



# Laboratory Studies to Support Rich Gas EOR

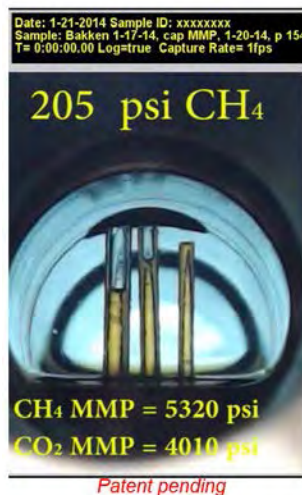
Steven Hawthorne, Ph.D. Principal Chemist

August 7, 2018

Critical Challenges. **Practical Solutions.**

# Rich Gas-Oil Fluid Behavior and Rock Extraction Studies

## MMP Studies



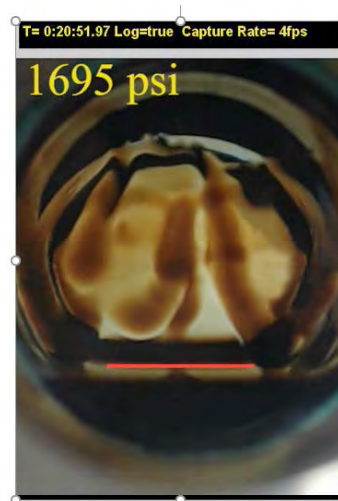
MMP of crude oil with rich gas components and different rich gas mixtures.

- Methane, ethane, and propane.

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



## Miscible Behavior Studies



How well do rich gas components mobilize crude oil hydrocarbons into the “miscible” upper phase?

Which rich gas components mobilize higher MW hydrocarbons better?

## Rock Extraction Studies



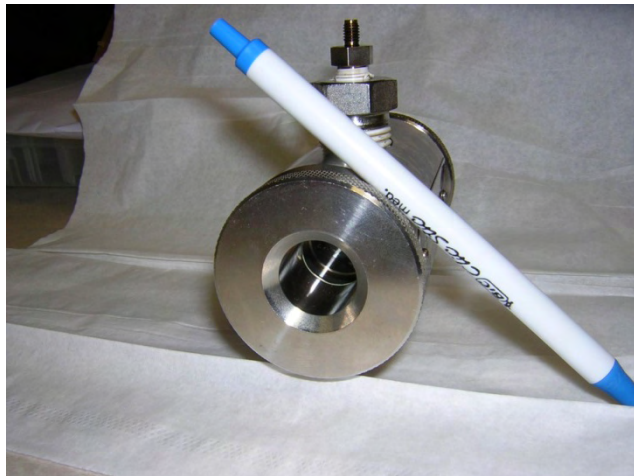
Determine ability of rich gas components to mobilize oil from the Bakken matrix.

- Methane, ethane, and propane at reservoir conditions.

### *3 basic lab experiments:*

- *MMP = multiple contact minimum miscibility pressure.*
- *Hydrocarbon compositions in the “miscible” phase.*
- *Bakken rock extractions at reservoir conditions.*

***MMP by vanishing  
interfacial  
tension/capillary rise.***

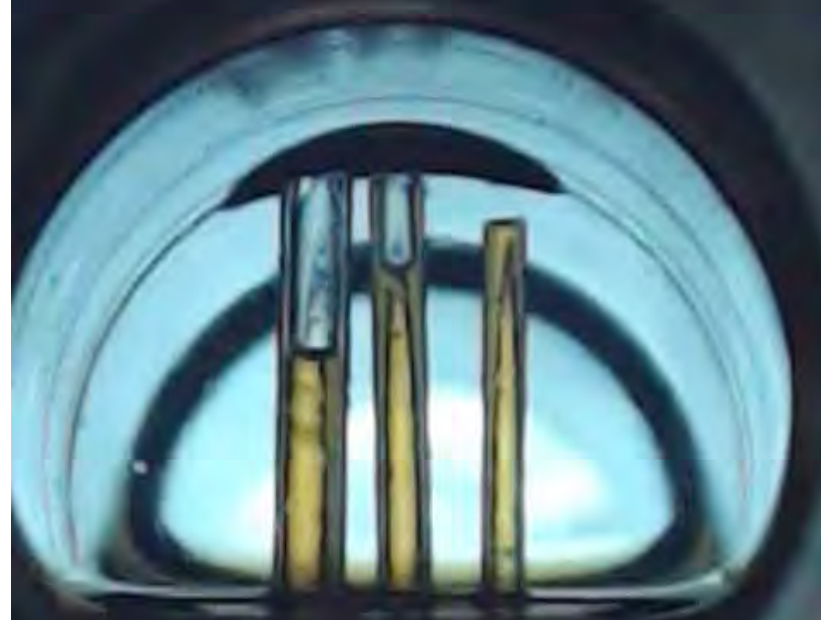


1.12, 0.84, 0.68 mm i.d.



Date: 1-21-2014 Sample ID: xxxxxxxx  
Sample: Bakken 1-17-14, cap MMP, 1-20-14, p 154  
T= 0:00:00.00 Log=true Capture Rate= 1fps

205 psi CH<sub>4</sub>



CH<sub>4</sub> MMP = 5320 psi

CO<sub>2</sub> MMP = 4010 psi

**Rapid and Simple  
Capillary-Rise/Vanishing  
Interfacial Tension Method To  
Determine Crude Oil Minimum  
Miscibility Pressure: Pure and  
Mixed CO<sub>2</sub>, Methane, and Ethane**

Steven B. Hawthorne, David J. Miller, Lu Jin, and Charles D. Gorecki

Energy & Environmental Research Center, University of North Dakota, 15 North 23rd Street, Stop 9018, Grand Forks, North Dakota 58202, United States

**energy&fuels**

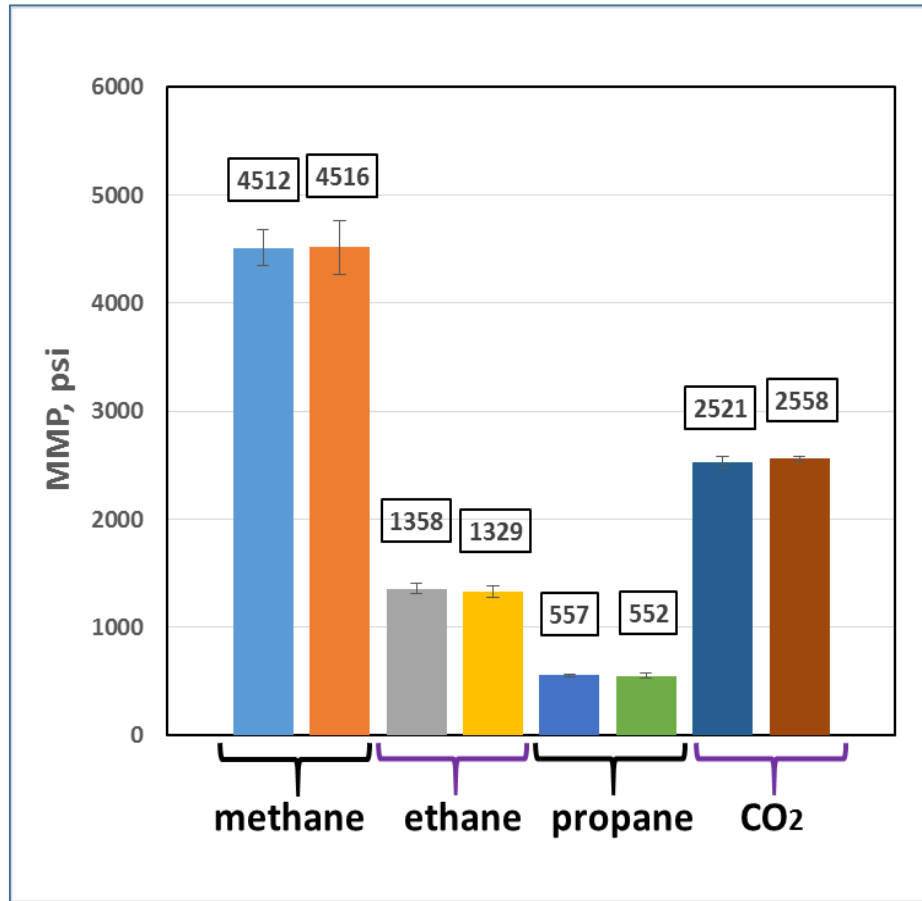
Reprinted from  
Volume 30, Number 8, Pages 6365–6372

***U.S Patent 9,851,339***

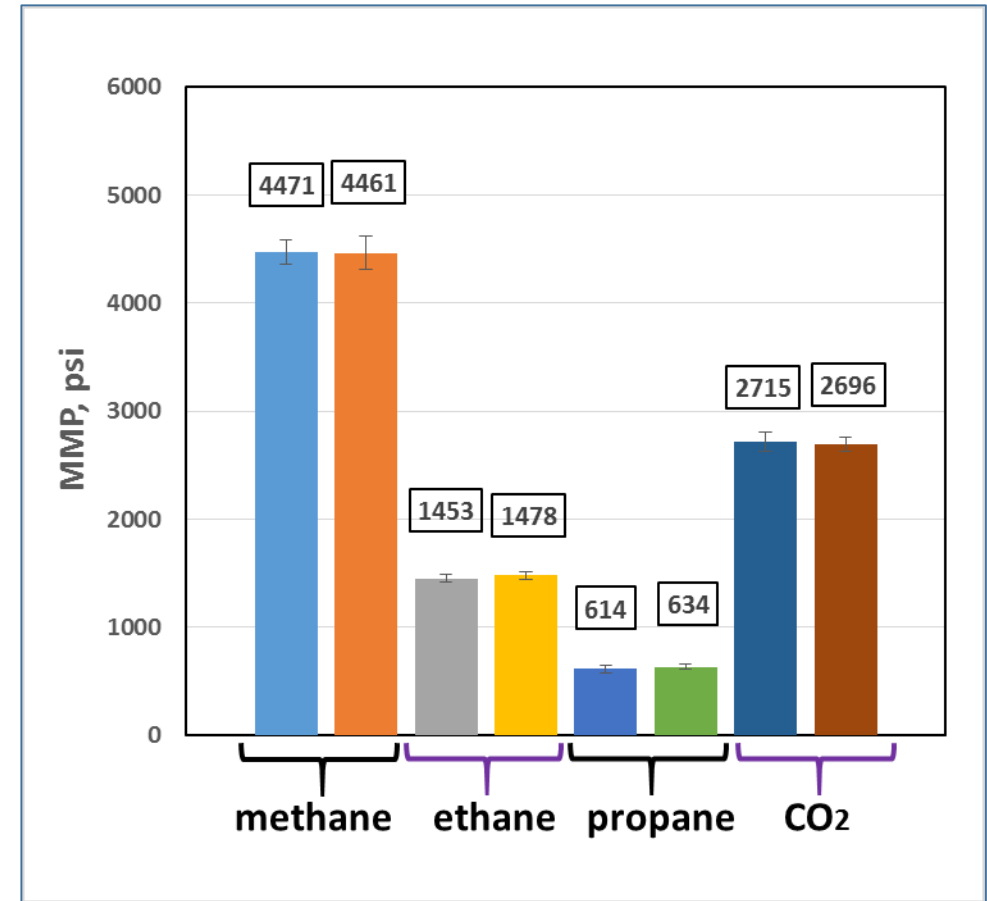
# Minimum Miscibility Pressure (MMP) with Methane, Ethane, Propane, and CO2\*

*The richer the gas, the lower the MMP !!*

### Bakken Crude Oil (230 F, 110 C)

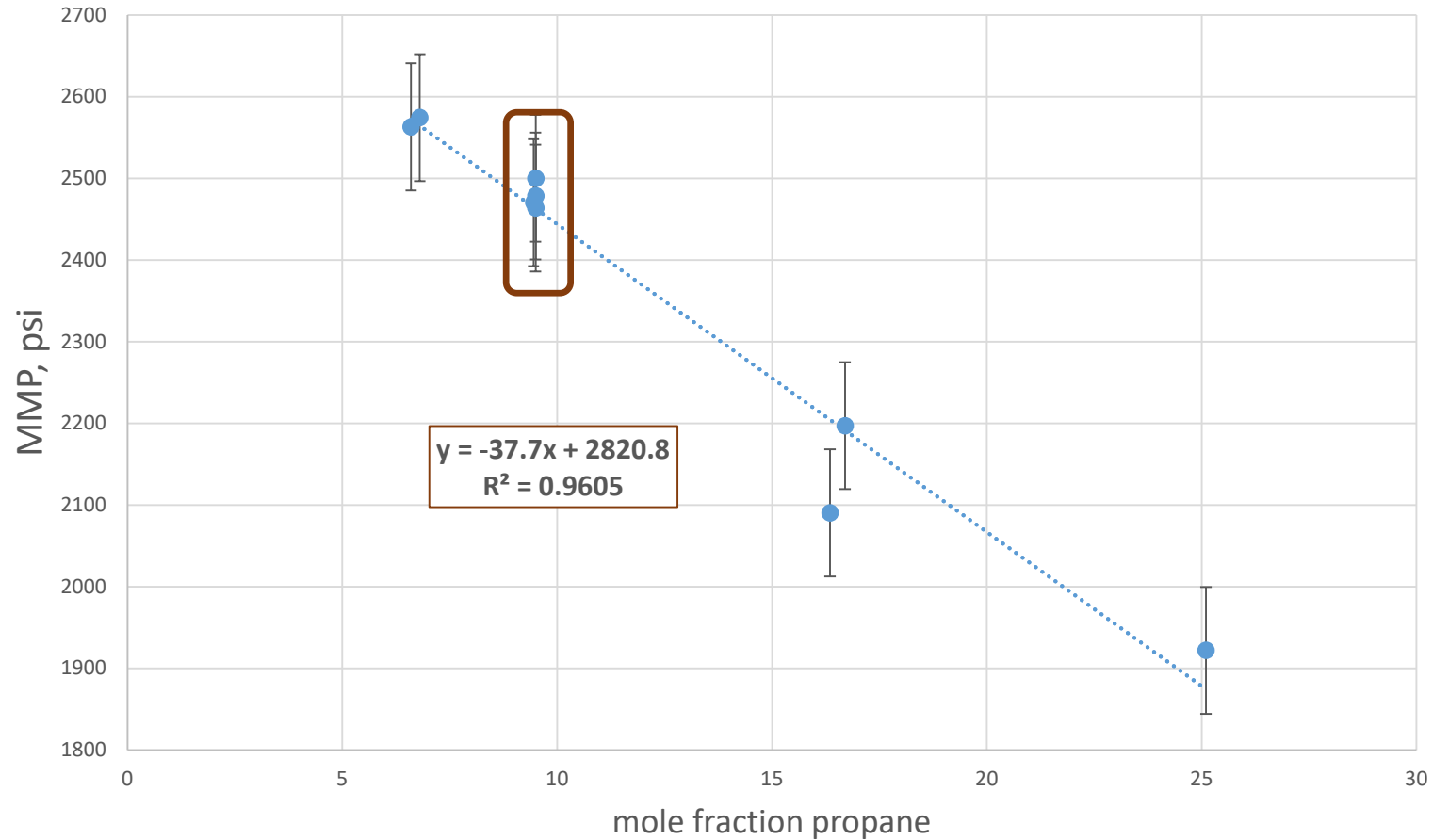


### Three Forks Crude (264 F, 129 C)



\* CO2 MMPs were determined under separate funding from the US Department of Energy, and are presented only for comparison purposes.

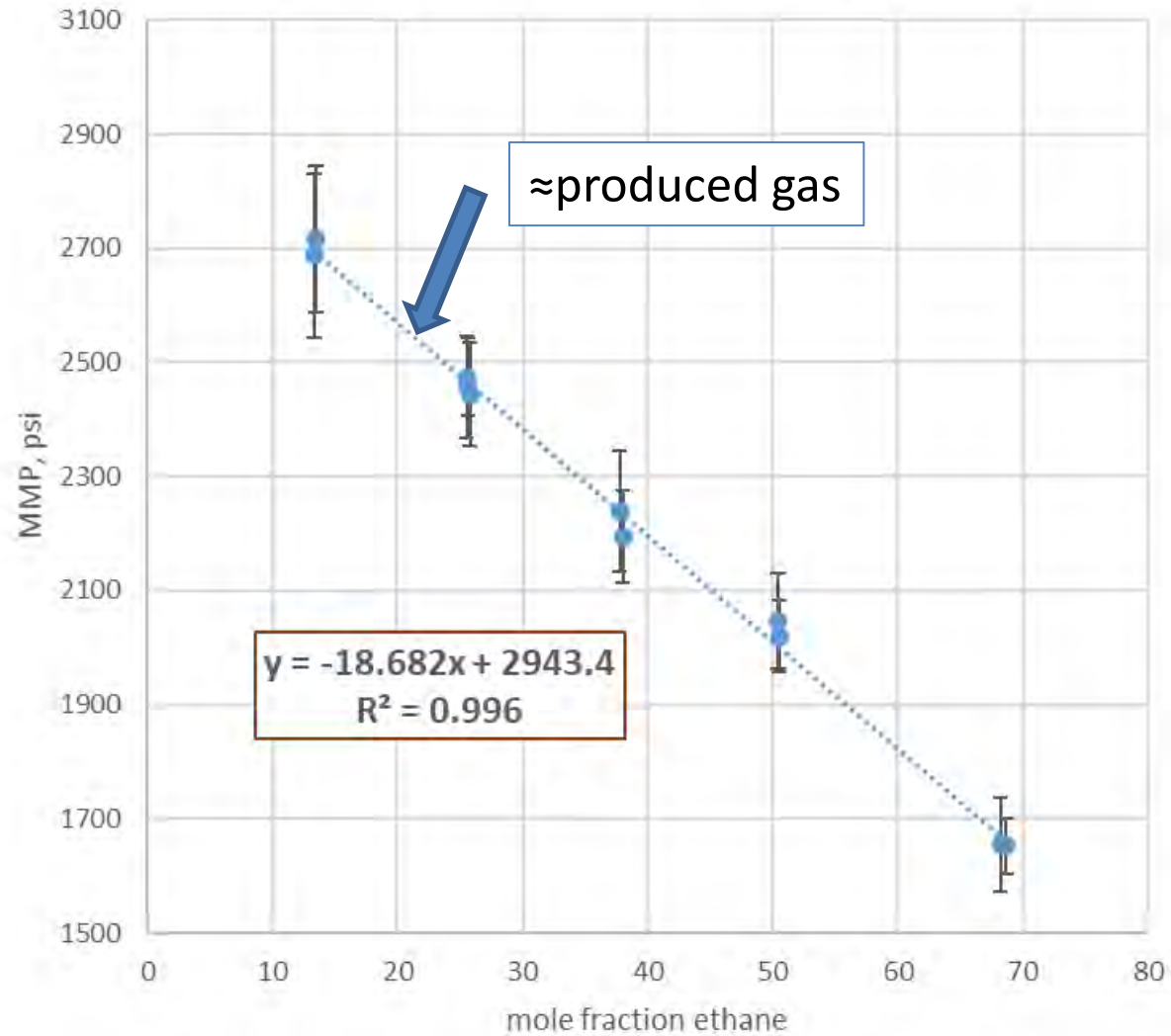
### Effect of propane on MMP with constant 3.1 C1/C2 ratio



***A typical 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 3483 psi, much higher than experimental value of 2480 psi.***

Effect of ethane with constant 7.3 C1/C3 ratio



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

### *3 basic lab experiments:*

- *MMP = multiple contact minimum miscibility pressure.*
- *Hydrocarbon compositions in the “miscible” phase.*
- *Bakken rock extractions at reservoir conditions.*



# Which crude oil hydrocarbons are dissolved into the gas-dominated upper “miscible” phase?



Date: 3-25-2013 Sample ID: Test ID  
Sample: BC 2300psi 42C)  
T= 1:16:20.36 Log=true Capture Rate= 1fps



10 mL gas  
10 mL oil

's' slows capture; 'f' captures faster; 'Q' is for Quit;  
'l' toggles logging; UP/DOWN/LEFT/RIGHT adjusts yellow box

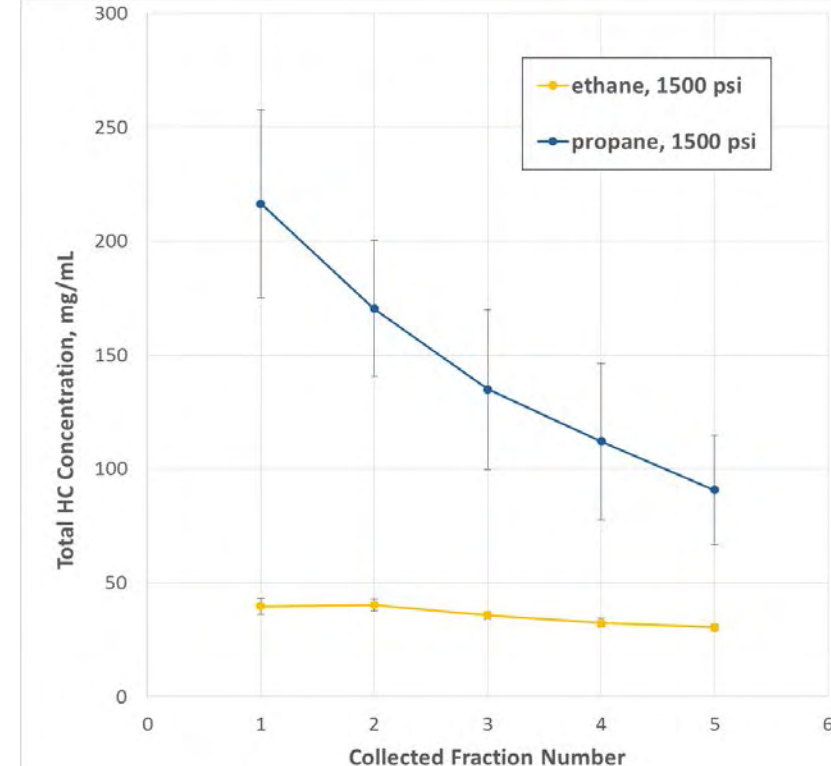
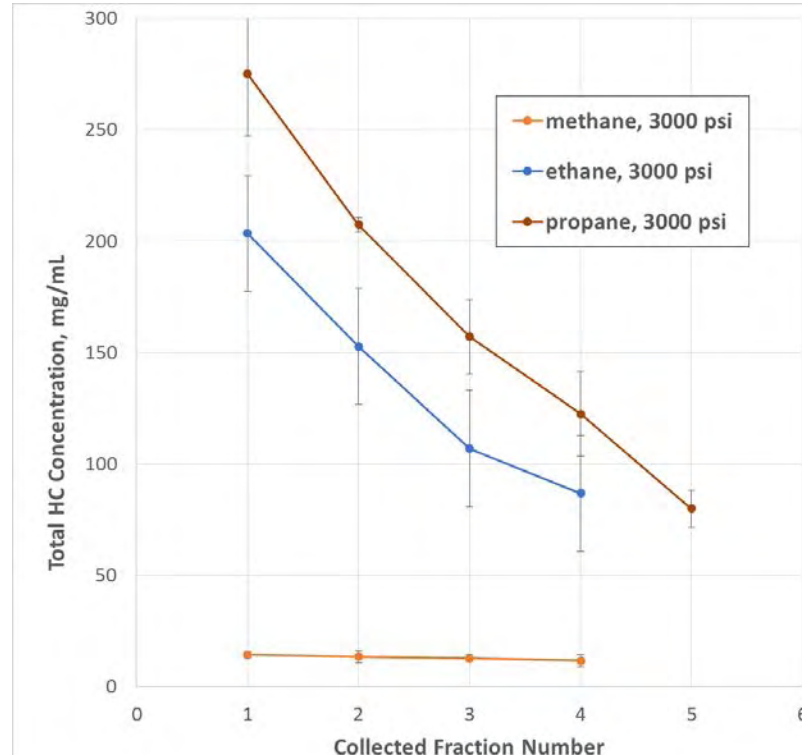
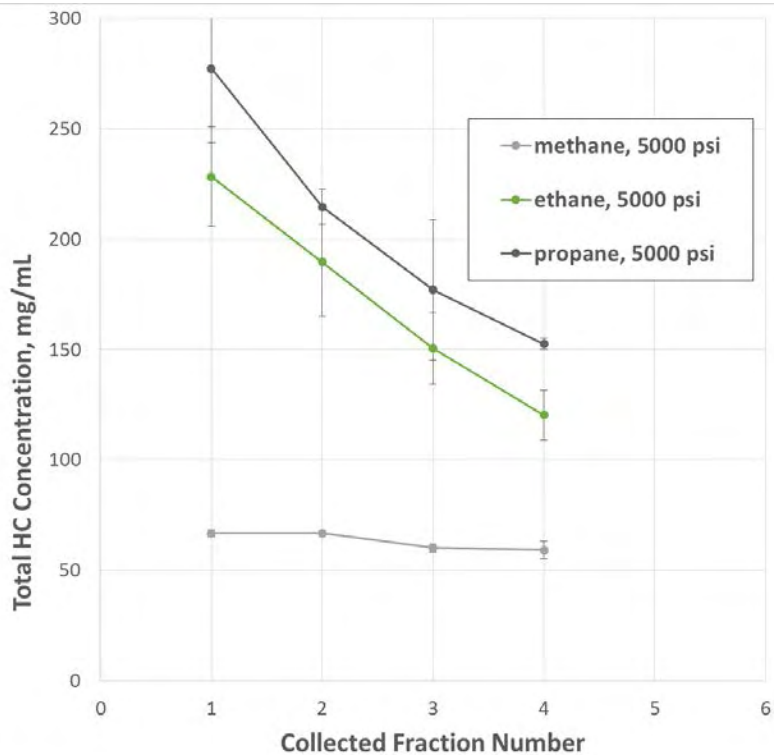
1. The gas is percolated through an oil column and equilibrated at reservoir temperature and pressure.
2. The upper “miscible” phase is sampled while maintaining reservoir T and P.
3. Dissolved HCs are collected analyzed by GC/FID

*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.*

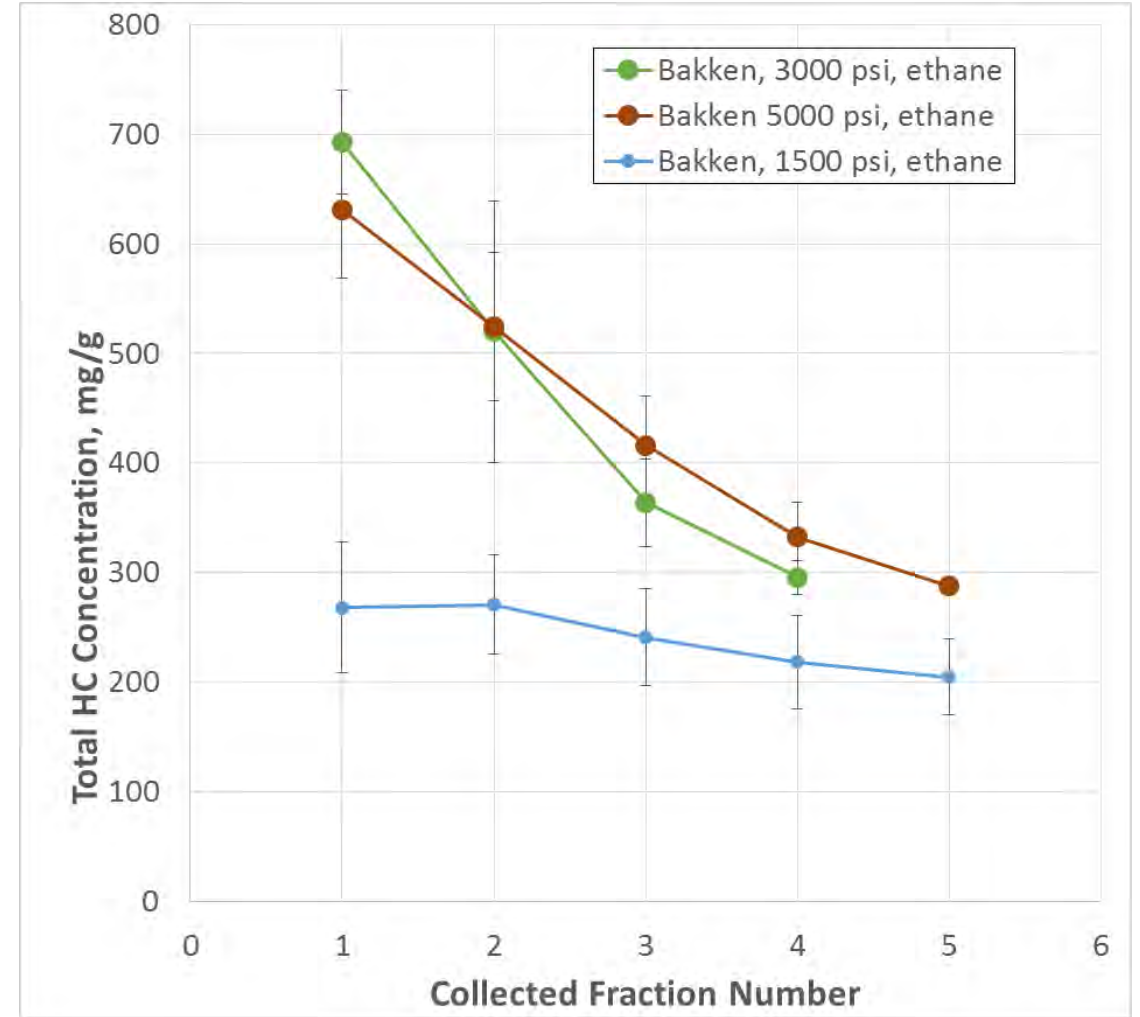
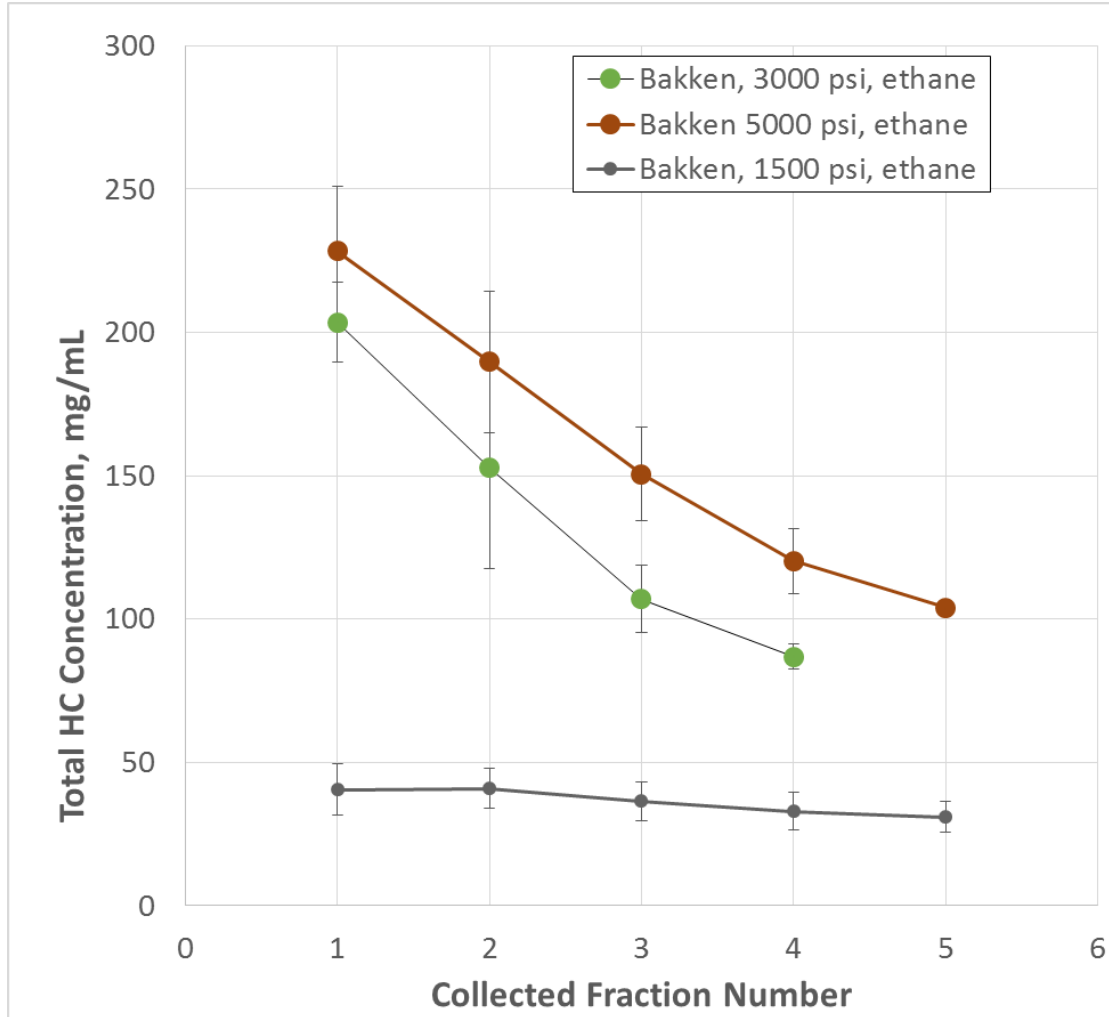
## Effect of fluid and pressure on hydrocarbons mobilized from Bakken crude oil at 230 °F (110 °C)

At 5000 psi, ethane and propane mobilize similar concentrations of hydrocarbons, but at lower pressures, ethane becomes much less effective. Methane is poor at any pressure.

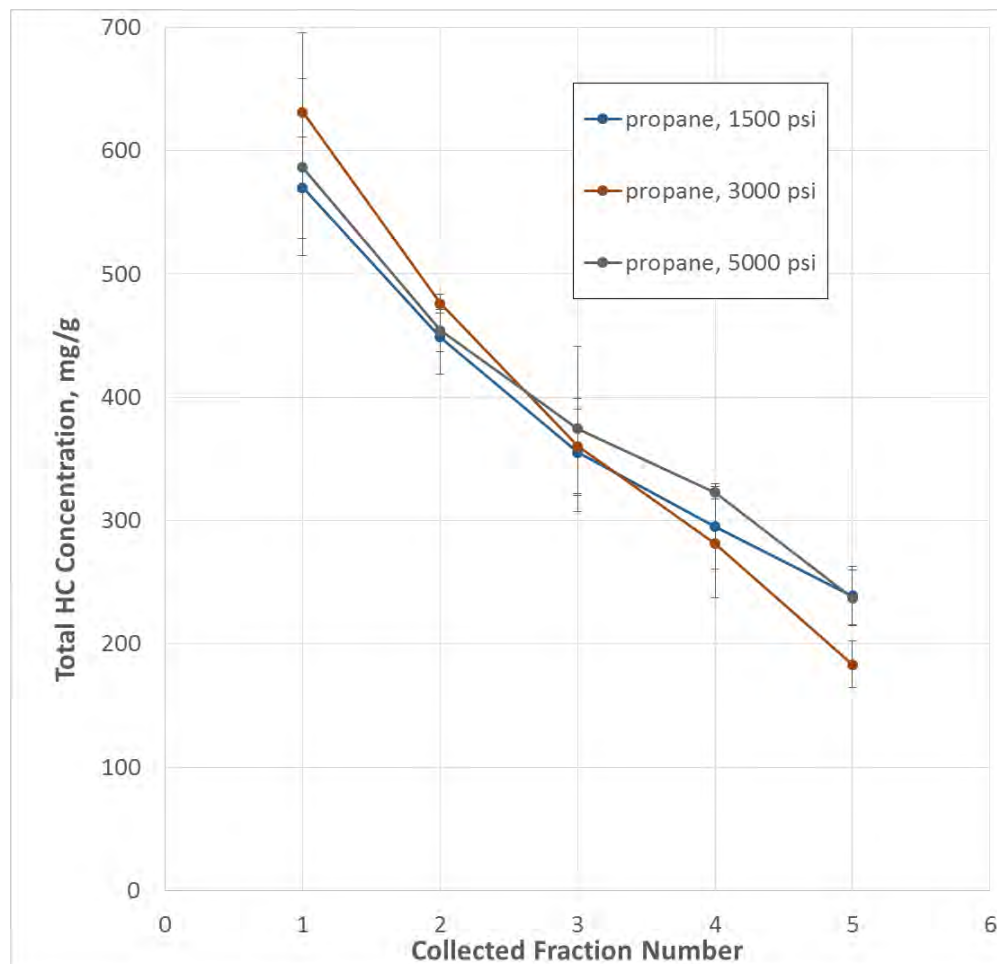
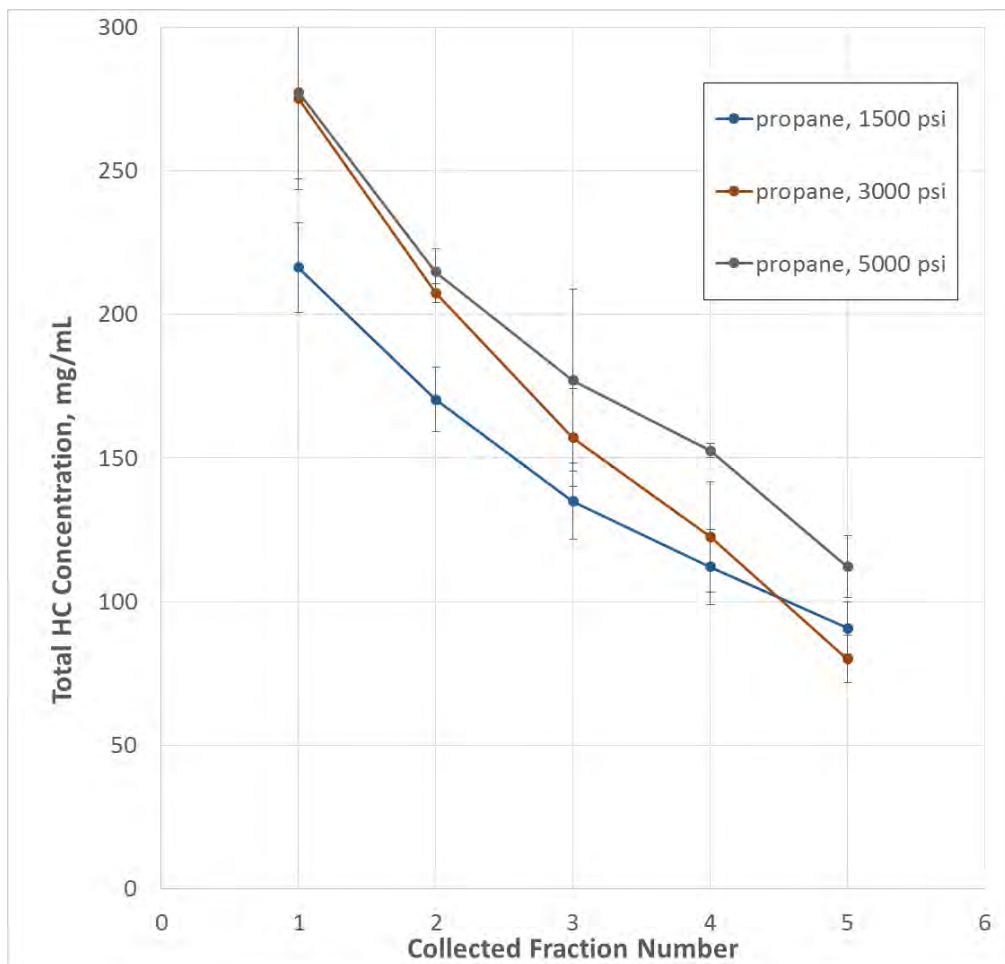


10 mL of crude oil was equilibrated with 10 mL of injected C1, C2, or C3 headspace at reservoir conditions before taking five sequential aliquots at 1-hour intervals. The error bars represent the standard deviation in hydrocarbon concentrations for triplicate experiments at each condition.

Just like for rock extractions discussed below, HC mobilization into the ethane “miscible” phase depends on pressure. Biggest improvement is between 1500 and 3000 psi.

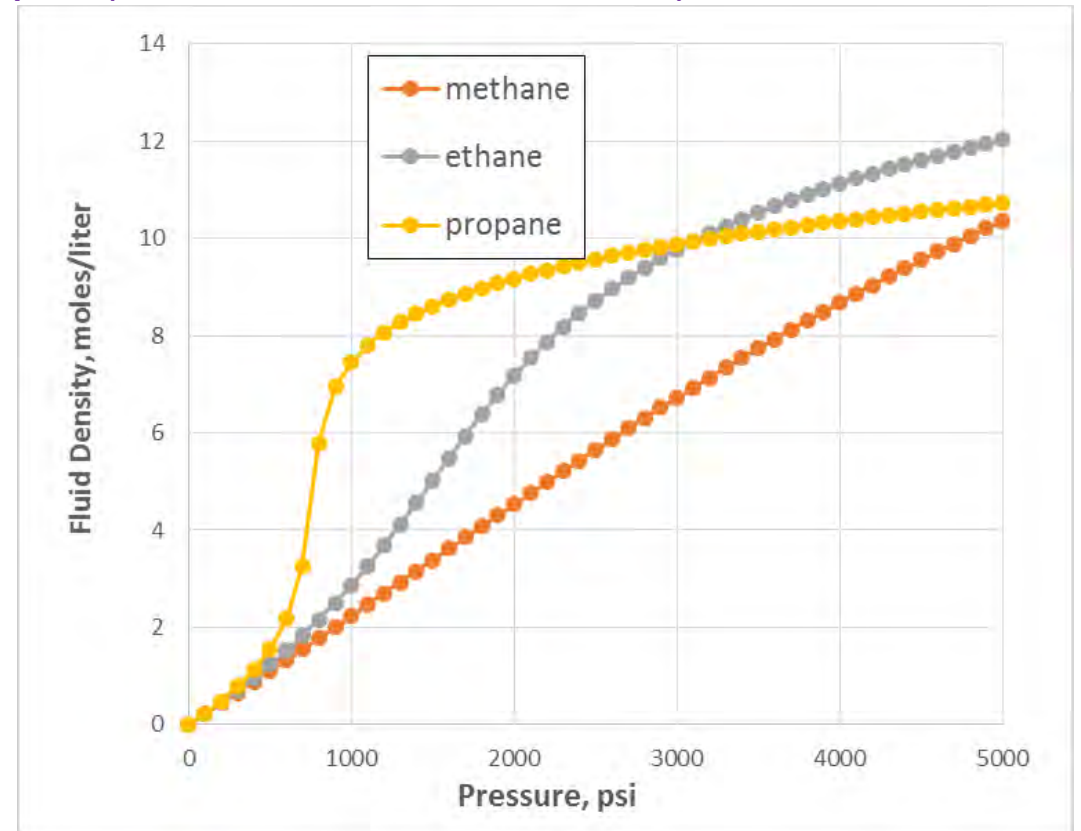
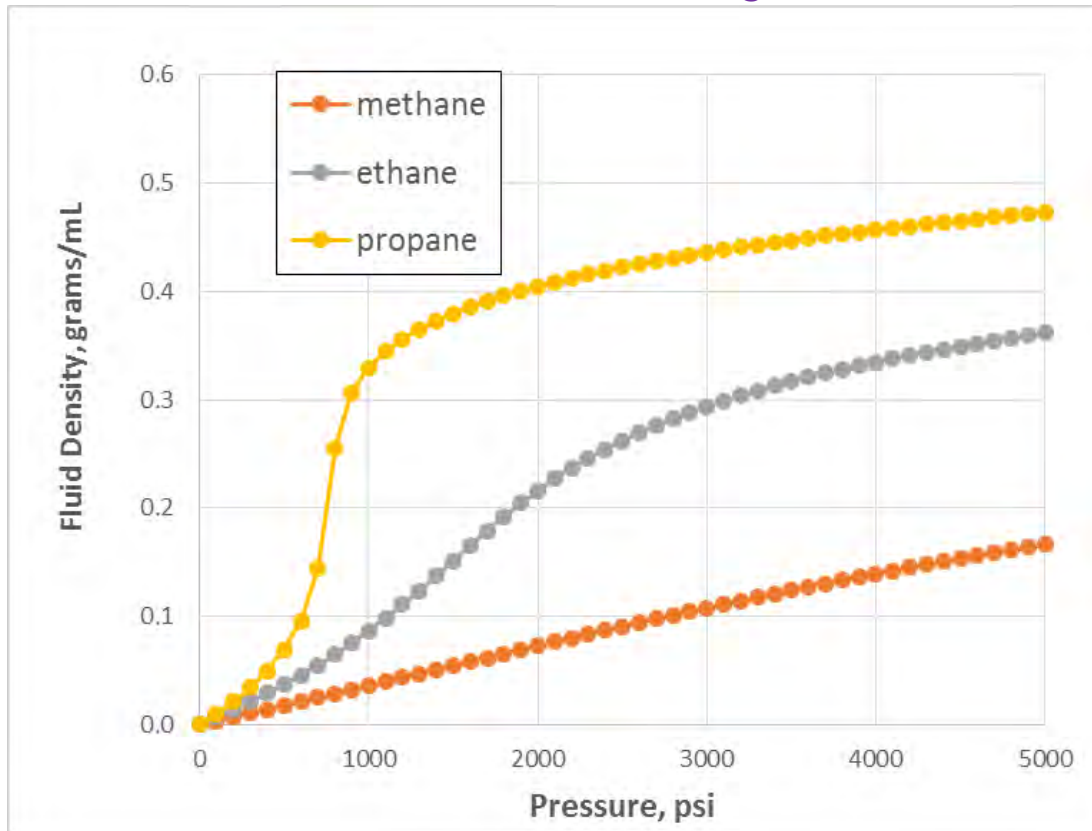


Just like for rock extractions discussed below, HC mobilization into the propane “miscible” phase has little dependence on pressure.



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 ethane, since propane's density does not change much above 1000 psi. (all values at 110 C, 230 °F)*



## **Summary**

*How effective are methane, ethane, and propane at mobilizing higher molecular weight hydrocarbons into the “miscible” phase?*

*Propane efficiently mobilizes hydrocarbons at all pressures from 1500 to 5000 psi, while ethane requires the higher pressures.*

*At 5000 psi, ethane and propane efficiently mobilize the heavier hydrocarbons (determined up to C36) effectively, but ethane is less efficient at lower pressures.*

*Methane ONLY mobilizes low MW hydrocarbons (smaller than ca. C12) at any pressure, leaving most mid- and higher-molecular weight hydrocarbons in the reservoir.*

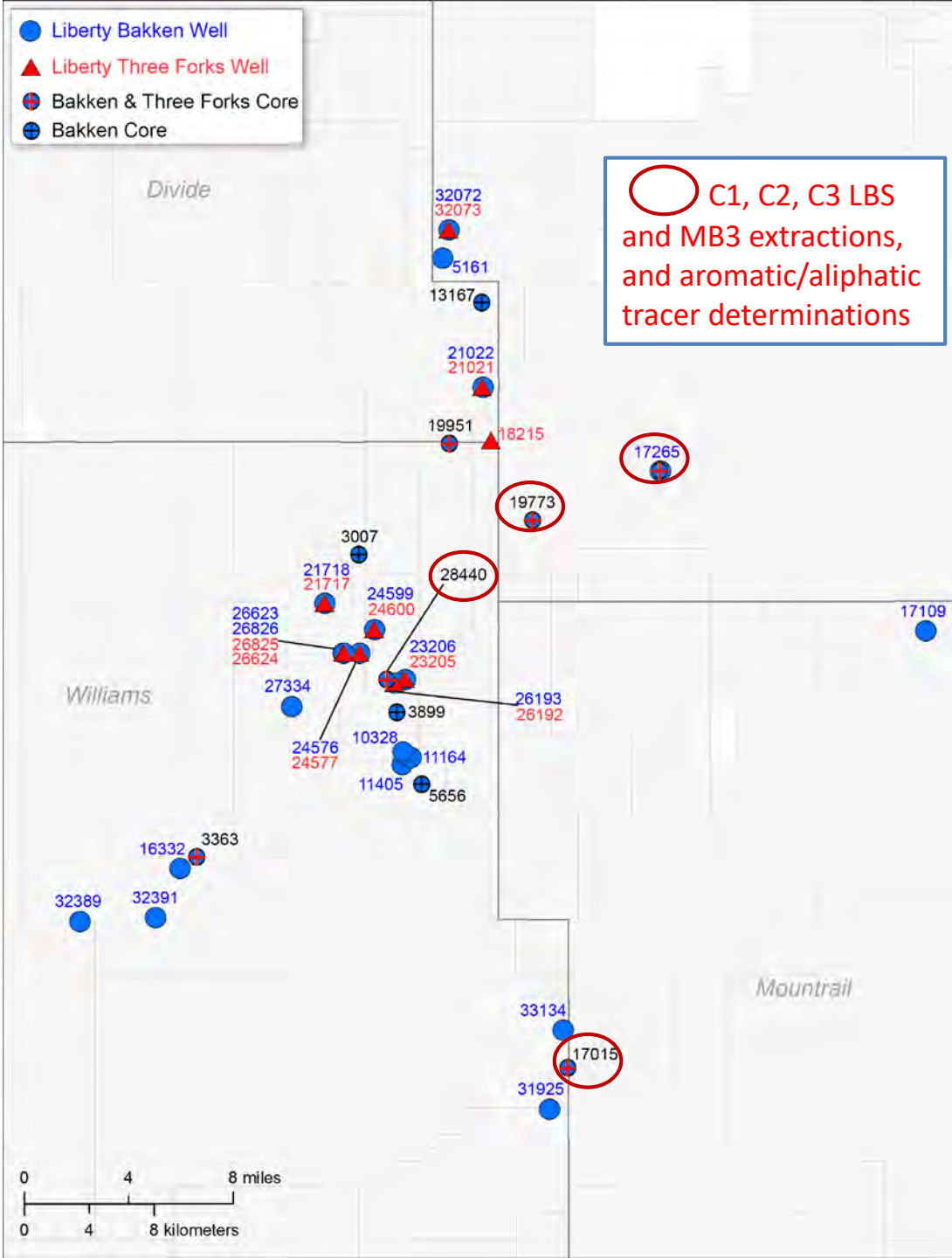
### *3 basic lab experiments:*

- *MMP = multiple contact minimum miscibility pressure.*
- *Hydrocarbon compositions in the “miscible” phase.*
- *Bakken rock extractions at reservoir conditions.*

24-hour exposures of Middle Bakken (11-mm rod) and Lower Bakken Shale (1-3.4 mm) at 110 C.

- Pure methane, ethane, and propane.
- Each at 1500, 2500, and 5000 psi

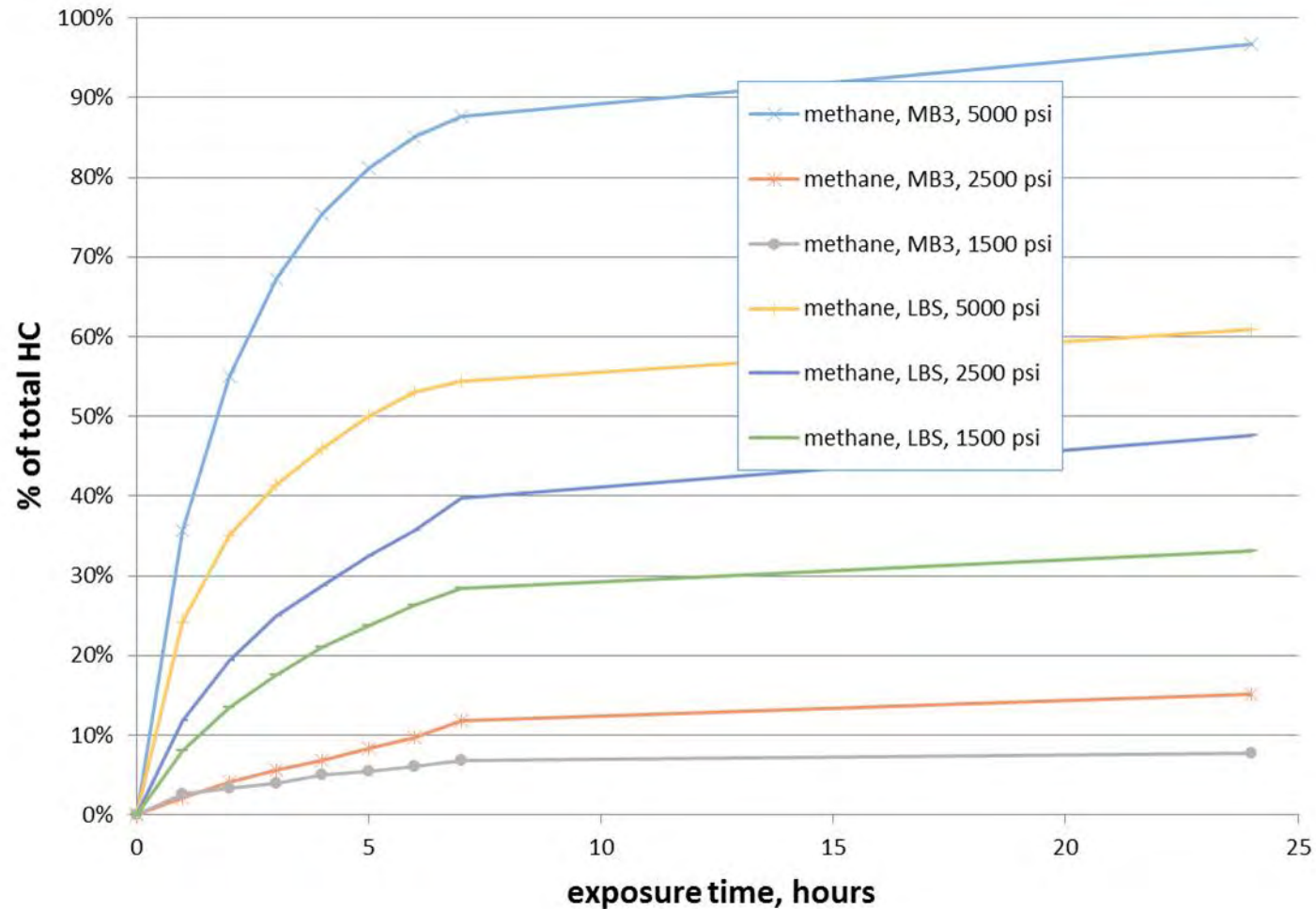




## Wells for LBS and MB3 rock samples.

- 4 well comparisons with C1, C2, and C3 LBS and MB3 extractions (5000 psi, 110 C, 24 hours).
- C1/C2/C3 extractions (and mixed) at different pressures.
- Effect of C1/C2/C3 extraction on shales for ESH rock-eval and vitrinite reflectance (National Resources, Canada).

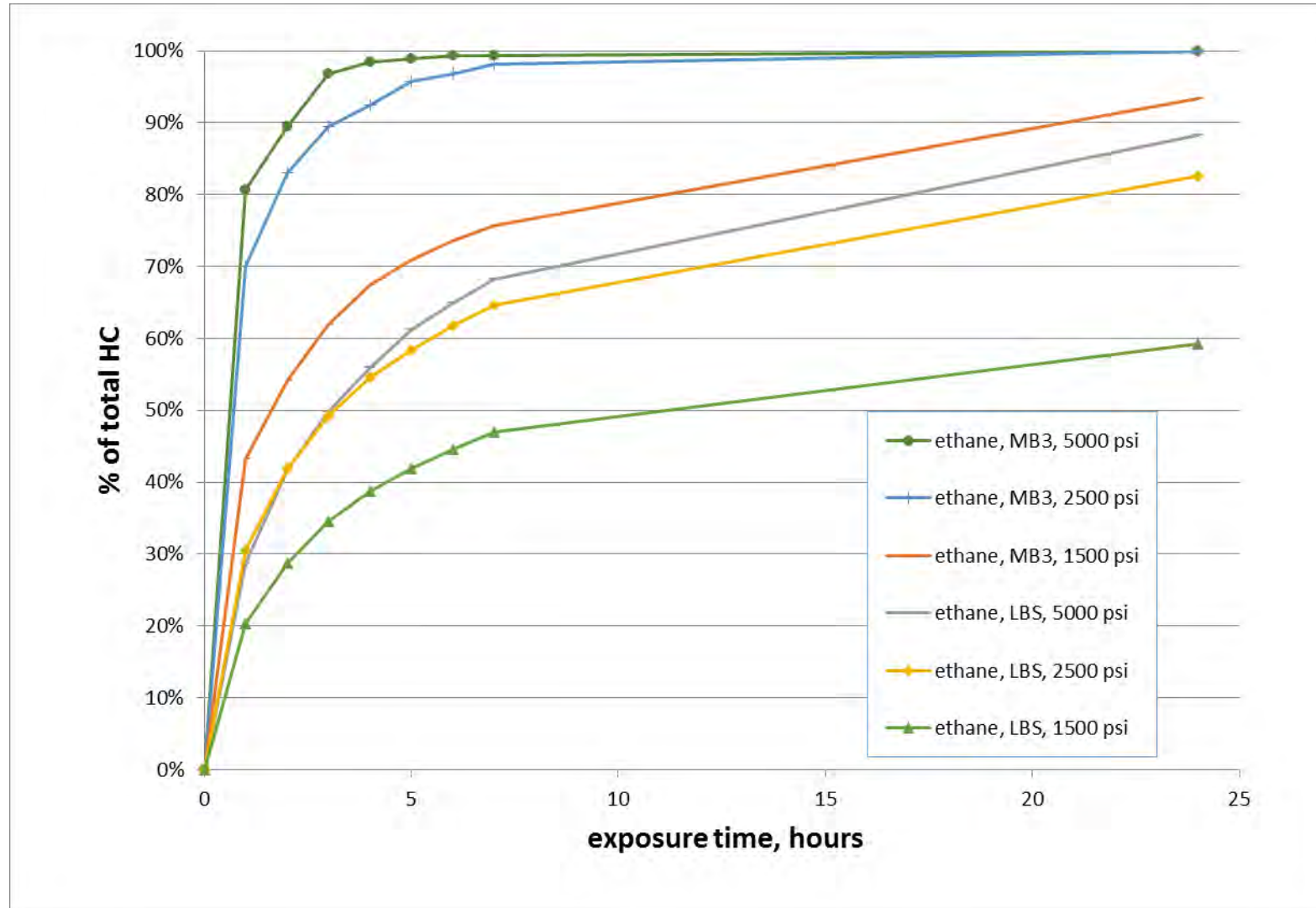
Methane recoveries from Middle Bakken and Lower Bakken Shale rocks are highly influenced by pressure, but are much lower than with ethane and propane, especially for mid- and higher-molecular weight hydrocarbons. (well 28440)



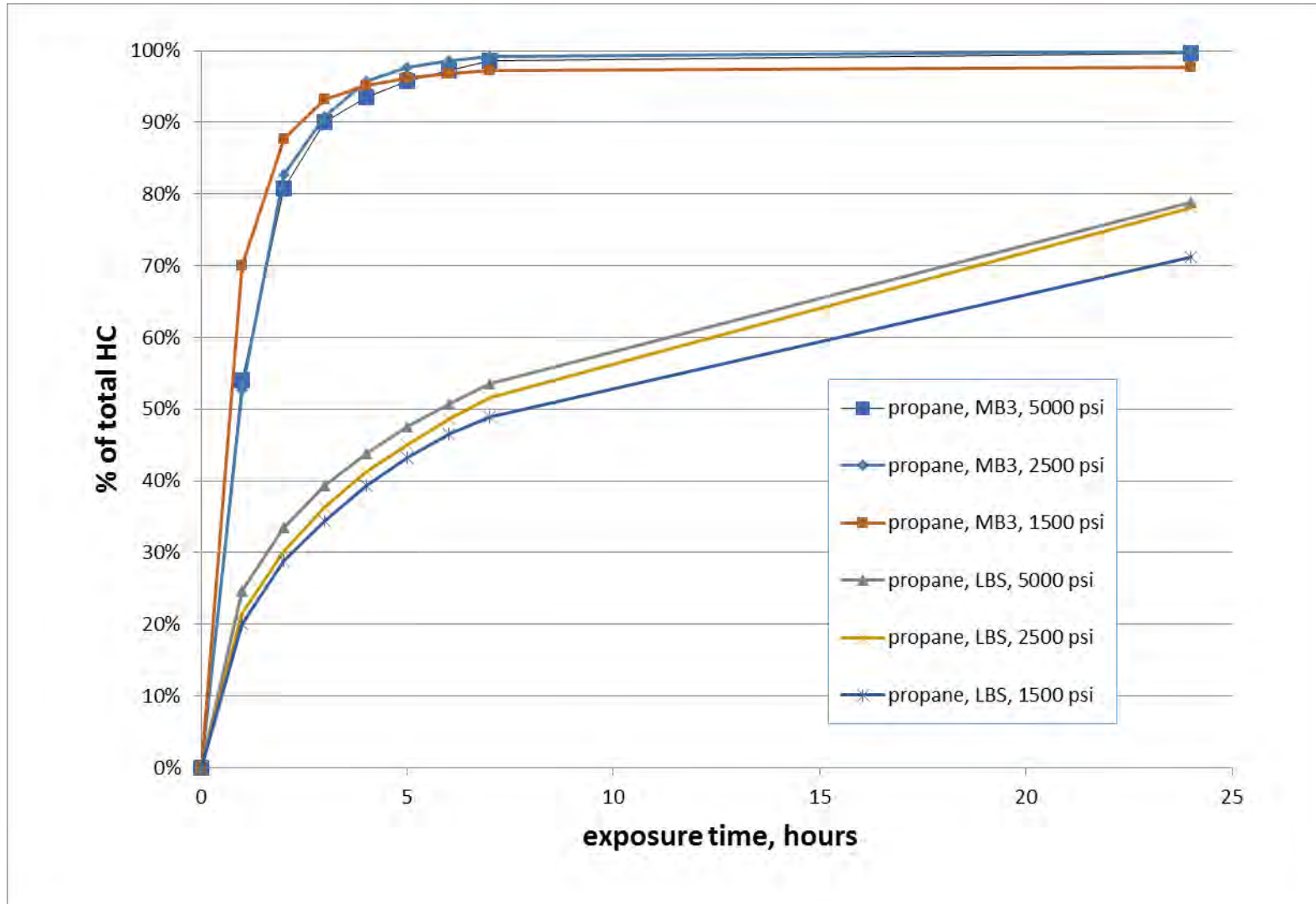
Methane simply can't extract the mid-MW HCs (ca. C12 and larger) that remain in the MB3 rocks at 1500 and 2500 psi.

Shales retain more lighter HCs, so methane artificially seems to do better with shales.

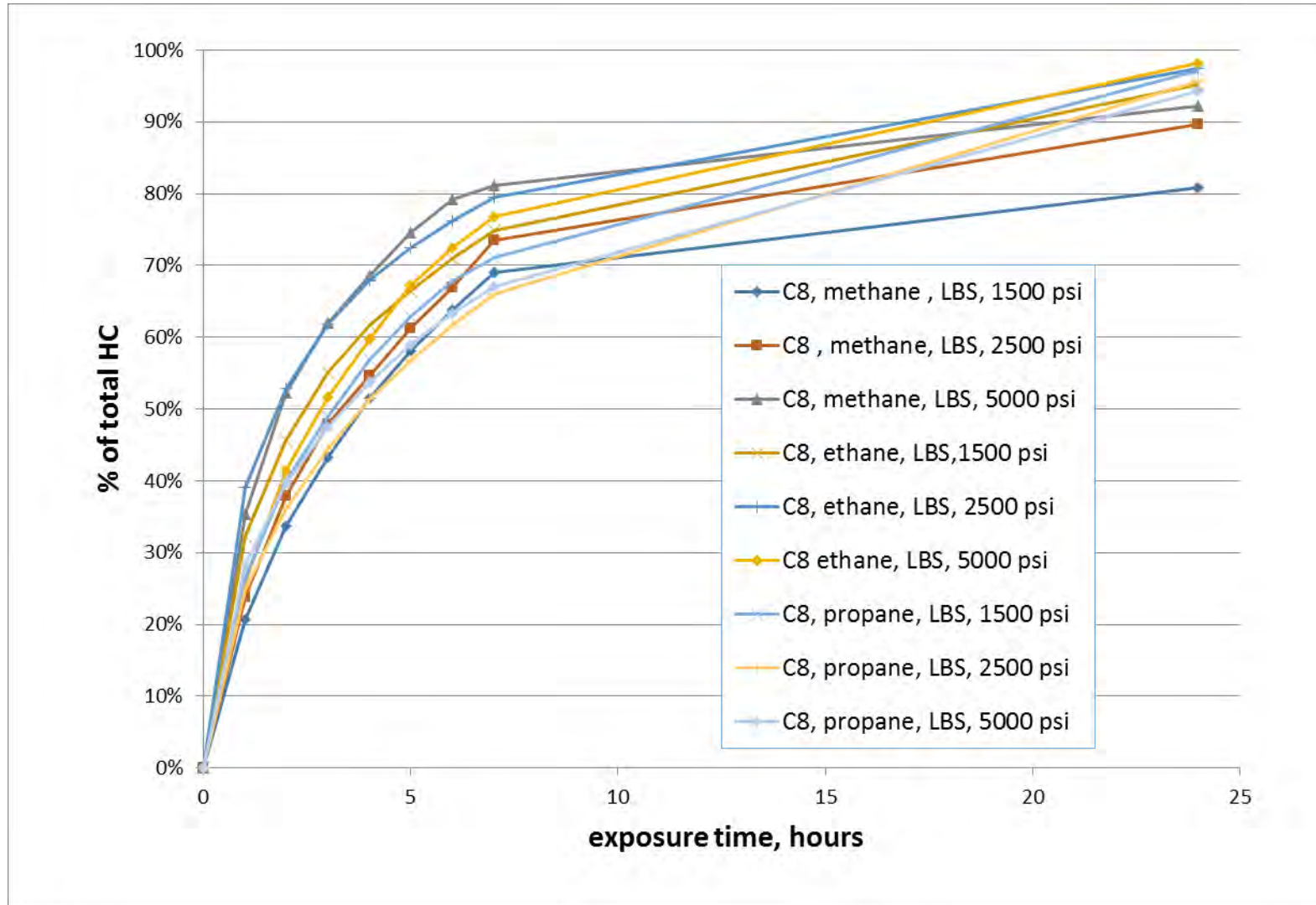
Total HC recovery from Middle Bakken and Lower Bakken Shale is affected by ethane pressure. Biggest improvement is between 1500 and 2500 psi. (well 28440)



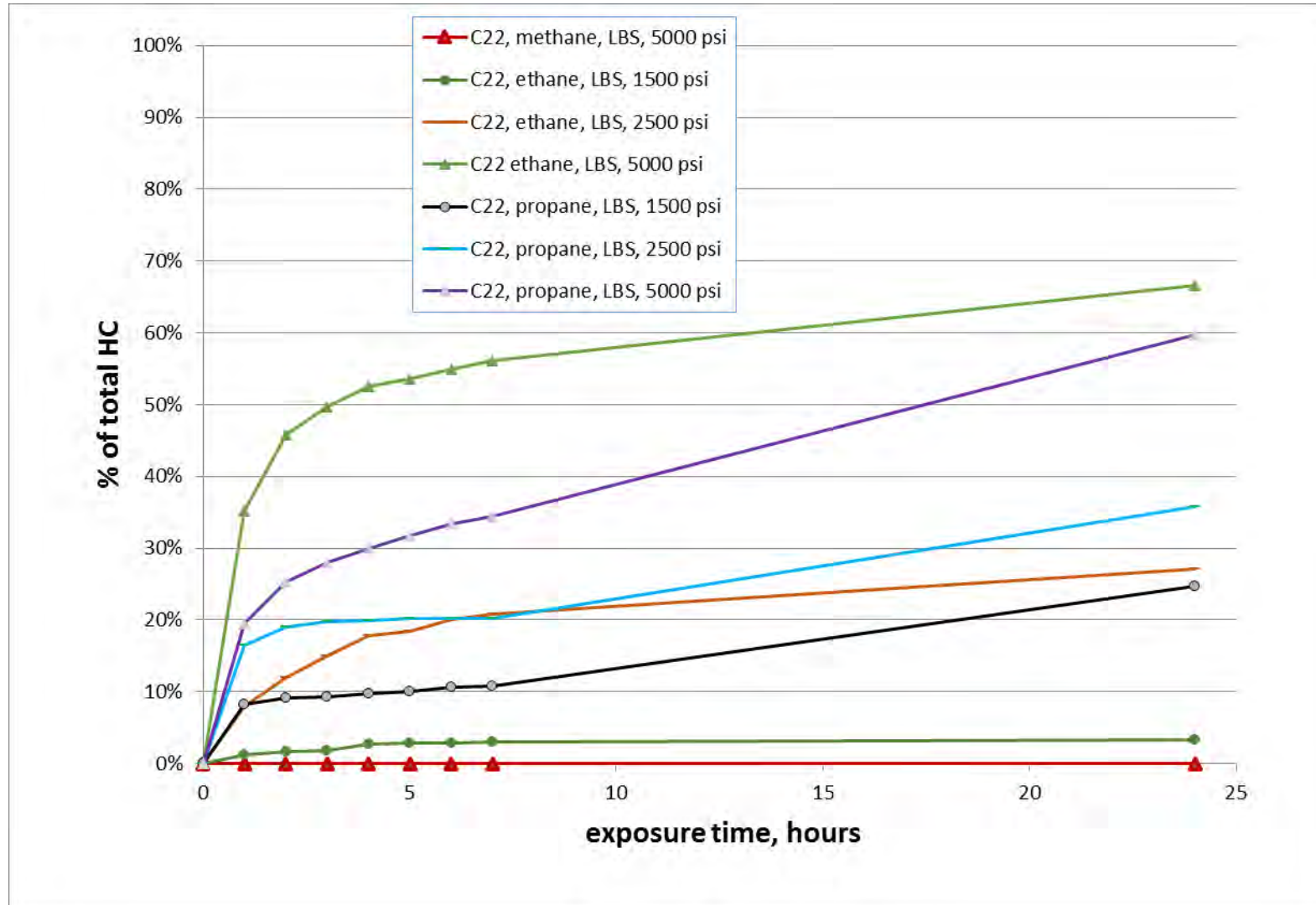
Total HC recovery from Middle Bakken (11-mm rod) and Lower Bakken Shale (1-3.4 mm) is not affected much by propane pressure.  
(well 28440)



C8 (octanes) recovery is similar for all fluids and pressures.  
Therefore, vaporization dominates C8 solubilities. (LBS, well 28440)



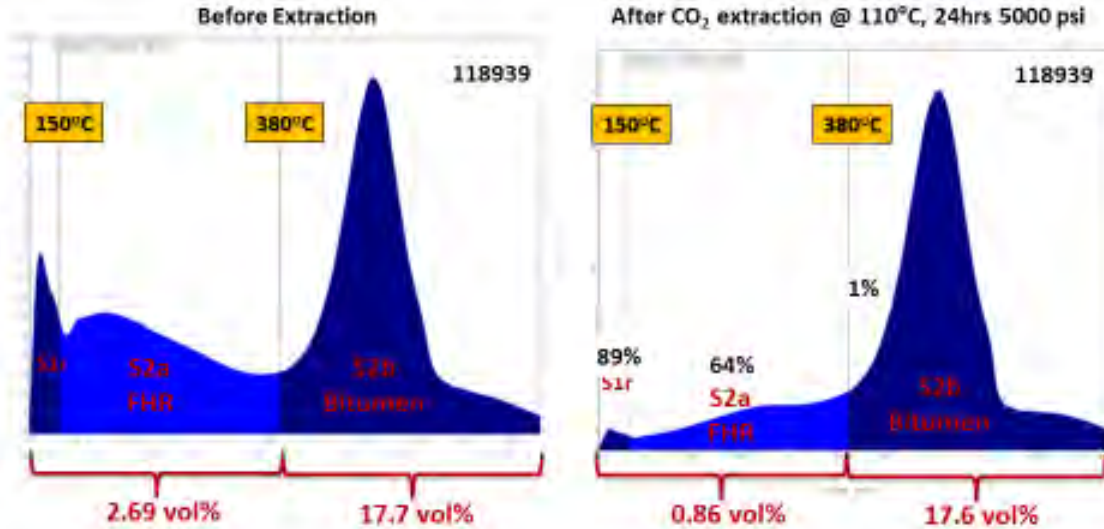
C22 (docosanes) recovery is not affected by propane pressure as much as ethane, but ethane recoveries at 5000 psi are the best. (LBS, well 28440)



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

Similar to their abilities to mobilize hydrocarbons into the “miscible” phase, propane is pretty effective at all pressures, ethane is most effective at higher pressures, and methane is much less effective at any pressure.

## Upper Bakken



Rock-Eval data (ESH cycle)

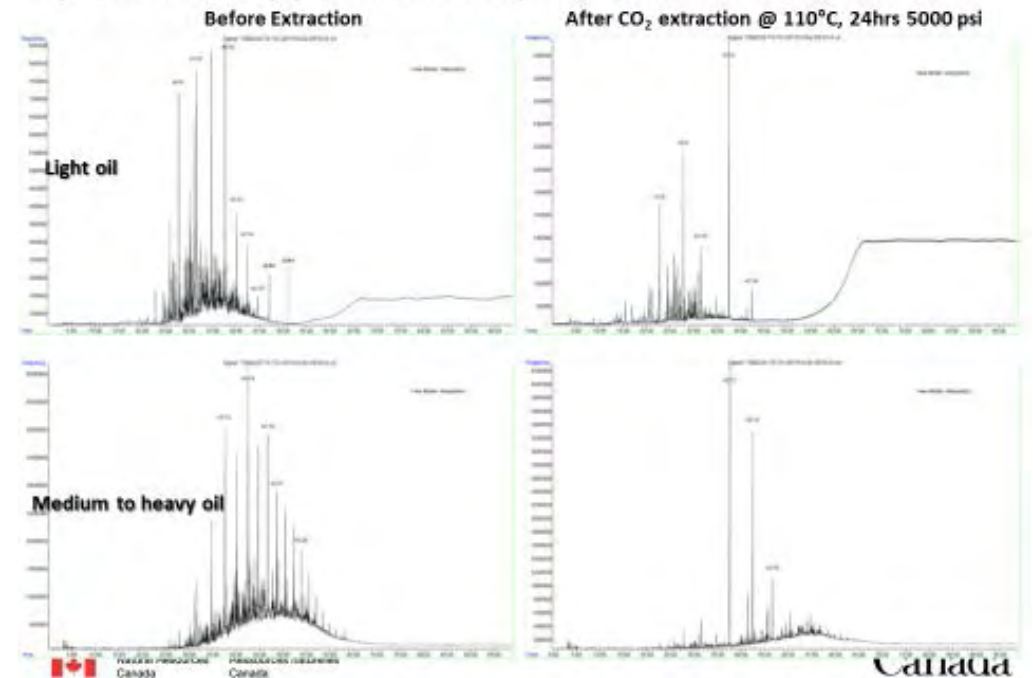


Canada

These techniques are being used to study shales extracted by C1, C2, and C3 at 1500 to 5000 psi.

Natural Resources Canada's extended heating rock-eval (ESH) and pyrolysis GC/MS support EERC's rock extraction results with CO<sub>2</sub>.

## Py-GC-MS, Upper Bakken (118939)





## In progress: Ternary mixtures of methane/ethane/propane.

- Perform “miscible” phase sampling and rock extractions with typical Bakken produced gas: mole ratio of 70/20/10 for C1/C2/C3.
- Additional “richer” mixtures planned (MMP work in progress, rock extractions planned).
- “Hail Mary” goal is to obtain sufficient mixed fluid data to support models that can estimate:
  1. MMP using mixed gases
  2. Mixed gases’ ability to solvate hydrocarbons into the “miscible” phase.
  3. Mixed gases’ ability to extract hydrocarbons from rock cores.

***And apply these insights to the Bakken reservoir!!***

## What should we also be doing?

- Determine sorption isotherms for C1/C2/C3 (and mixtures) in Bakken shales and Middle Bakken (Utilization factor? Storage capacity? Oil desorption mechanisms?).
- Better understand matrix hydrocarbon/rich gas component interaction(s) and subsequent oil production mechanisms. (Including ESH rock-eval, pyrolysis GC/MS with Natural Resources Canada.)
- Perform volumetric swelling studies. (The next big recovery mechanism may be based on oil swelling, and perhaps not so much on hydrocarbon extraction.)
- Develop predictive models on mixed fluid behavior (e.g., MMP) based on experimental results.

## Summary:

### How do methane, ethane, and propane compare as EOR fluids?

*(In short, the richer the gas the more oil can be produced!)*

- MMP, “miscible” phase sampling, and rock extractions all agree that:
  - 1. Propane and ethane are both MUCH more effective than methane at lowering MMP, dissolving hydrocarbons, and extracting oil from Bakken rocks.
  - 2. Methane doesn’t do anything well.
  - 3. Propane doesn’t care much about pressure (above 1500 psi), but ethane needs higher pressures.
  - 4. Propane and ethane are effective at mobilizing heavier hydrocarbons.
  - 5. Mixed C1/C2/C3 lowers MMP more than expected based on their pure fluid MMPs.

# CONTACT INFORMATION

## **Energy & Environmental Research Center**

University of North Dakota  
15 North 23rd Street, Stop 9018  
Grand Forks, ND 58202-9018

**[www.undeerc.org](http://www.undeerc.org)**

701.777.5256 (phone)

701.777.5181 (fax)

**Steven Hawthorne, Ph.D.**  
**Principal Research Chemist**  
shawthorne@undeerc.org

