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Laboratory Studies of Rich Gas Interactions with Bakken Crude Oil to Support Enhanced Oil Recovery

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Abstract

Primary recovery factors for Bakken wells are typically less than 10%, and there is a need for enhanced oil recovery (EOR). Reduction of rich gas flaring from the Bakken is also a high priority, suggesting that there may be an opportunity to use rich gas as a working fluid for EOR. However, the fundamental mechanisms controlling rich gas interactions with the Bakken reservoir fluids are not well understood. In particular, different pressures and rich gas mixtures (i.e., ratios of methane, ethane, and propane) may affect the fluid phase behavior of oil and rich gas as measured by minimum miscibility pressure (MMP) as well as by changing the solvent strength of the injected fluid for oil hydrocarbons. Lab studies are being conducted to determine the effect of different rich gases on their potential to enhance Bakken crude oil recovery. These include measuring the MMP of Bakken crude oil with different candidate gas injectants and measuring the hydrocarbon composition in the “miscible” phase generated by crude oil/injectant exposures.

MMP values were measured for pure ethane, methane, and propane and are now being measured with different combinations of those gases including stable ternary methane–ethane–propane mixtures. MMPs are measured using a modified capillary rise/vanishing interfacial tension technique. Experiments to determine the effects of rich gas fluid composition and pressure on the mobilization of hydrocarbons from Bakken crude oil are also being conducted with different gases, gas mixtures, and pressures. These studies show that true chemical miscibility (single phase in all proportions of crude oil and injectant) between injected fluids and crude oil is not attained under reservoir-relevant temperature and pressure conditions, but rather the fluids exist in two phases including a lower crude oil-dominated phase in equilibrium with an upper, injectant gas-dominated phase. Different fluids and pressures change the compositions of mobilized hydrocarbons in the rich gas-dominated upper phase and the bulk crude oil-dominated lower phase, and are being determined by collecting and analyzing the gas-dominated phase at equilibrium with the bulk crude oil.

The results show that, in terms of MMP, propane is superior to ethane, and both fluids are much better than methane. For rich gas mixtures, it is expected that the richer the gas, the lower the MMP. Based on the ability to solvate crude oil hydrocarbons into the mobile “miscible” phase, propane is the most

efficient at 3000 psi, ethane is next, and methane is much poorer. The same trends occur for their abilities to solvate higher-molecular-weight hydrocarbons. Molar densities of the different fluids indicate that higher pressures may increase their effectiveness, especially of ethane, and these experiments are currently being conducted. These data sets will support industry in their determination of the most effective rich gas compositions and operating conditions for EOR.

Introduction

As of January, 2019, oil production from the Bakken Petroleum System in the Williston Basin exceeded 1.4 million barrels per day (NDIC, 2019), despite primary recovery factors of only 6 to 10% for a typical well (LeFever and Helms 2008, Nording and Helms 2010). Since the reservoir is estimated to have 4.5 to 20 billion barrels of recoverable oil (U.S. Energy Information Administration 2013, Flannery and Kraus 2006), even small increases in recoveries would yield significant quantities of crude oil.

While enhanced oil recovery (EOR) using CO₂ has been employed for decades in conventional reservoirs, the use of CO₂ for EOR projects in unconventional plays like the Bakken may be limited by insufficient economically-viable supplies of CO₂ (Kuuskraa and Wallace 2014, Azzolina et al 2016). In addition, because tight shale plays like the Bakken often produce gas that is too rich for pipeline-quality natural gas (McGuire et al. 2016), there is increasing interest in using rich gas hydrocarbons for EOR as well as to reduce CO₂ emissions from rich gas flaring (Sibbald et al. 1991, Zick 1986, Chang et al. 1993). Despite this interest, there are few experimental studies and results available to support the development of EOR projects with rich gas hydrocarbons. Therefore, the purpose of the present study is to investigate the abilities of methane, ethane, propane, and produced gas mixtures for attaining MMP with Bakken crude oil, and also to determine their abilities to solvate crude oil hydrocarbons (both in terms of total oil dissolved, as well as the molecular weight distribution of the hydrocarbons) in the injectant gas-dominated phase.

Methods

MMPs were determined using a vanishing interfacial/capillary rise technique described in detail in (Hawthorne et al. 2016). In brief, 3 mL of a typical Bakken crude oil was placed into a high-pressure view cell which had previously been purged with the test fluid. The cell contained three glass capillaries having different diameters with their bottom ends suspended in the crude oil as shown in Figure 1.

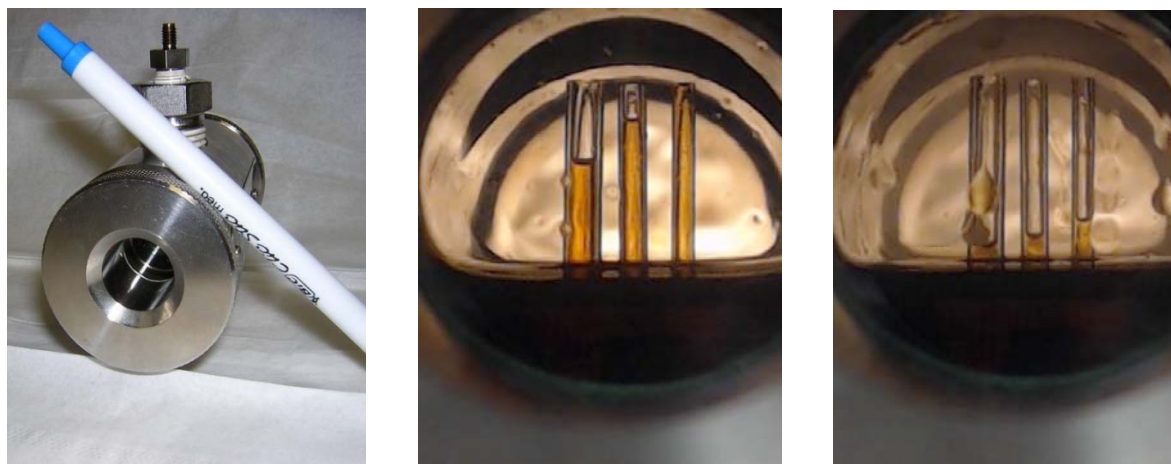


Figure 1. High pressure view cell used for the MMP determinations (left). The center photo shows the pool of Bakken crude oil in the bottom of the cell, and the height of the oil in the three capillaries at the initial low pressure of ethane. (Capillary inner diameters from left to right are 1.12, 0.84, and 0.68 mm.) The photo on the right shows the oil height in each capillary as the ethane pressure is raised and the interfacial tension between the ethane injectant and the bulk crude oil approaches zero near the MMP.

The view cell and oil were heated to 110 °C in a gas chromatographic oven which had been modified to have a view window in the oven door. The cell was heated to 110 °C for one hour, then the pressure of the test gas in the cell was increased in ca. 50 psi increments until the height of the oil in the three capillaries approached zero (i.e., approached zero interfacial tension between the gas and oil phases). A plot of the oil height in each capillary versus the injectant gas pressure was extrapolated to zero height, with the intercept on the pressure axis being the MMP (Figure 2) (Hawthorne et al. 2016).

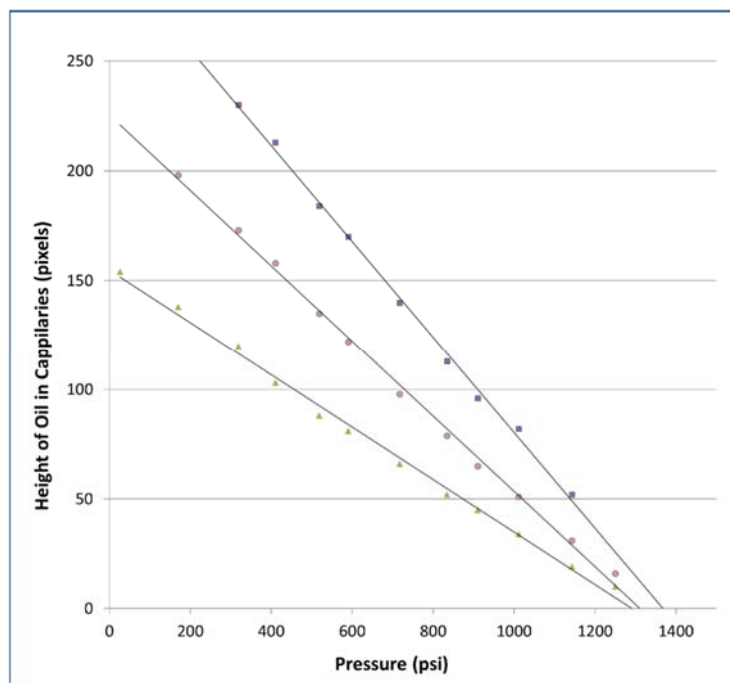


Figure 2. Plot of oil height versus different pressures of injected ethane for the three different capillary diameters shown in Figure 1. The MMP with ethane for this trial was 1323 +/- 40 based on the extrapolation of the three capillaries' oil heights to zero.

The method for collecting and analyzing the crude oil hydrocarbons was recently developed and applied to determine the abilities of methane, ethane, and CO₂ to dissolve hydrocarbons by coming to equilibrium at reservoir temperature with a crude oil from a conventional sandstone reservoir. Details of the method are given in (Hawthorne and Miller 2019). In brief, a high-pressure view cell was adapted to contain a 10-mL reservoir for the crude oil (Figure 3). The view cell was then heated to 110 °C for one hour, followed by slowly adding the test gas via the bottom of the oil reservoir so that the gas had to contact the 10-mL oil sample before reaching the gas-dominated upper phase (top of the cell in Figure 3). The oil/gas mixture was left to come to equilibrium, and the upper phase hydrocarbons were “sipped” through the tube inserted into the upper phase via a heated flow restrictor which allowed the gas phase and its dissolved hydrocarbons to percolate through 15 mL of methylene chloride. (Note that the pressure and temperature were maintained at the test conditions during the equilibration time and the sampling time so that any pressure/temperature changes during equilibration and sample collection were infinitesimal.) After each ca. 5-mL sample was collected, the remaining oil was left to equilibrate with fresh injectant gas for an additional hour before the next fraction was collected. Octadecylbenzene was added to each fraction as an internal standard, and each extract was analyzed by high-resolution gas chromatography coupled with a flame ionization detector (GC/FID) (Hawthorne and Miller 2019).

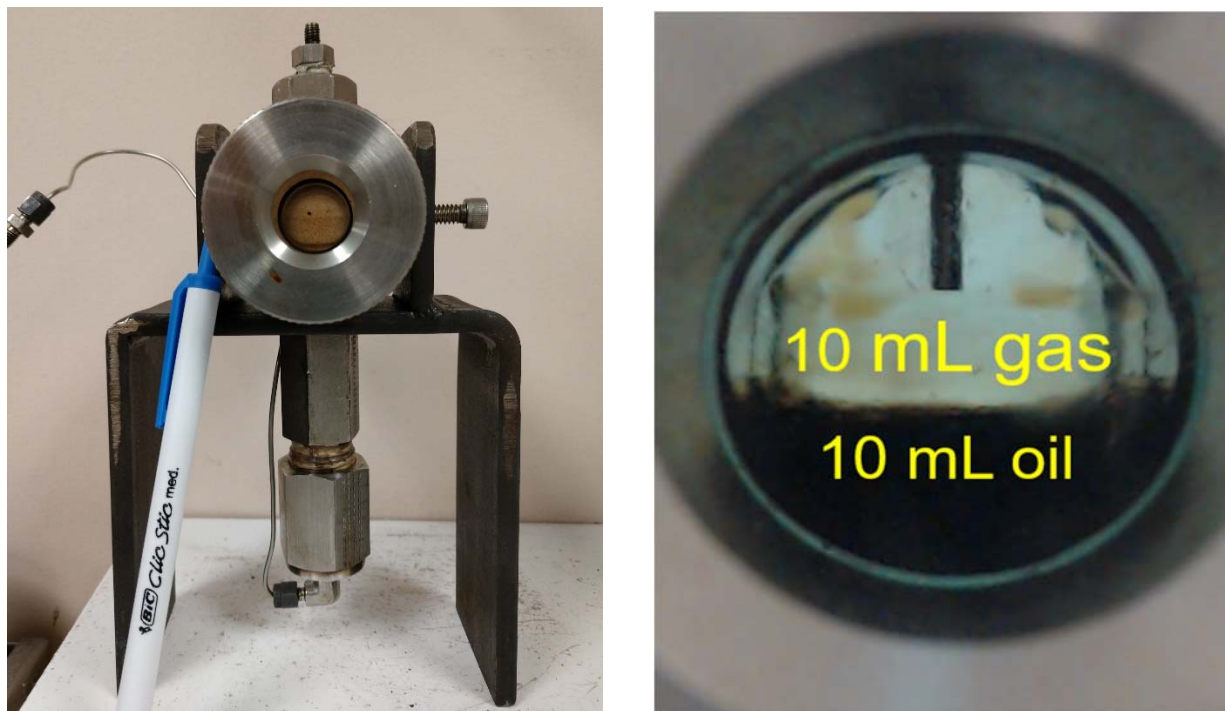


Figure 3. High pressure view cell (left) modified to include a 10-mL oil reservoir that allows the injectant gas to be introduced at the bottom so that it percolates through the 10-mL oil column. The photo on the right shows the sampling tube which is used to “sip” off the upper gas-dominated phase. During the sampling procedure the gas inlet to the cell is left open to the ISCO 260D syringe pump operated in the constant pressure mode so that there is no significant pressure change in the cell at any time in the experiment.

Results

A comparison of the MMP values for a typical Bakken crude oil (API 38.7) are shown in Figure 4, which shows dramatic differences in the ability of the three light hydrocarbons to attain MMP. Methane required 4516 psi for MMP, while ethane only required 1323 psi, and propane only required 552 psi, results that clearly demonstrate that if produced gas is used for EOR, the richer the gas, the more effective it should be. It is also interesting to note that the MMP for the same crude oil using CO₂ was reported to be about 2540 psi (Hawthorne et al. 2016). Thus, CO₂ only requires about one-half the pressure to attain MMP than methane, while ethane requires about one-half the pressure of CO₂, and propane requires about one-half the pressure of ethane.

The same Bakken crude oil was used to determine the ability of three gases to dissolve crude oil hydrocarbons via vaporization gas drive as described above and in (Hawthorne and Miller, 2019). Figure 5 compares the total hydrocarbon concentrations in the gas-dominated upper phase for 4 or 5 sequential exposures of the 10-mL oil sample. Similar to the MMP results, both ethane and propane are far superior to methane, and propane is superior to ethane. Figure 5 also shows declining concentrations of oil with each subsequent exposure with ethane and propane, which is consistent with liquid/liquid partitioning rather than saturation solubility as the mechanism that determines the concentration of oil hydrocarbons in each collected fraction. For example, the first propane fraction dissolved about 17% of the 10-mL oil sample, the second fraction dissolved about 17% of the remaining ca. 8.3 mL of oil, and so on for each subsequent fraction. (See reference (Hawthorne and Miller 2019) for a detailed explanation of the liquid/liquid partitioning mechanism.)

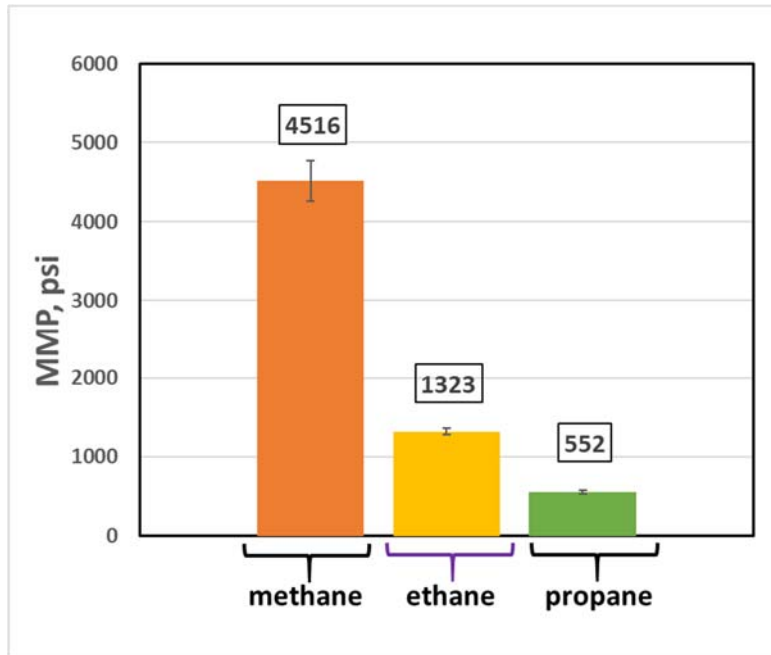


Figure 4. MMP values for a typical Bakken crude oil using pure methane, ethane, and propane. The error bars (one standard deviation) are derived from the MMP values from the three different-diameter capillaries used in each experiment.

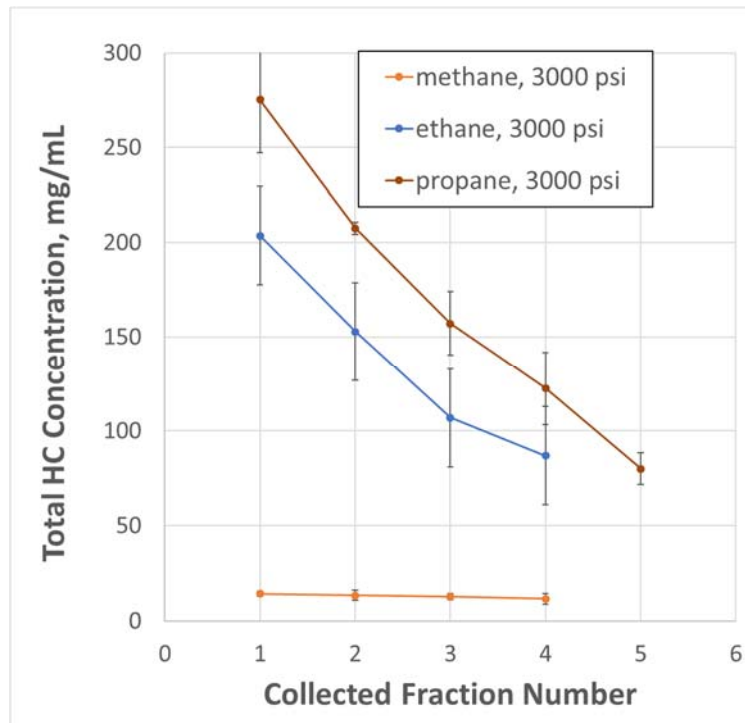


Figure 5. Total crude oil hydrocarbons mobilized into the upper gas-dominated phase via vaporization gas drive with methane, ethane, and propane at 3000 psi. The error bars represent one standard deviation based on triplicate experiments with each fluid.

In addition to solvating much less oil, methane only dissolves the lightest hydrocarbons as shown in Figure 6, while the hydrocarbons mobilized by both ethane and propane show essentially the same molecular weight distribution as the original crude oil.

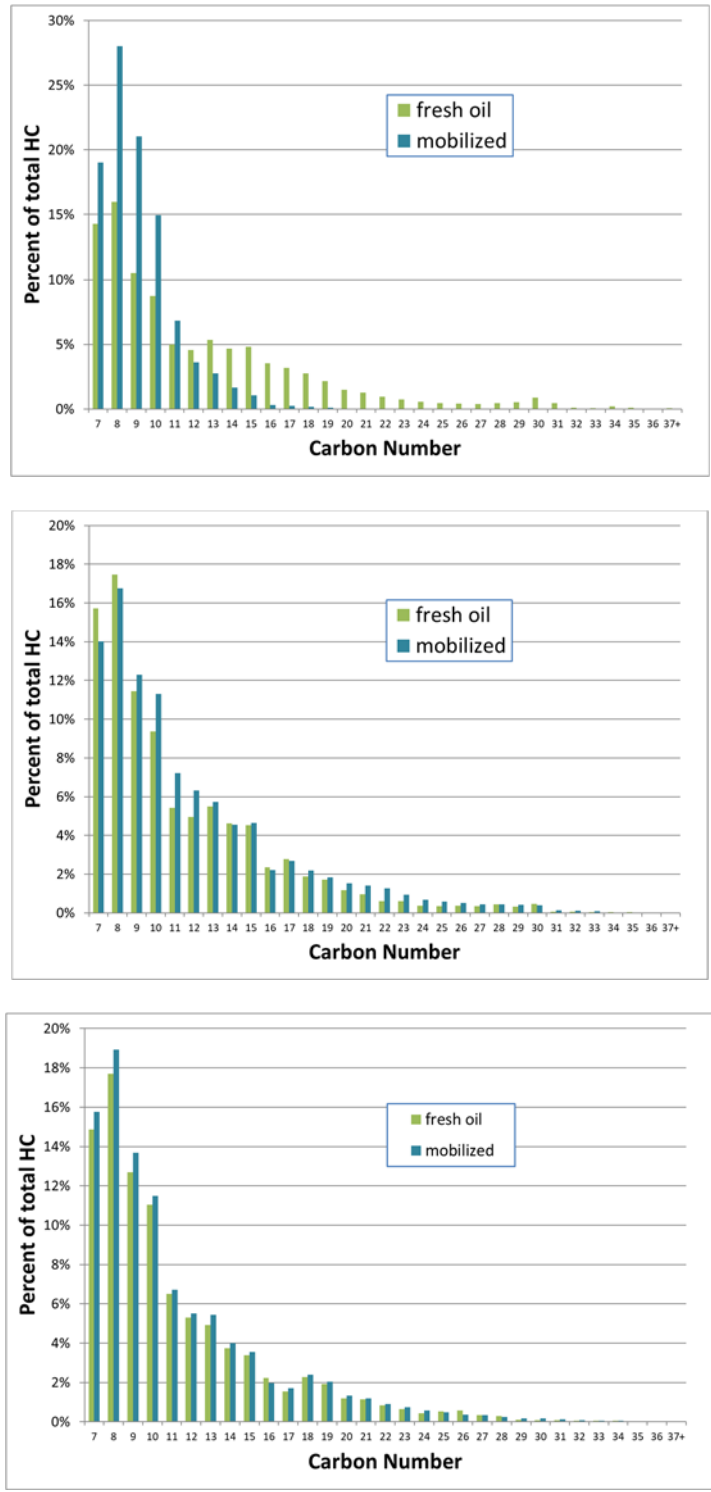


Figure 6. Comparison of the hydrocarbon molecular size (carbon number) mobilized by methane (top), ethane (middle), and propane (bottom) at 3000 psi and 110 °C.

Discussion

The MMP results shown in Figure 4 clearly show that the use of relatively high concentrations of ethane and/or propane in injectant gas should be much more effective for attaining MMP at lower pressures than gases rich in methane. While different mechanisms (other than achieving miscible flood conditions as for a conventional permeable reservoir) may control oil recovery in tight-fractured unconventional reservoirs (Hawthorne et al. 2013), these MMP results do indicate that richer gases should be more effective EOR fluids than leaner gases.

The comparisons of the three fluids to mobilize crude oil hydrocarbons via vaporization gas drive at 3000 psi (110 °C) also show the same trend as MMP, i.e., propane is superior to ethane, and both are far superior to methane. Methane is very poor at dissolving mid- and high-molecular weight hydrocarbons, and nearly all of the total oil dissolved by the methane consists of dodecanes (C12) and smaller, which is likely to result in the deposition of the middle- and heavier-molecular weight hydrocarbons. In contrast, the hydrocarbons dissolved by both ethane and propane show essentially the same molecular weight distributions as the original oil. Thus, as was the case for MMP, these results indicate that richer gases will be more effective for mobilizing heavier hydrocarbons (and causing less deposition) than leaner gases.

Although ethane is not as effective as propane in these lab studies, its use as a relatively pure EOR fluid may be reasonable in some shale plays because the rich gas produced from these plays have high concentrations of low-value ethane that needs to be removed (along with higher-value propane) to produce pipeline-quality gas (McGuire et al. 2016).

Conclusions

The results of these laboratory studies clearly indicate that richer gases will be more effective than leaner gases for EOR, whether EOR is being performed in conventional or unconventional tight-fractured reservoirs. The additional studies needed to determine the effectiveness of different produced gas compositions at different pressures are currently being conducted.

Acknowledgements

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References

- Azzolina, N.A., Peck, W.D., Hamling, J.A., Gorecki, C.D., Ayash, S.C., Doll, T.E., et al. 2016. How Green is My Oil? A Detailed Look at Greenhouse Gas Accounting for CO₂-Enhanced Oil Recovery (CO₂-EOR) Sites. *Int'l. J. Greenhouse Gas Control* **51**:369-379.
- Chang, H.L., Lo, T.S., Ring, W.W. 1993. The Effects of Injectant-Enrichment Level on Oil Recovery in Horizontal, Gravity-Tongue-Dominated Enriched-Gas Drives. Presented at the 1993 SPE Western Regional Meeting, Anchorage, AK, May 26-28. SPE 26084.

- Flannery, J., Kraus, J. 2006. *Integrated Analysis of the Bakken Petroleum System*. American Association of Petroleum Geologists Search and Discovery; article no. 10105.
- Hawthorne, S.B., Gorecki, C.D., Sorensen, J.A., Steadman, E.N., Harju, J.A., Melzer, S. 2013. Hydrocarbon Mobilization Mechanisms from Upper, Middle, and Lower Bakken Reservoir Rocks Exposed to CO₂; In *Unconventional Resources Conference*; Society of Petroleum Engineers: Calgary, AB, Canada, Nov. 5-7. DOI: 10.2118/167200-MS.
- Hawthorne, S.B. and Miller, D.J. 2019. A Comparison of Crude Oil Hydrocarbon Mobilization by Vaporization Gas Drive into Methane, Ethane, and Carbon Dioxide at 15.6 MPa and 42 °C. *Fuel* **249**:392-399. <https://doi.org/10.1016/j.fuel.2019.03.118>.
- Hawthorne, S.B., Miller, D.J., Jin, L., Gorecki, C.D. 2016. Rapid and Simple Capillary-Rise/Vanishing Interfacial Tension Method to determine Crude Oil Minimum Miscibility Pressure: Pure and Mixed CO₂, Methane, and Ethane. *Energy Fuels* **30** (8):6365-6372.
- Kuuskräa, V. and Wallace, M. 2014. CO₂-EOR Set For Growth as New CO₂ Supplies Emerge. *Oil Gas J* 92-105.
- LeFever J.A., Helms L.D. 2008. Bakken Formation Reserve Estimates. North Dakota Geological Survey White Paper, Bismarck, North Dakota: North Dakota Geological Survey; p 6.
- McGuire, P.L., Okuno, R., Gould, T.L., Lake, L.W. 2016. Ethane-Based EOR: An Innovative and Profitable EOR Opportunity for a Low Price Environmental. Presented at the SPE Improved Oil Recovery Conference, Tulsa, OK, April 11-13. SPE-179565.
- Nordeng, S.H., Helms, L.D. 2010. Bakken Source System – Three Forks Formation Assessment: North Dakota Dept. Mineral Resources, p 22.
- North Dakota Industrial Commission (NDIC) website accessed April 26, 2019. <https://www.dmr.nd.gov/oilgas/mprindex.asp>
- Sibbald, L.R., Novosad, Z., Costain, T.G. 1991. Methodology for the Specification of Solvent Blends for Miscible Enriched-Gas Drives. *SPE Res. Eng.* August, 373-404.
- U.S. Energy Information Administration. 2013. Technically Recoverable Shale Oil and Shale Gas Resources – An Assessment of 137 Shale Formations in 41 Countries outside the United States: U.S. Department of Energy; Washington, DC. www.eia.gov/analysis/studies/worldshalegas/pdf/fullreport.pdf (accessed 2013).
- Zick, A.A. 1986. A Combined Condensing/Vaporizing Mechanism in the Displacement of Oil by Enriched Gases. Presented at the SPE Annual Technical Conference and Exhibition, New Orleans, Oct. 5-8. SPE-15493.