Investigating CO_2/oil interactions with high pressure videos and a new capillary rise MMP method.

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Presented at the 19th Annual CO_2 Flooding Conference

December 11-13, 2013, Midland, Texas

How meaningful is MMP?

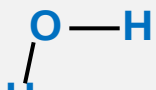
Does “miscibility” really occur?

Does anything interesting happen below and above MMP?

What happens as pressure drops below injection pressure?

Full disclosure: I am an analytical chemist.

Basic Properties of Three Fluids

	**Not linear**
	Permanent dipole moment
	Wets minerals well
	Solvates polars, but not nonpolars (sort of)
O=C=O	**Linear**
	No permanent dipole moment
	Polarizable
	“Wets” minerals a little
	Solvates nonpolars and moderately polar compounds, (but not very well)
H_3C-CH_3 (hydrocarbons)	
	No dipole moment
	Not polarizable
	Poor at wetting minerals
	Solvate nonpolars

Why is CO_2 "special?"

- CO_2's critical T and P are close to "normal" values. Therefore, we operate with liquid, gaseous, and supercritical states.

- CO_2 is "polarizable." That is, it tries to mimic the polarity of it's surroundings (but doesn't do it very well).

- CO_2 is highly compressible, even as a liquid. Accurately controlling mass flows (etc.) is VERY difficult.

- CO_2 shows VERY large J-T cooling and heating. Temperature changes every time you move CO_2, and depressurization can cause freezing. Significant cooling/heating occurs even without a phase transition (and is huge with phase change).

Definitions of "Miscibility"

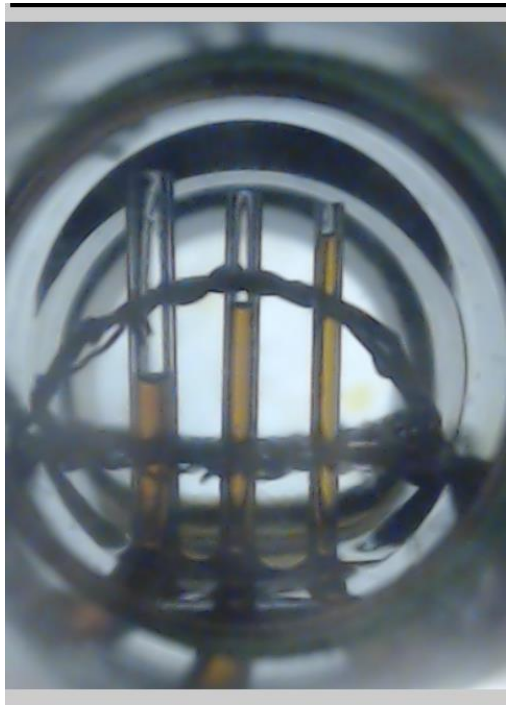
To a chemist: miscible fluids mix in any ratio without forming two phases (e.g., alcohol and water).

To a PVT lab: 90% of the oil in a 50 foot "slim tube" of sand came out in 1.2 pore volumes.

To a petroleum engineer: "I don't care as long as I get more oil."

EERC approach (via Rao, et al.): vanishing interfacial tension.

MMP by capillary rise.



Patent pending

Sequeira thesis, LSU, 2006

MMP is when there is no interfacial tension between CO_2 and oil phases.

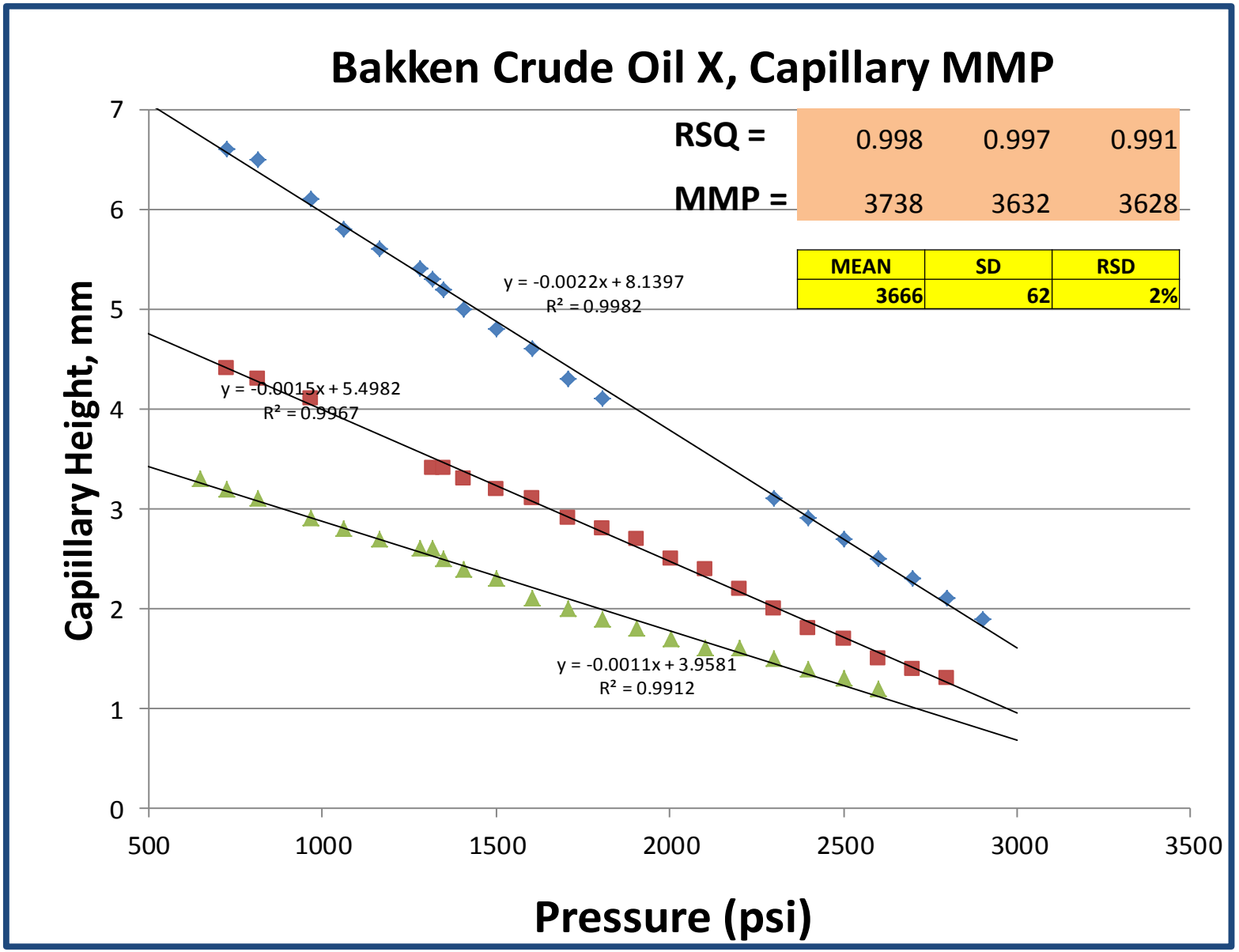
Based on measuring interfacial tension at various pressures.

- Requires measured density of both phases at each P. ($$$)
- Requires accurate capillary i.d.
- Must extrapolate MMP from a curved plot.

EERC modification greatly simplifies the apparatus (<<<$$), and is much faster.

- Simply measure capillary height vs. pressure.
- Yields linear plots with many data points per plot.
- Allows multiple conditions to be evaluated.

MMP by capillary rise.



Method is now rapid (cheap) enough to ask interesting questions (to me, at least !).

For example:

"How reproducible are the MMP values the lab gives me?"

"How might reservoir oil MMP change during CO_2 EOR?"

"How do methane and NGLs affect the performance of recycle CO_2?"

"How important is reservoir temperature in determining MMP?"

"What is the effect of different gases on MMP?"

MMP values by capillary rise method.

Bakken Crude (110 C)

Reproducibility?

Well 2, trial 1	3564 ± 43
Well 2, trial 2	3674 ± 64
Well 2, trial 3	3429 ± 158
Mean	3556 ± 123

Effect of reservoir T on MMP?

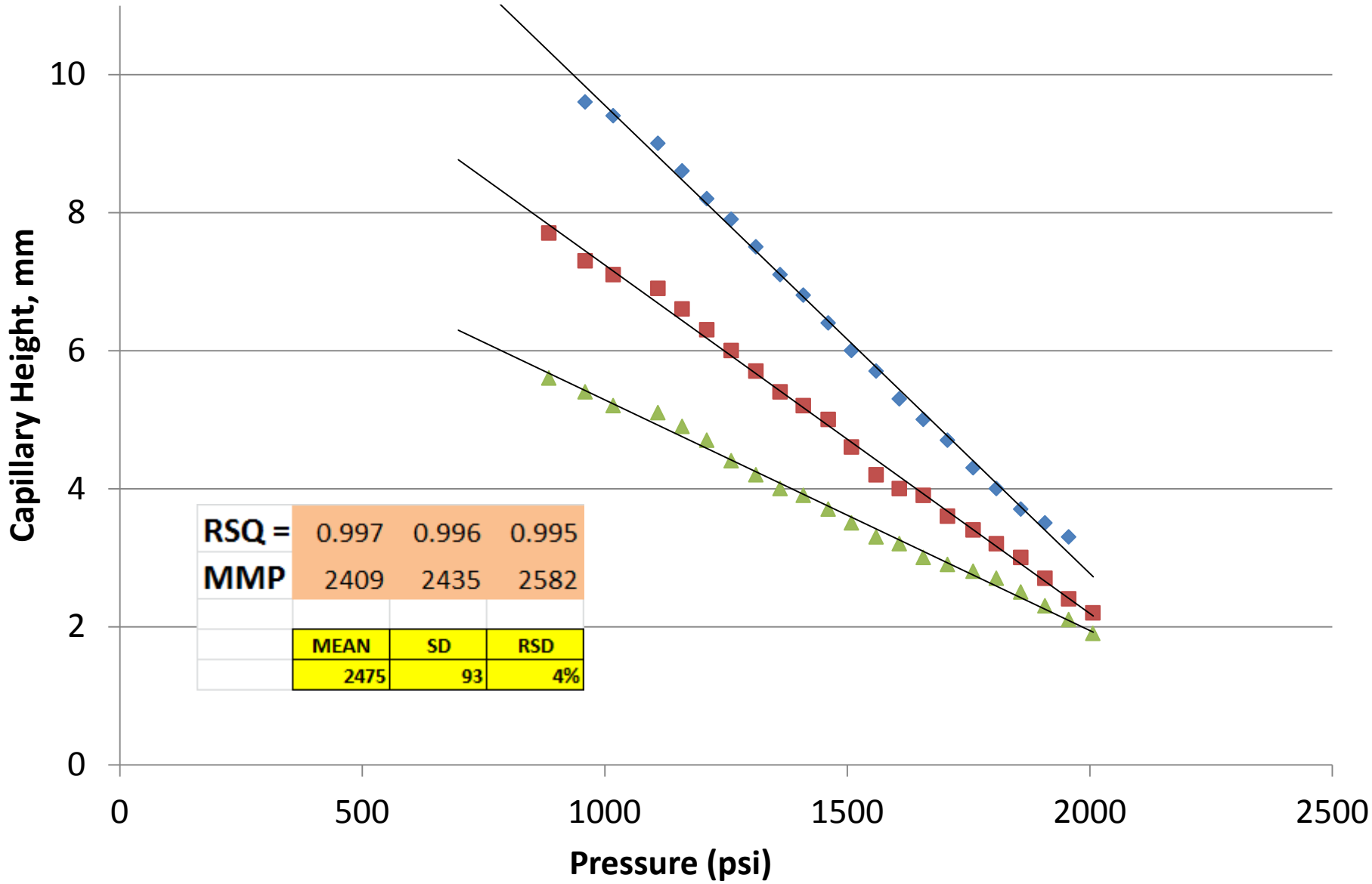
Well 3, 110 C	2685 ± 27
Well 3, 42 C	1316 ± 24

Pure CO_2 density ca. 0.4 at both conditions.

Effect of CO2 exposure on MMP?

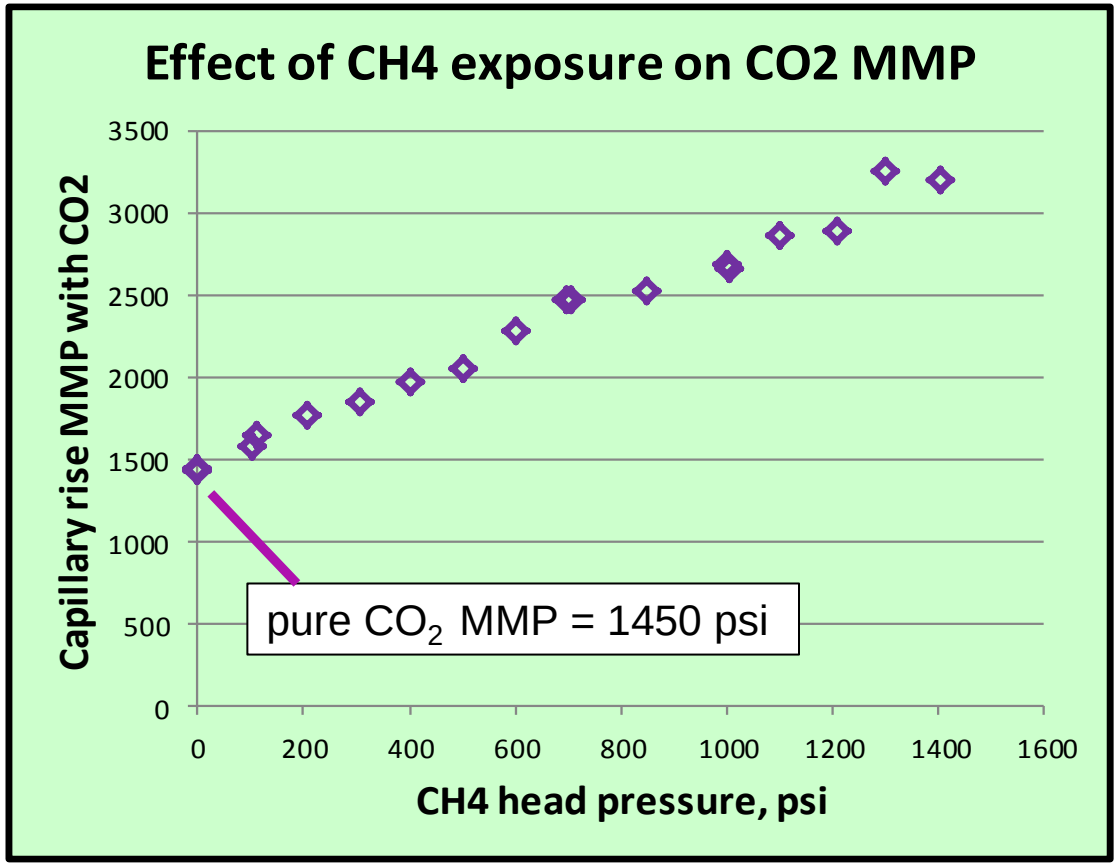
Well 2, ***before*** CO2 exposure	3556 ± 123
Well 2, ***after*** 3000 psi CO2	3270 ± 17

Conventional Reservoir Crude Oil, Capillary Rise MMP with 700 psi Methane



RSQ =	0.997	0.996	0.995
MMP	2409	2435	2582
	MEAN	SD	RSD
	2475	93	4%

What is the effect of various gases on MMP?.
(conventional reservoir oil)



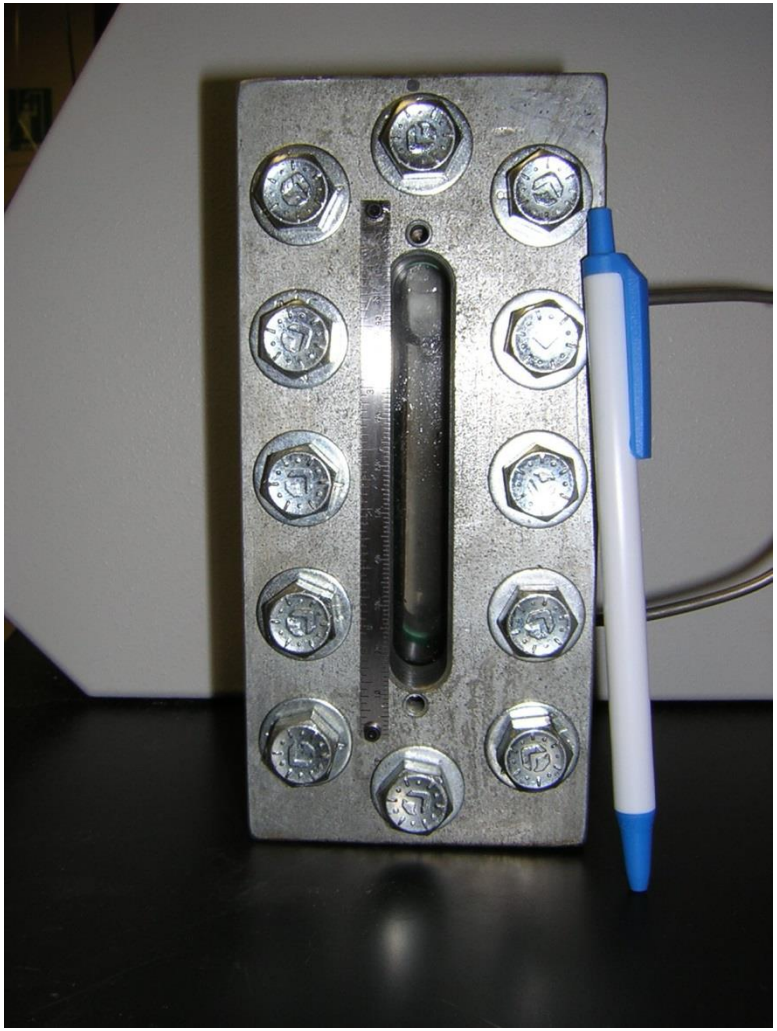
MMP with pure CH4

MEAN	SD	RSD
3793	111	3%

Does anything interesting happen above and below MMP?

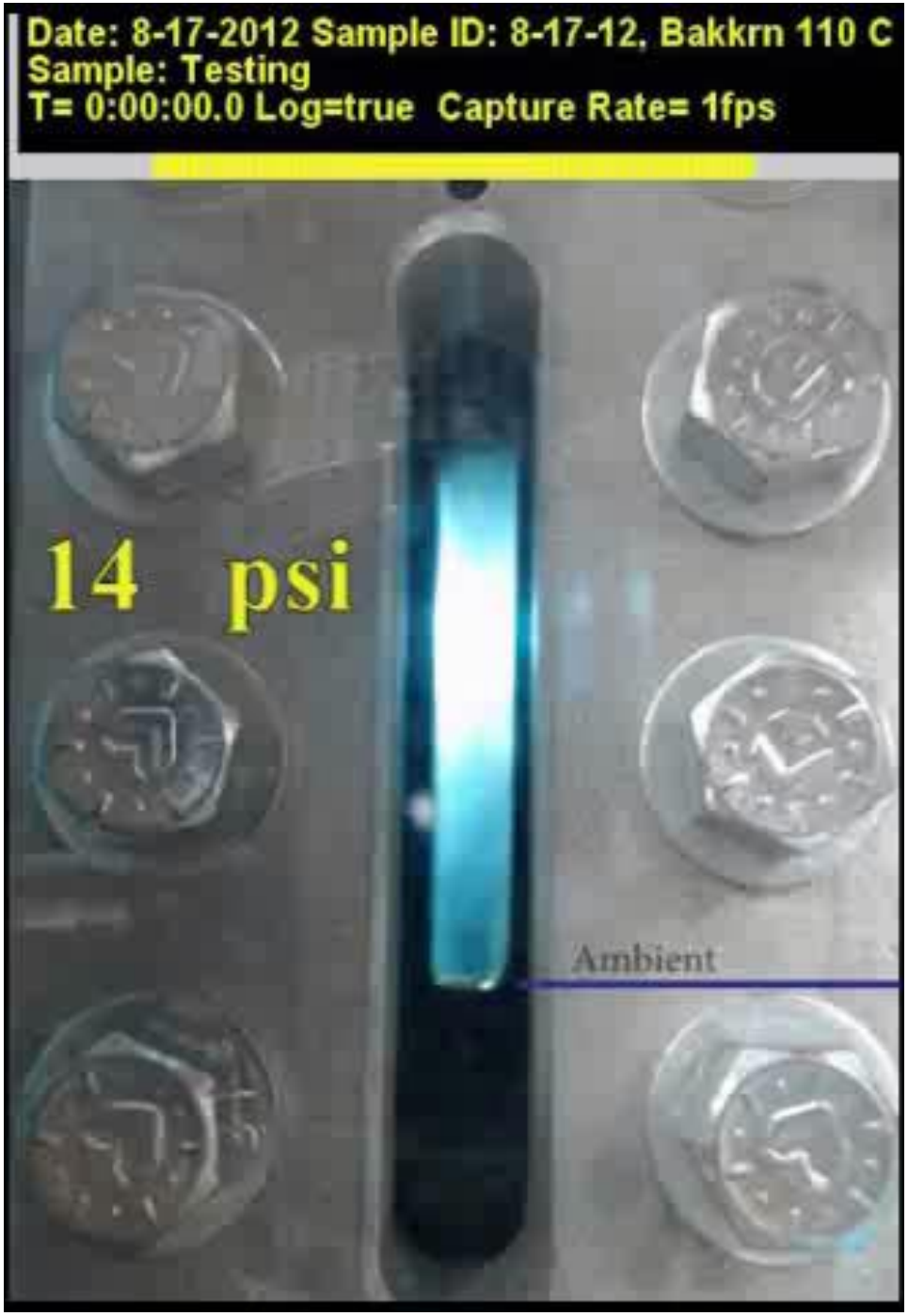
Bakken crude/CO_2 behavior, 110 ^oC

CO_2 pressure increased from ambient to 5000 psi, then reduced back to ambient.



Bakken Crude Oil

110 °C (230 F)
MMP = 2800 psi



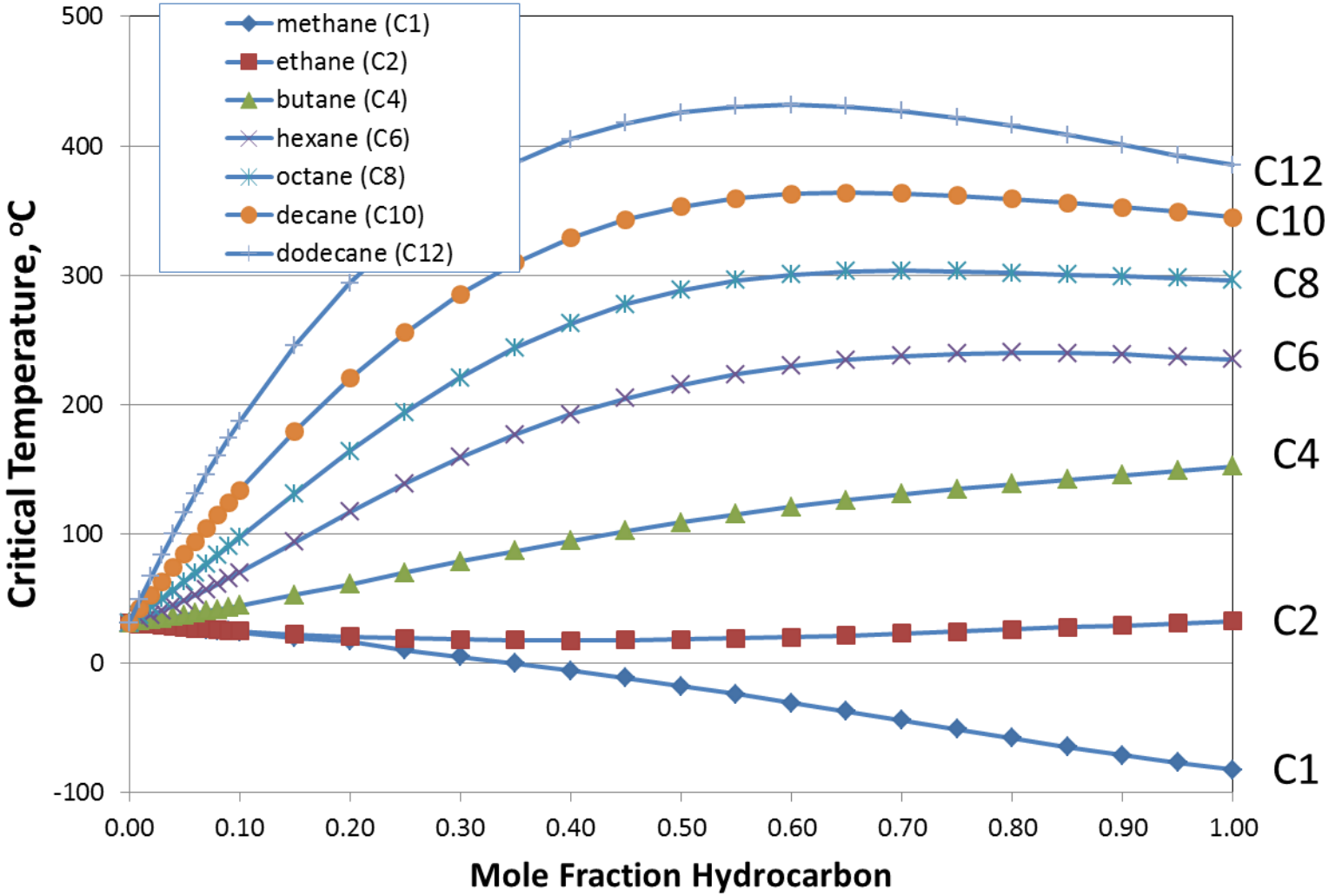
Does anything interesting happen above and below MMP?

Conventional crude/CO_2 behavior, 42 ^oC

CO_2 pressure increased from ambient to 2300 psi, then reduced back to ambient.

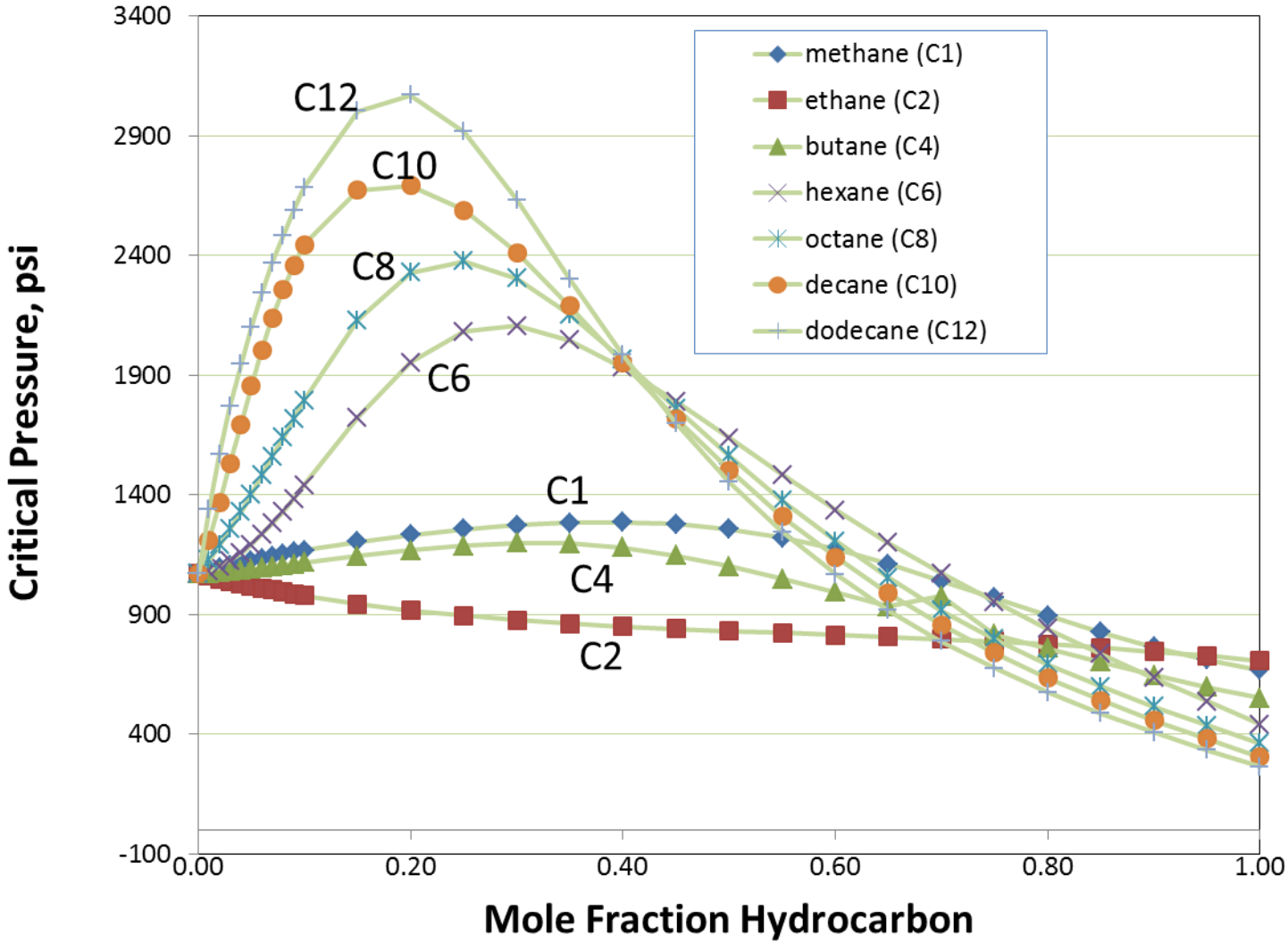
Where do these “extra” phases come from?

Dissolved Hydrocarbons Affect the Critical Temperature (a lot)



NIST Standard Reference Database, 23. Version 9.0, “Reference Fluid Thermodynamic and Transport Properties”

Dissolved Hydrocarbons Affect the Critical Pressure (a lot)

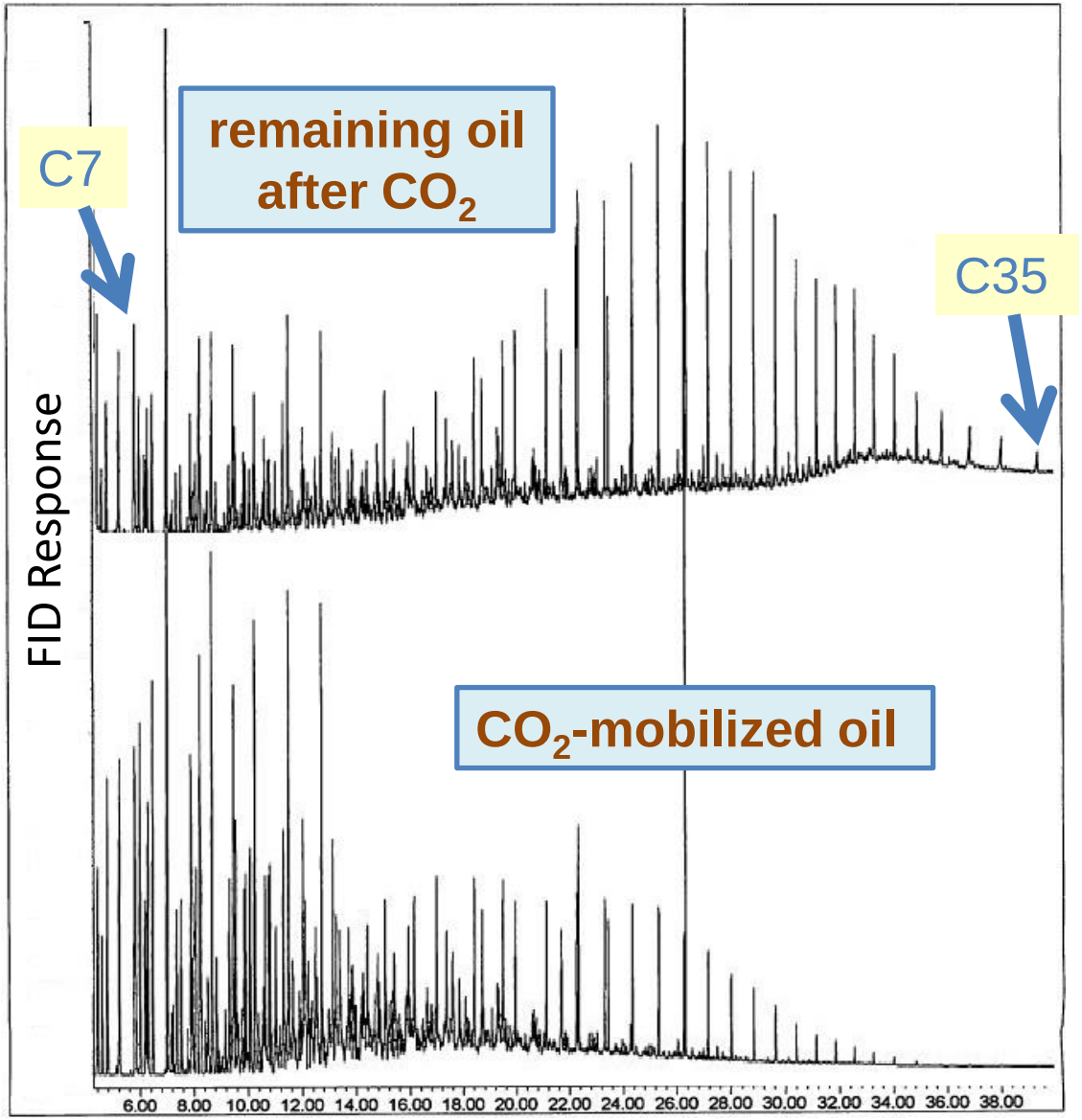


NIST Standard Reference Database, 23. Version 9.0, “Reference Fluid Thermodynamic and Transport Properties”

Is there MW selectivity in CO_2-mobilized hydrocarbons—both as the pressure is rising, and then falling below injection pressure?

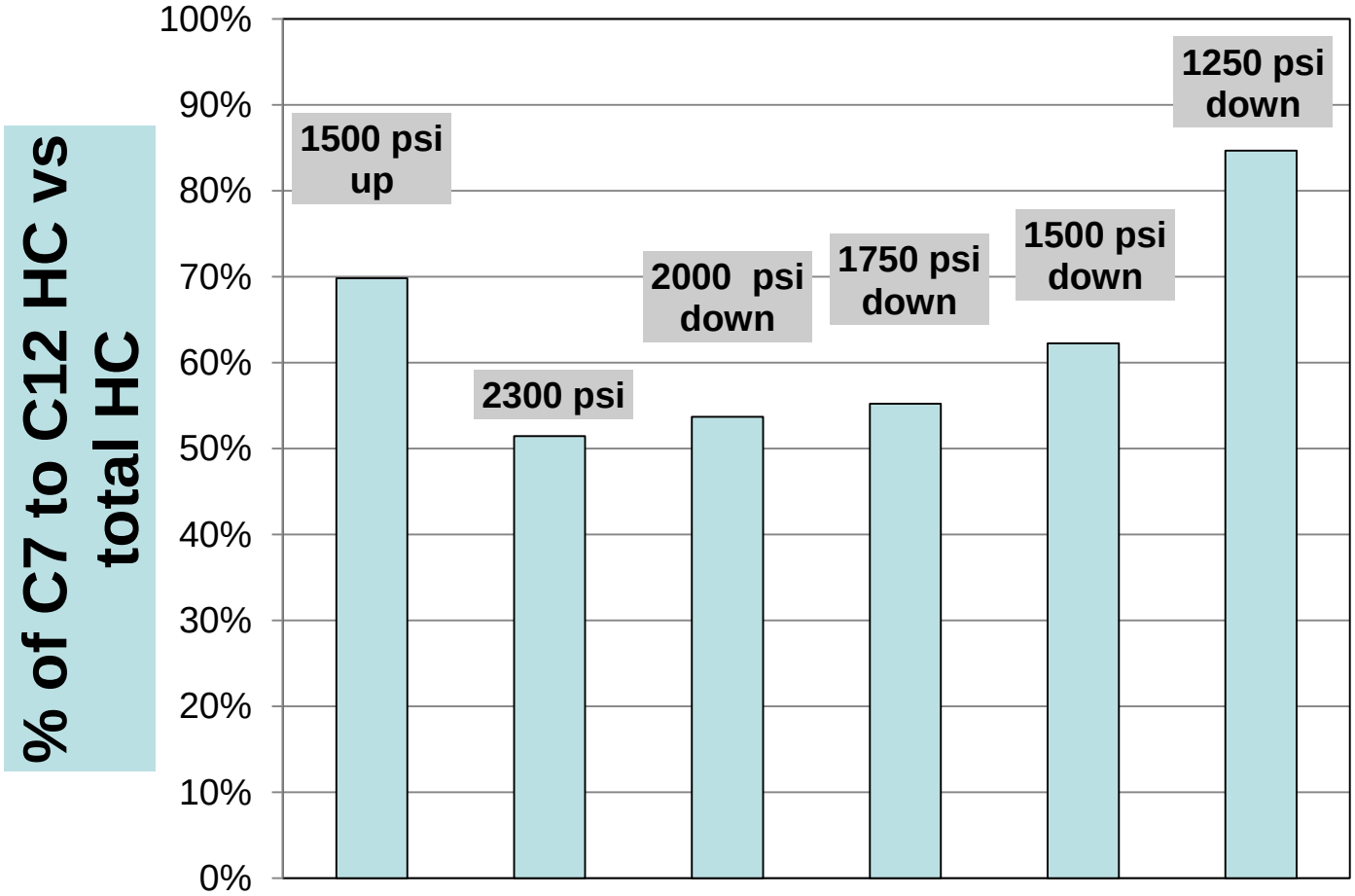
15 mL oil pressurized for ca. 1 h between each sample collection (ca. 5X at each condition).

Each pressure was tested with new oil.


C7
remaining oil after CO_2
C35
FID Response
CO_2-mobilized oil
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00 36.00 38.00
Retention Time (Minutes)

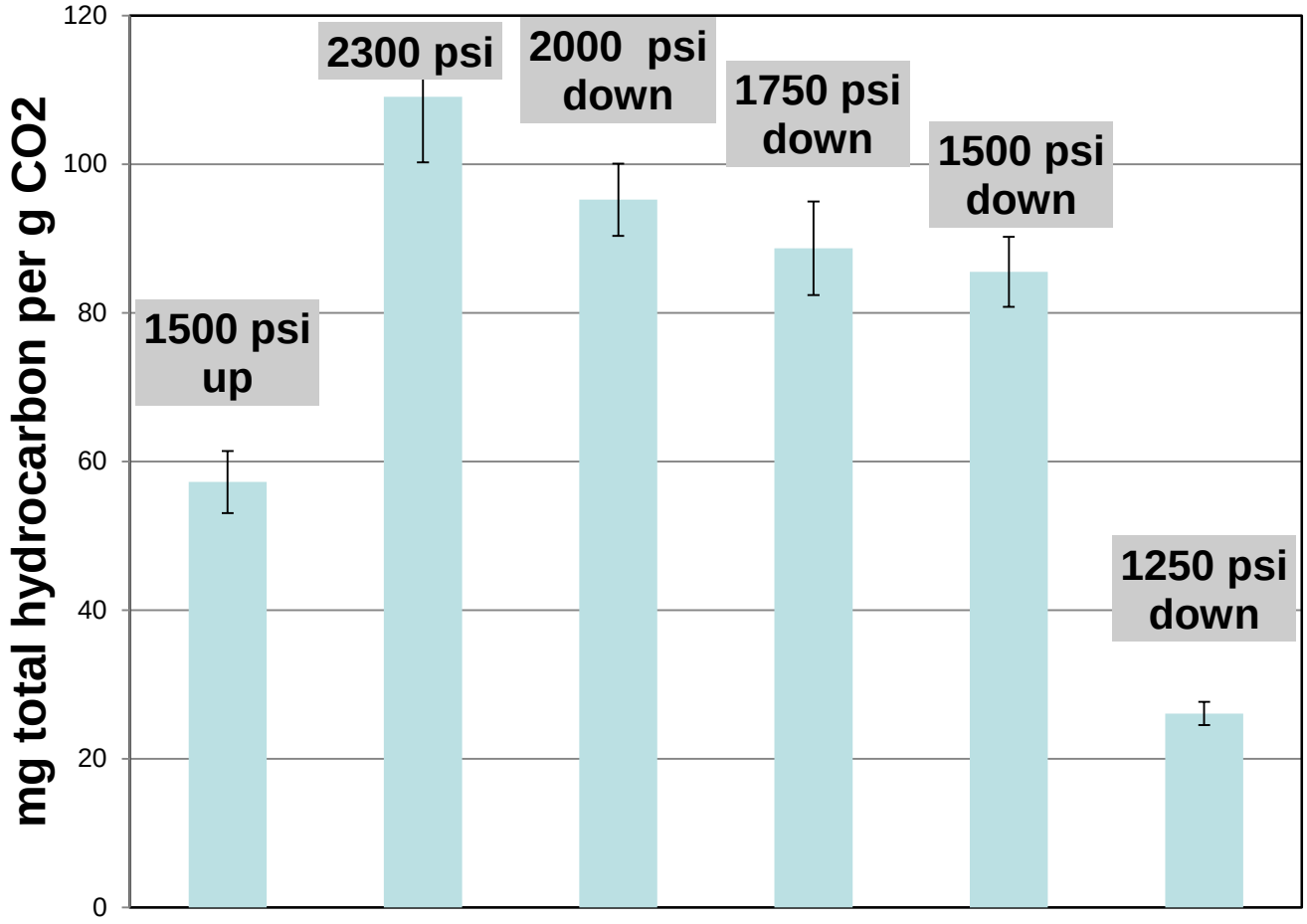
CO_2 selectively mobilizes lighter hydrocarbons, especially at lower pressures.

(Heavier hydrocarbons will be left in the reservoir.)



Mobilized oil almost doubles from MMP (1450 psi) to injection pressure.

Some oil is lost as pressure is reduced to MMP, then much is lost below MMP.



Observations and Preliminary Conclusions

1. Capillary rise method allows rapid determinations of MMP under varying conditions, and with various fluids.

2. Slim tube is a powerful tool to design EOR in conventional reservoirs, but it does not measure "miscibility." (And may not apply to unconventional plays?)

3. "MMP" is not a magic number. Lots of oil mobilization occurs below MMP. Lots of oil deposition occurs above MMP.

4. True miscibility does not happen. However, formation of an extra CO_2/oil mobile phase does occur. *(A functional definition of multiple contact miscibility.)*

Future Experiments (near term)

1. Comparison with slim rube results using live oil.

2. Effects of hydrocarbons (and nitrogen) in recycle CO2.

3. Changes in produced oil MMP during EOR.

4. Determining the effect on MMPs of different flare gas compositions.

5. Try to better understand the multi-phase behavior of oil and CO2 below, at, and above MMP.

6. Apply these insights to unconventional plays like the Bakken.

Acknowledgments

This material is based upon work supported by the U.S. Department of Energy, National Energy Technology Laboratory under Award Nos. DE-FC26-08NT43291 and DE-FC26-05NT42592.

The support of Marathon Oil Company; TAQA North, Ltd.; Continental Resources, Inc.; and the North Dakota Industrial Commission (Oil and Gas Research Council) is also gratefully acknowledged as is the support of the members of the PCOR Partnership Program.

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