, blah, blah, blah……

Lab tests show preference to produce lower MW HCs during EOR. What do field tests show?

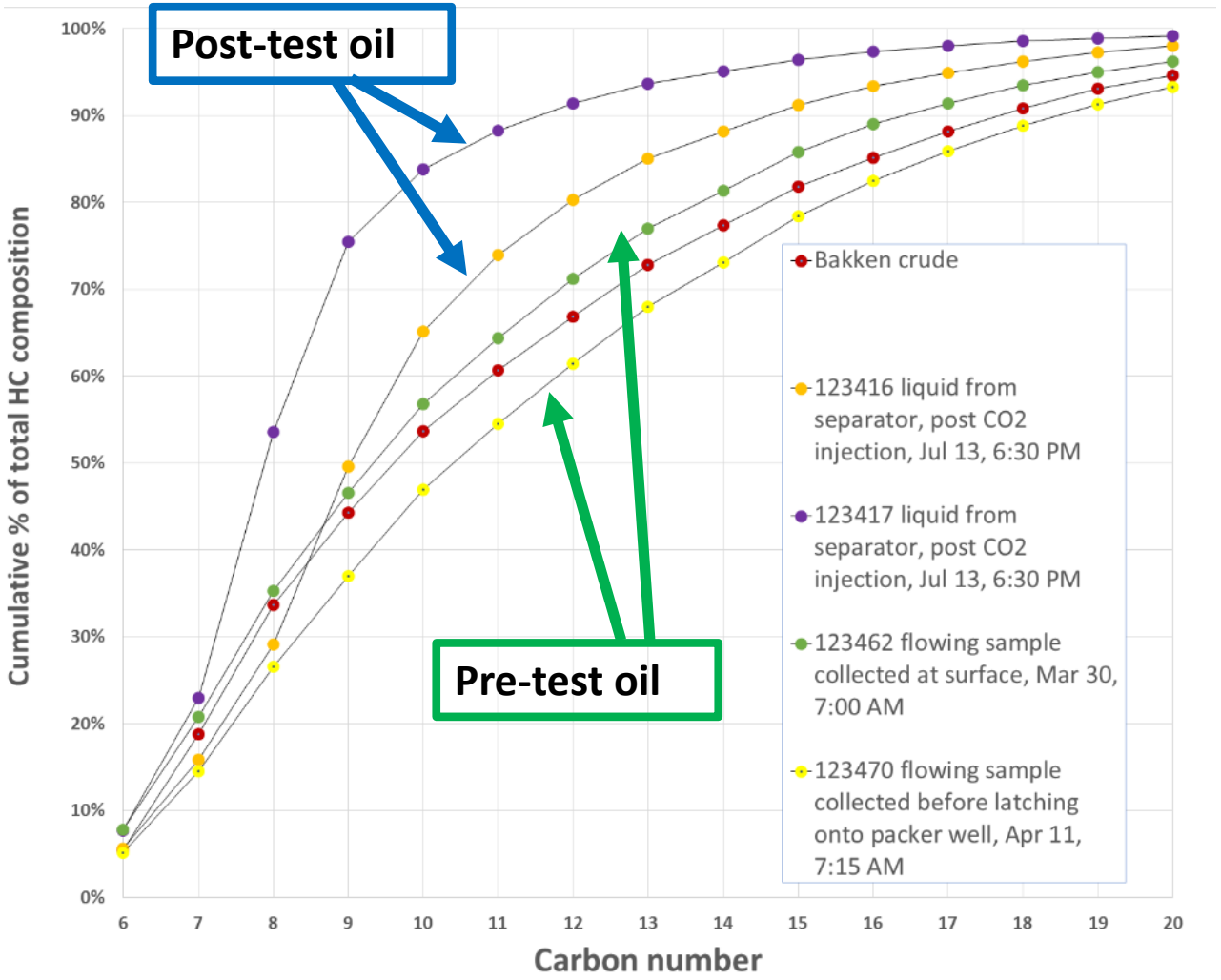
Hypotheses to be tested in a vertical well:

1. CO_2 can be injected into an unstimulated Bakken reservoir.
2. The injected CO_2 can interact with the in-place fluids, resulting in subsequent mobilization of hydrocarbons and storage of CO_2.

Down-hole pressure was about 3X the MMP.



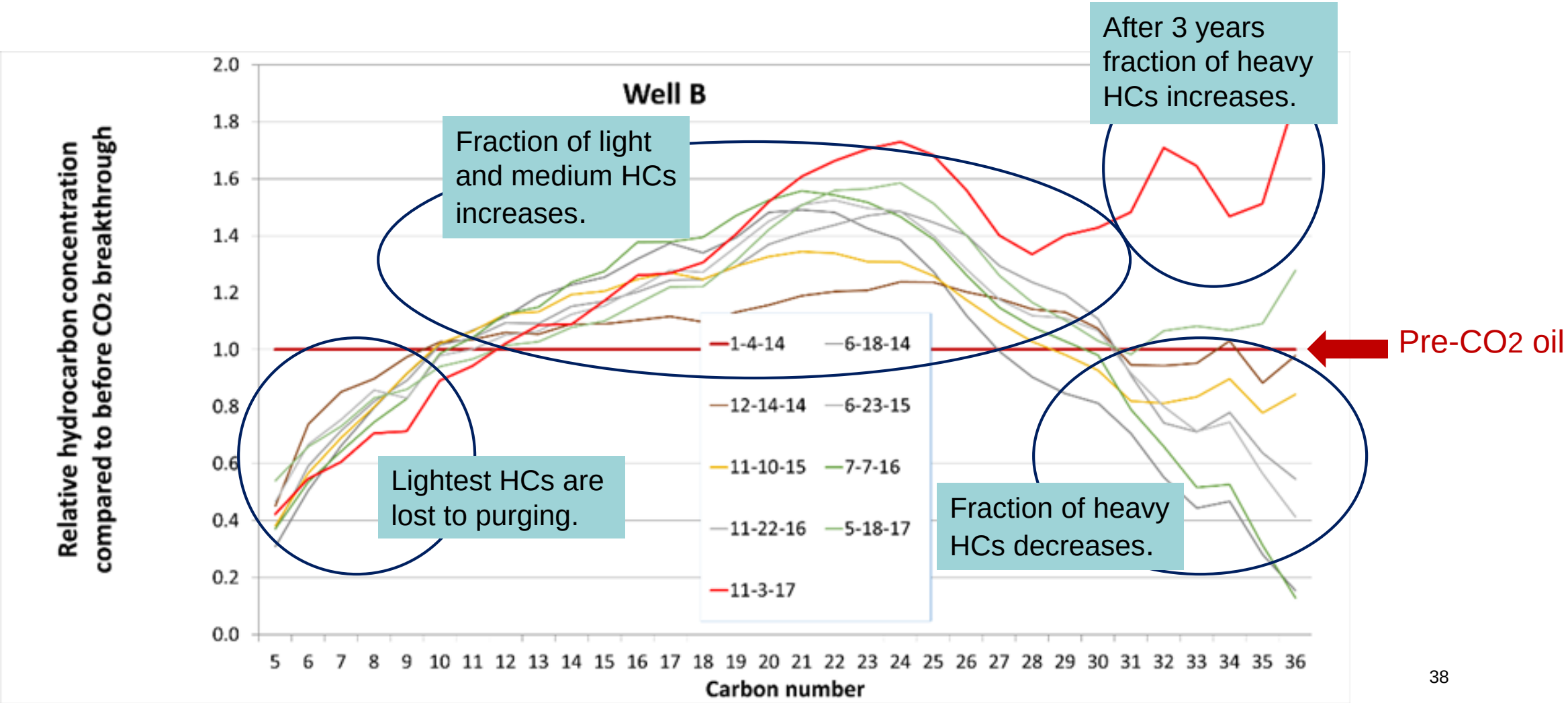
Pre- and Post- CO2 Injection Changes in Produced Oil Molecular Weight



- **There was an significant shift towards the lower molecular weight hydrocarbons as a result of the CO_2 injection.**
- **These data suggest that the CO_2 did penetrate the matrix of the Middle Bakken, interacted with the oil therein, and preferentially mobilized a lighter oil, despite a down-hole pressure 3X higher than MMP.**

Molecular weight distributions of produced crude oil before and after CO_2 breakthrough during CO_2 EOR in a conventional Powder River Basin field.

Reservoir pressure was maintained at 2300 to 2900 psi vs. 1400 psi MMP.



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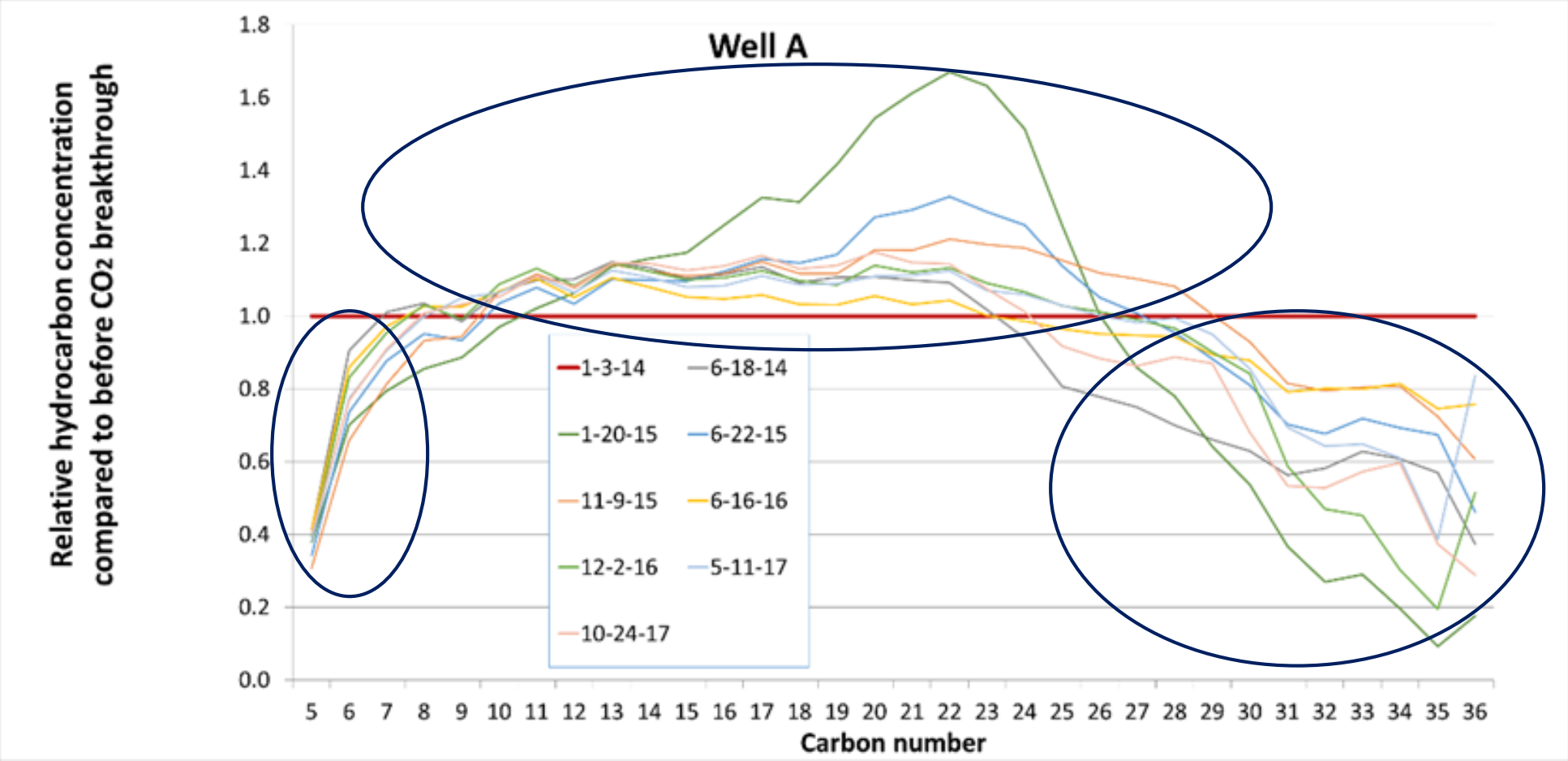

Summary: Effect of pressure on HC recoveries from Middle Bakken and Lower Bakken Shale rocks with methane, ethane, propane, and CO_2.

Total HC recovery shows little pressure dependence with propane, but higher pressures are needed for higher MW HCs.

Pressure matters for total HC recovery with ethane and CO_2, and matters even more for higher MW HCs.

Ethane recovers total HCs and higher MW HCs better than propane at higher pressures, but not at lower pressures. These results correlate with ethane and propane molar density.

Methane only recovers the most volatile HCs, with some improvement at 5000 psi (also correlating with molar density).

MMP is NOT a "line in the sand." Higher pressures yield faster/higher oil recoveries regardless of MMP.

Summary:
How do methane, ethane, propane, and CO_2 compare as EOR fluids?

(In short, the richer the gas and the higher the pressure, the more oil can be produced!)

- **Based on minimum miscibility pressure (MMP), propane is superior to ethane, ethane is superior to CO_2, and all three are superior to methane.**
- **Based on "miscible" phase sampling and rock extractions, higher pressure is always better regardless of MMP (though the effect with propane is not so significant).**
- **Molar density is a better way to compare fluids' capabilities than simple pressure considerations.**
- **Results suggest maintaining reservoir pressure prior to gas injection for IOR/EOR could be effective.**
- **Produced gas MMP, "miscible" phase sampling, and rock extractions are more encouraging than pure gas results may suggest.**
- ***But remember! These are lab tests that address MMP, vaporization/solvation of bulk oil with injected gases, and recovery of oil from rock core samples. They do not encompass all the realities of a reservoir injection.***

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