URTeC: 2671596

Extraction of Oil from the Bakken Shales with Supercritical CO_2

Lu Jin, Steven Hawthorne, James Sorensen,* Lawrence Pekot,
Bethany Kurz, Steven Smith, Loreal Heebink, Nicholas Bosshart, José Torres,
Chantsalmaa Dalkhaa, Charles Gorecki, Edward Steadman, John Harju
Energy & Environmental Research Center, Grand Forks, ND, United States.

This paper was prepared for presentation at the Unconventional Resources Technology Conference held in Austin, Texas, USA, 24-26 July 2017.

Abstract

The Bakken petroleum system is one of the largest unconventional plays in the United States, with over 10,000 wells drilled in the past 10 years. The main target of this drilling has been two of the non-shale low-permeability units: the Middle Bakken Member and the Three Forks Formation. Although well logs and core data show that there is significant oil content in the two shale members—the Upper and Lower Bakken, the oil transport behavior in these source rocks is still not well understood.

The Energy & Environmental Research Center (EERC) conducted a series of experiments to investigate the rock properties of the two shale members, how fluids flow through them, and how flow may be induced. Twenty shale cores were collected (eight Upper Bakken samples and twelve Lower Bakken samples) from six wells in three North Dakota counties to ensure the samples were representative of the shales in the most productive areas of the Bakken. Six primary mineralogical components were detected in the samples through x-ray diffraction (XRD) analysis. High-pressure mercury injection tests showed that pore throat radii are less than 10 nanometers for most pores in both the Upper and Lower Bakken samples. Such small pore sizes yield high capillary pressure in the rock and make fluid flow difficult. Total organic carbon (TOC) content was measured, and kerogen was characterized by Rock-Eval/TOC pyrolysis, which indicated considerable TOC present (10–15 wt%) in the shales. However, oil and gas are difficult to mobilize from organic matter using conventional methods.

Field experience has shown that hydrocarbon extraction with supercritical CO_2 is effective for extracting hydrocarbons (up to C20+) from conventional reservoirs. Additionally, laboratory experiments indicated that supercritical CO_2 interacts with the oil associated with the organics, solvating the oil so that it can be extracted at reservoir temperature and pressure. A systematic experimental procedure was carried out to reveal the potential for extracting hydrocarbons from the shale samples under typical Bakken reservoir conditions (e.g., 5000 psi and 230°F). Results from 20 samples showed that supercritical CO_2 enables extraction of a considerable portion (15%–65%) of the hydrocarbons from the Bakken shales within 24 hours. The results may be used to improve modeling and forecasting the effects of CO_2 enhanced oil recovery (EOR) and suggest the possibility for increasing ultimate recovery, and possibly CO_2 storage, in some areas of the Bakken Formation.

Introduction

In the last decade, the boom of unconventional resource development has been a great success for the American oil industry. Several giant unconventional plays, including the Bakken, Eagle Ford, and Niobrara, etc., have dramatically increased oil production in the United States.[1-5] Horizontal drilling and multistage hydraulic fracturing technologies make it profitable to unlock oil and gas from the extremely tight rocks. Horizontal wells are typically around 10,000 feet long with 20 to 40 hydraulic fracture stages per well. In the Bakken alone, over 10,000 wells have been drilled in the past 10 years, which have produced more than 1 billion barrels (bbl) of oil and positioned North Dakota as the second-largest oil producer in the United States.[6-10] The Bakken petroleum system (BPS) has four units with moderate to high oil saturation: the Upper Bakken, Middle Bakken, and Lower Bakken Members and the Three Forks Formation. Currently, most of the producing wells in the BPS are completed in the two tight non-shale units, i.e., Middle Bakken and Three Forks, which have average porosities of 4%–8% and permeability in microdarcy levels.[8-9,11-14] The reservoirs in Middle Bakken and Three Forks are tight but naturally fractured, which makes oil production respond exceptionally well to long laterals and multistage fracture stimulation. Since horizontal wells have a large drainage area and the Bakken oil is generally light, with around 40% of light components (C1–C4) in the reservoir oil, gas expansion provides the main energy for the current production (primary depletion) stage.[6,10-15] However, gas–oil ratios have increased, and water cuts have been rising in many wells in recent years, which indicate pressure depletion in the two non-shale units. The depletion may impact well performance as well as ultimate oil recovery in the reservoirs. Figure 1 shows the number of producing wells and oil production performance in the BPS. It is clear that more producing wells do not yield higher oil production rate after 2015.[15] According to the key research institutes and major operators in the Bakken Formation, the estimated recovery factors of the BPS range from 3% to 10% and from 15% to 20% for some of the best areas of the play.[8-15] Such estimates of recovery factor are considered very low compared to that observed in conventional oil reservoirs, where oil recovery factors usually range from 30% to 50%.[16-24] Therefore, new drilling targets and producing technologies become important to prevent rapid production decline and improve oil recovery in the BPS.[25-28]

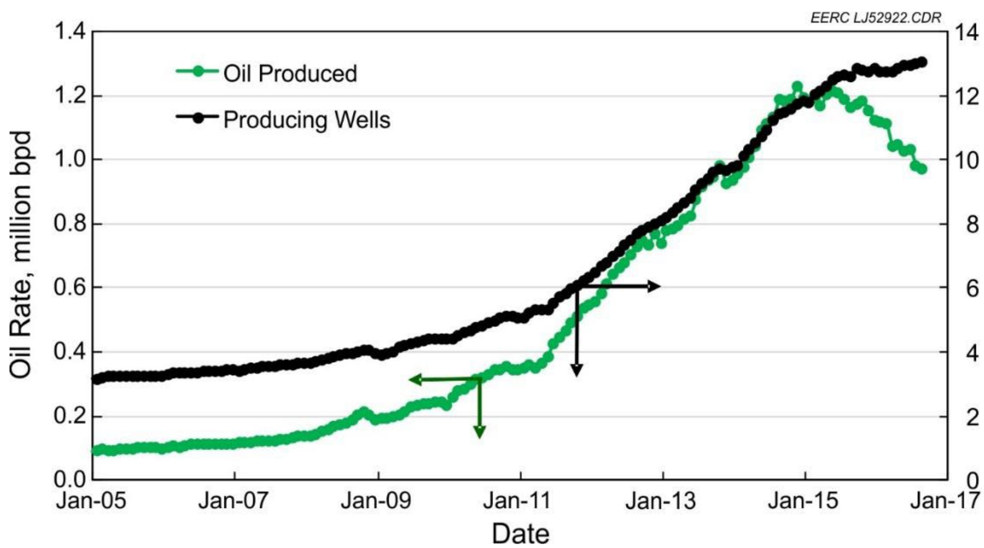

Figure 1. Oil production performance in the Bakken.

The Upper and Lower Bakken units are organic-rich shales, which are considered to be world-class source rocks in the Williston Basin and are sourcing reservoirs in the BPS. It is estimated that 10 billion to 400 billion bbl of oil has been generated from these shale units, charging both unconventional and conventional plays in the basin.[29-33] Although these shale units are not currently the main targets for drilling in the Bakken, production experience in other unconventional plays has shown that oil could also be produced from the shales and the production could be profitable.[5,16,30] For instance, the Eagle Ford shale formation is the source rock for both sandstone (Woodbine) and carbonate (Austin and Buda) hydrocarbon reservoirs in Texas. Recent production activities in the Eagle Ford unconventional play have demonstrated that the source rock is able to produce significant volumes of gas and oil.[34] Studies also showed that supercritical CO_2 could effectively extract oil from organic-rich shales in complex matrices, even when the oil is trapped in the tiny pore space and flow in the reservoir is difficult under original conditions. [6,10,25-26,35-36]

To better understand the shale properties in the Bakken and further evaluate the oil production potential of the BPS, the Bakken shale units were characterized, and supercritical CO_2 was used to extract oil from the shale samples in this study.

Rock and Fluid Distribution in the Formation

Oil produced from the Middle Bakken and Three Forks is sourced from the Upper and/or Lower Bakken members, respectively. The two shale members can be easily identified from well logs and core samples, and these shales are usually used to create a subsurface correlation within the basin.[33,37] Figure 2 shows typical logs recorded from a well in the Bakken. The high gamma ray readings in the Upper and Lower Bakken Members indicate the high shale content, while the high values of resistivity indicate there may be considerable clay content and hydrocarbon saturation in these intervals. Core samples and drill cuttings show that both Upper and Lower Bakken Members consist of laminated, brown to blacks marine shale. Many samples contain open fractures and some filled ptygmatic fractures, as well as pyrite features, which have been observed in field emission scanning electron microscopy (FESEM) images, as shown in Figure 3.[37-40] Compared to the shale members, the Middle Bakken and Three Forks have low readings of gamma ray and resistivity. The minerals are highly variable and consist of an interbedded sequence of siltstones, sandstones, and limestones rich in silt and sand, etc., as shown in Figure 4. Figure 4 also includes an FESEM image showing clay particles in microfractures. Natural fractures ranging from nano- to macrometer scale have commonly been found in the Middle Bakken and Three Forks units.[6,26]

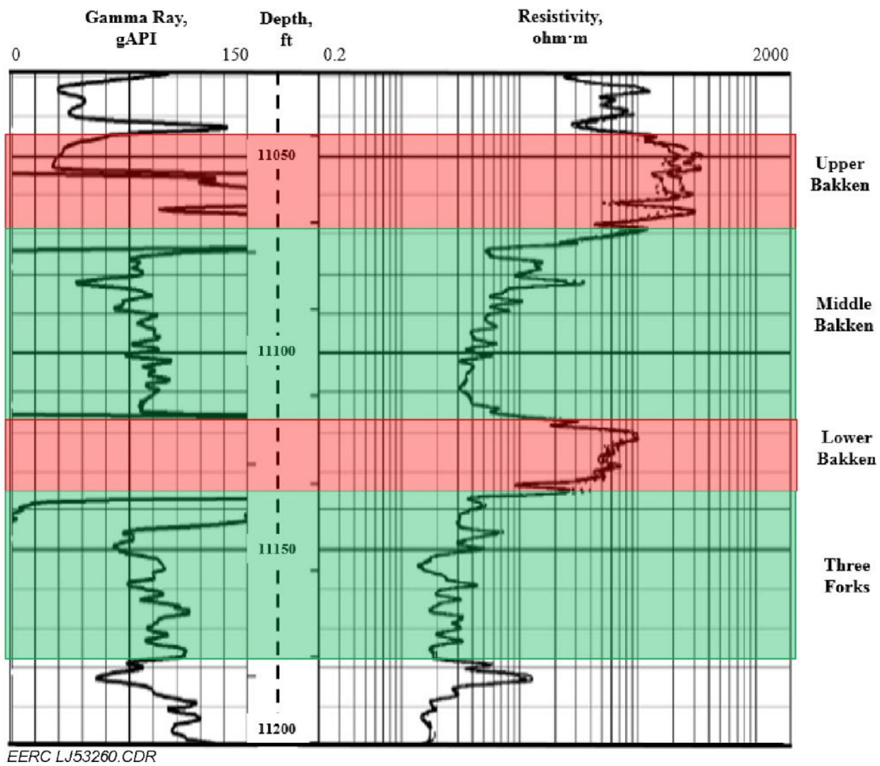

Figure 2. Typical gamma ray and resistivity logs showing the division of units in the BPS.

Oil sampling and analysis have shown that Bakken oil is generally very light, with a high percentage (>50%) of light-medium components (C1–C7) in the oil under reservoir conditions.[13,41-42] Figure 5 shows a typical phase envelope of Bakken oil. The oil is in a liquid state under reservoir conditions where pressure is greater than 3000 psi; however, it separates into liquid and gaseous states when pressure drops. As a result, gas escapes, and only a part of the oil is left in the core when it is brought to the surface. Therefore, the oil saturation in the core samples measured under lab conditions is usually lower than that under reservoir conditions. An alternative way to estimate the in situ hydrocarbon saturation is to measure the water saturation in the rock samples under net confining stress and then calculate hydrocarbon saturation using a volumetric balance equation: $S_h = 1 - S_w$, where S_h and S_w are hydrocarbon and water saturations, respectively.

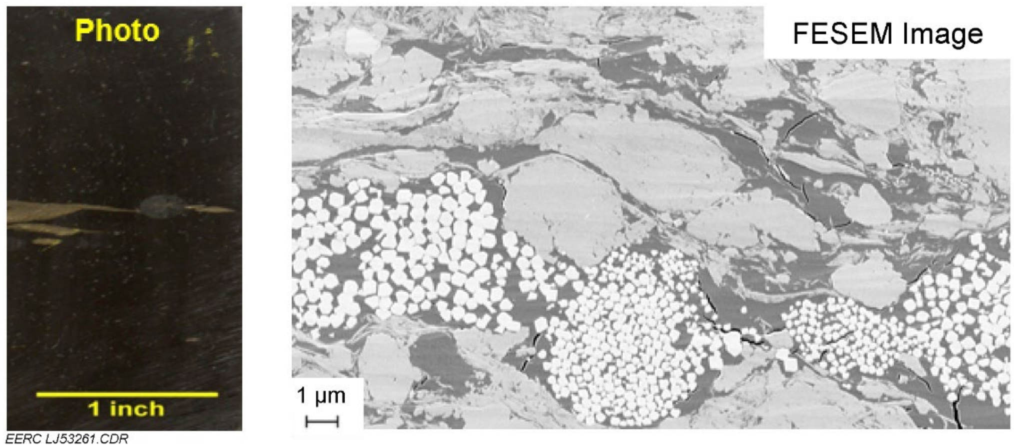

Figure 3. Photo and FESEM image of Bakken shale. White represents pyrite spherules, dark gray represents organic matter, light gray represents mineral grains, and black represents porosity.

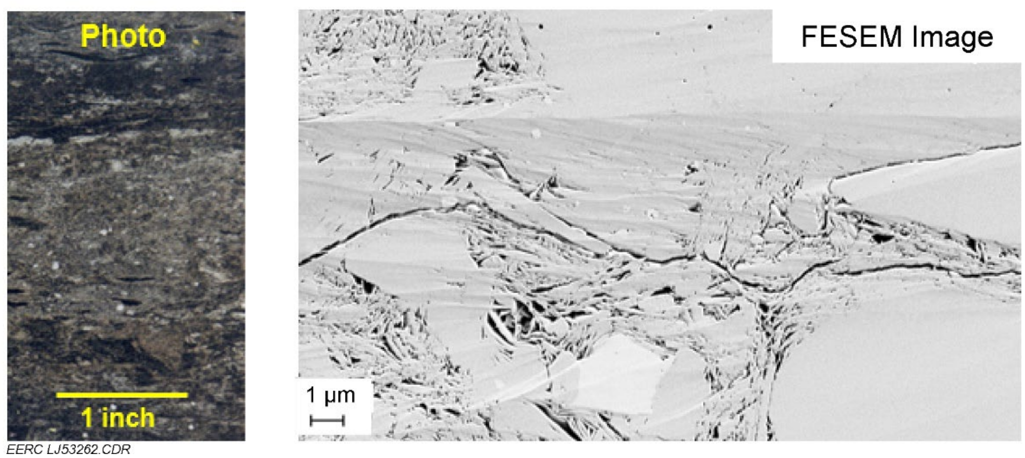

Figure 4. Photo and FESEM image of Middle Bakken rock.

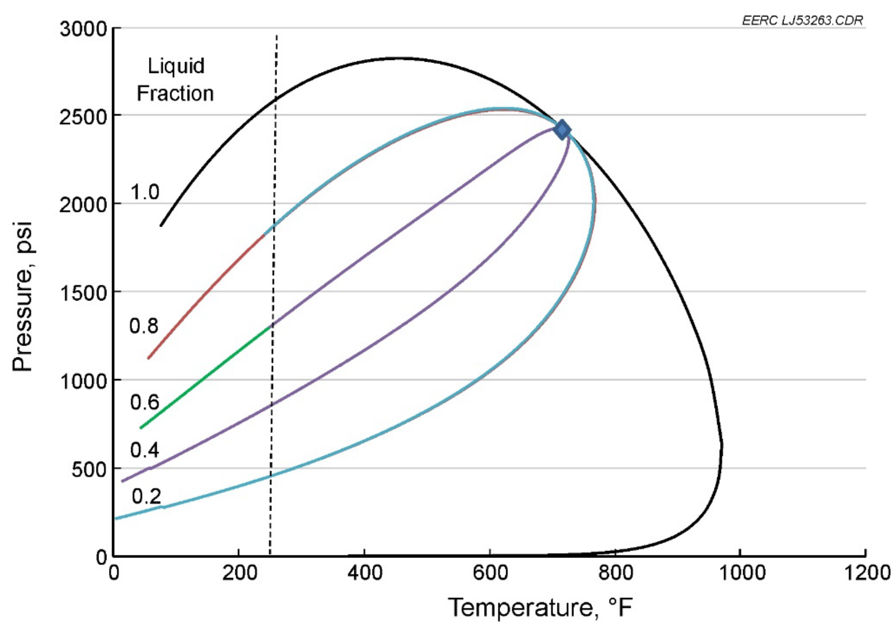

Figure 5. Phase envelope of Bakken oil.

Dozens of rock samples (cores and drill cuttings) were collected from a well (referred to as Well A hereafter) for rock and fluid saturation analysis. The well is located in McKenzie County, North Dakota, which is one of the most productive areas of the BPS. The well is completed with 29 hydraulic fracture stages in the Three Forks Formation, and it has shown good production performance since the well was put into production. Water saturation and TOC content were measured under a net confining stress of 2000 psi. Based on the volumetric balance equation, the hydrocarbon saturation (including both oil and gas) was calculated and is shown on the left side of Figure 6. An evident correlation between hydrocarbon saturation and TOC can be observed from the figure: higher TOC yields greater hydrocarbon saturation in the shale members. Recent studies showed that kerogen is usually oil-wet, and it has a smaller pore throat size than inorganic rocks in the Bakken.[43-44] The small pore throat size induces a larger capillary force, confining oil inside of the pore space.[45-48] Oil adsorption in the shale could also be remarkable because of the strong interaction between alkane molecules and organic materials, together with the widespread nanometer pores in kerogen.[48]

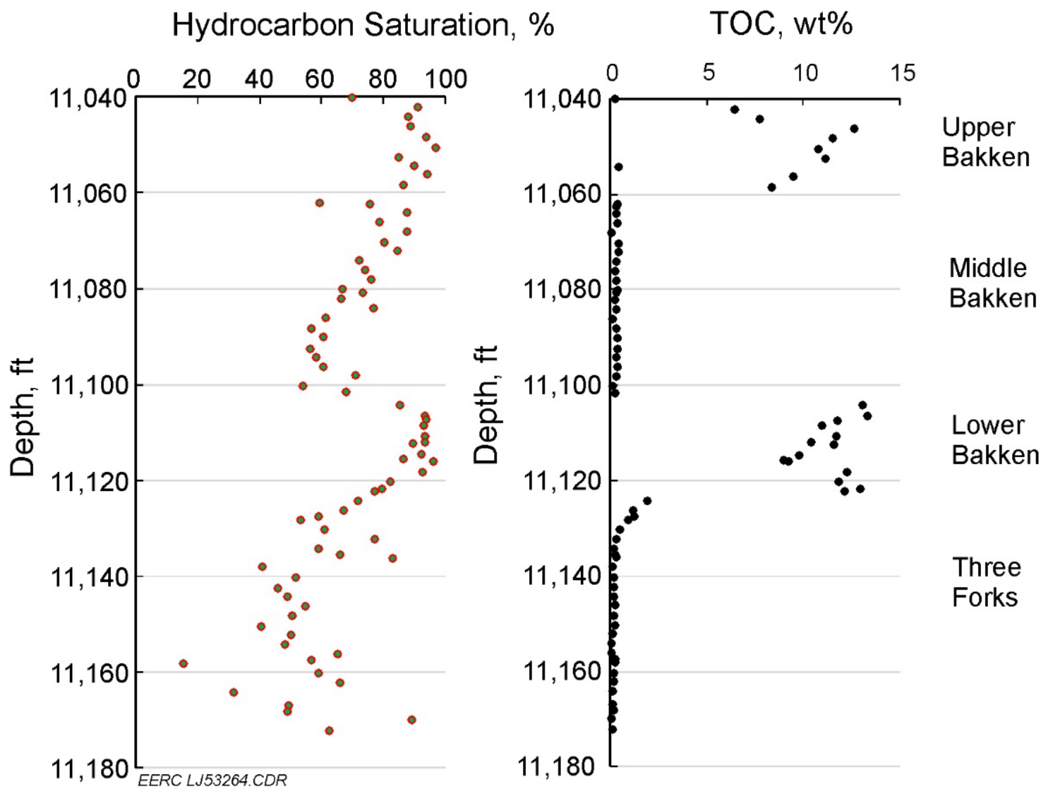

Figure 6. Hydrocarbon saturation and TOC distribution along Well A in the BPS.

Characterization of Bakken Shales

Twenty shale cores were collected—eight Upper Bakken samples and twelve Lower Bakken samples—from six wells in three North Dakota counties (Mckenzie, Mountrail, and Dunn) to ensure the samples were representative of the shales in the most productive areas of the Bakken, as shown in Figure 7. Six primary mineralogical components were detected in the samples through x-ray diffraction (XRD) analysis, as shown in Figure 8. The figure clearly indicates that quartz and illite are the major components in the matrix of Bakken shales; the two minerals account for 67% of total matrix weight. The weight percent of chlorite, dolomite, and pyrite varies from 3% to 6%. Ankerite and albite are found in some samples; however, their contents are less than 2% on average. Other minerals like calcite and rutile are also identified in a few samples, but their weight percent is generally small. High-pressure mercury injection tests showed that pore sizes are less than 10 nanometers (Figure 9) for most pores in both the Upper and Lower Bakken samples, and the mean pore throat radii are around 3.5 nm, as shown in Figure 10. Such small pore sizes yield high capillary pressure in the rock and make fluid flow difficult.[10-11]

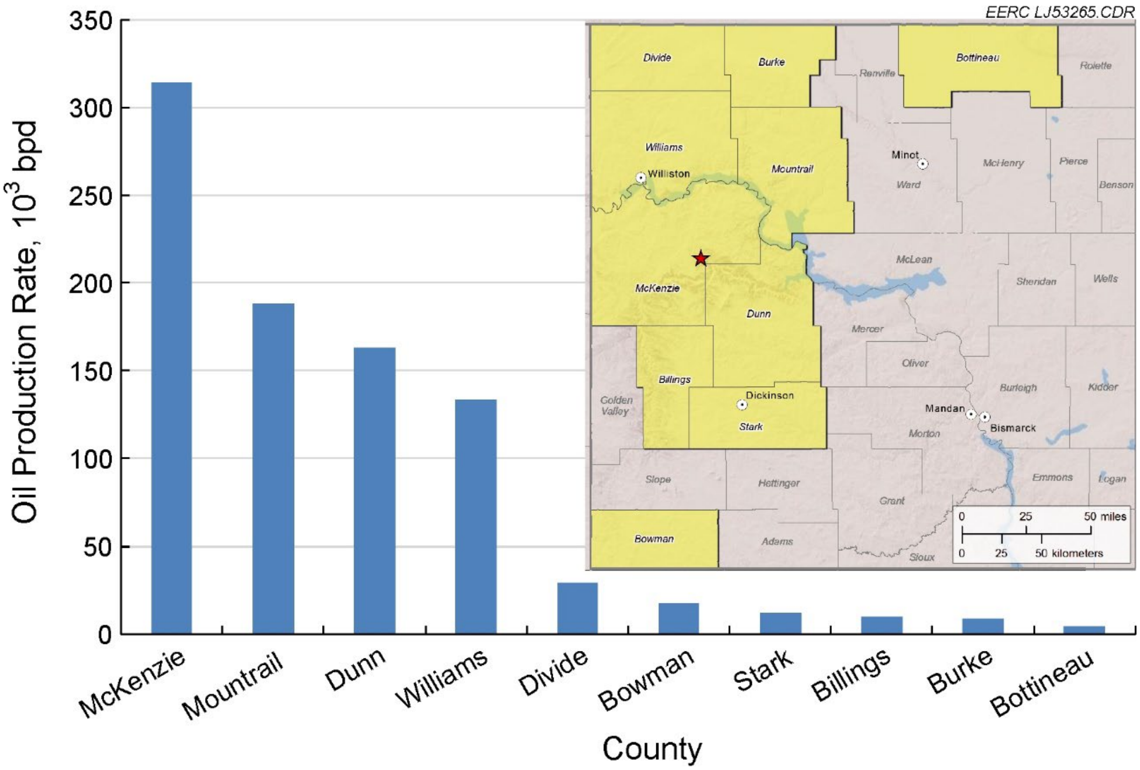

Figure 7. Oil production performance of North Dakota counties (yellow) in the Bakken Formation. Red star denotes Well A.

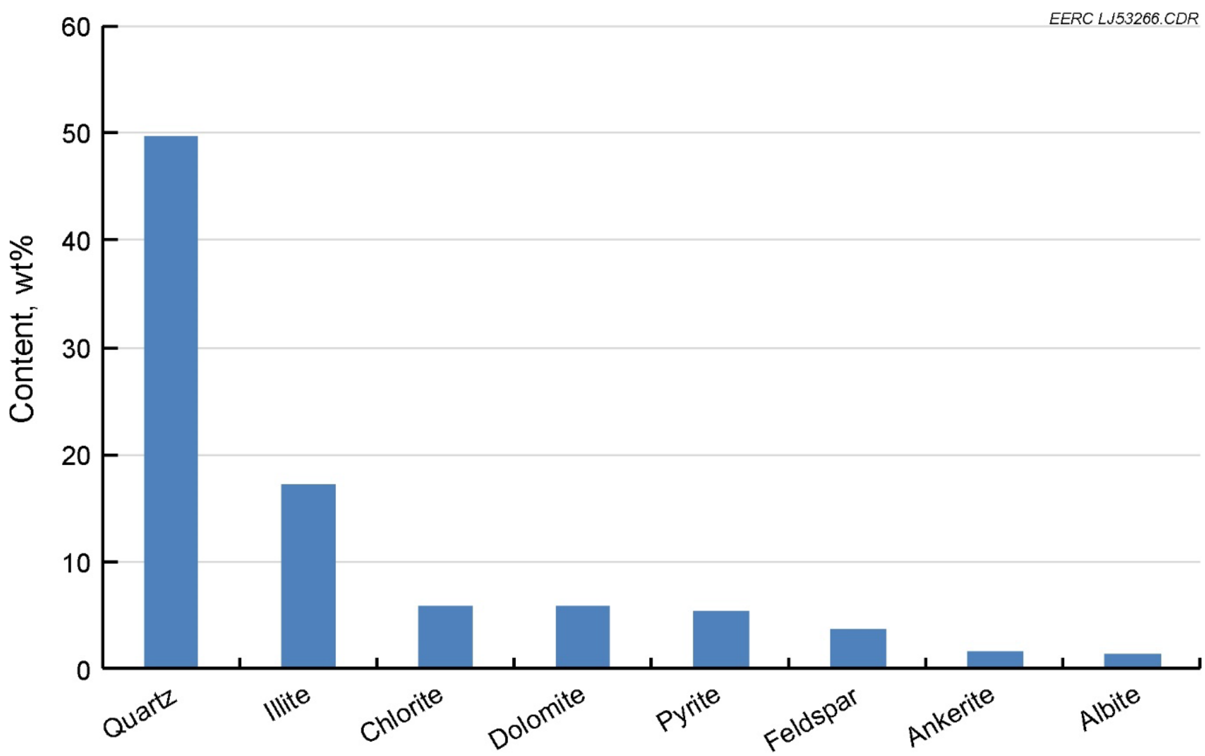

Figure 8. Main minerals found in Bakken shale samples using XRD.

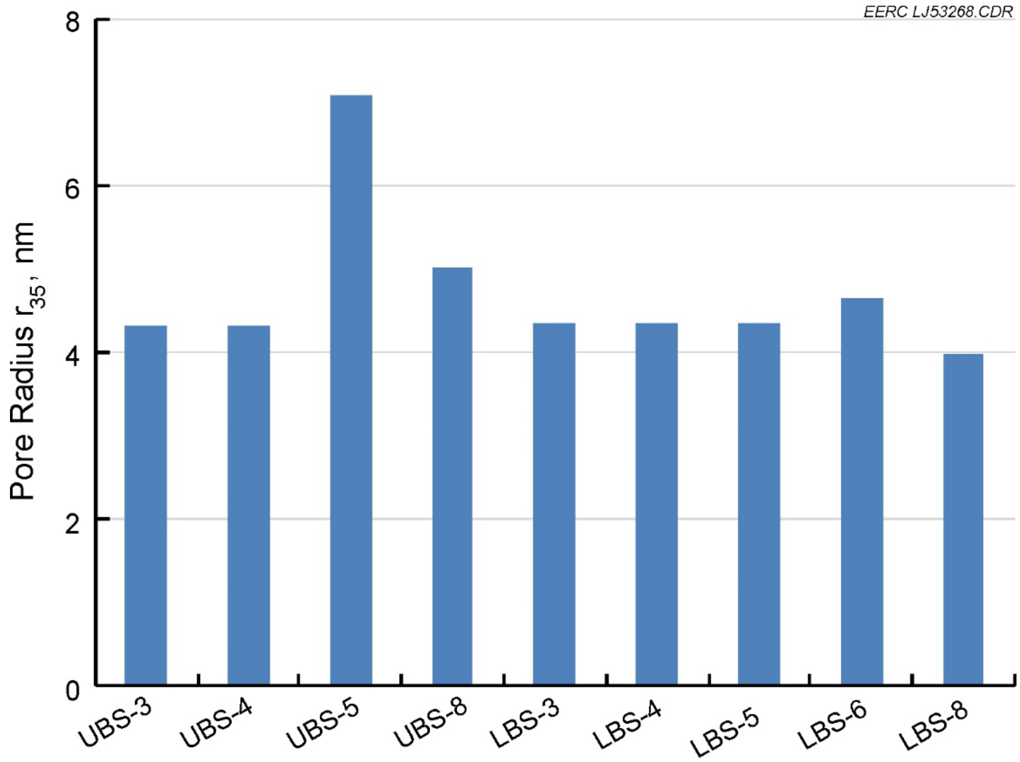

Figure 9. Pore size measured in Bakken shale samples.
Note: UBS, Upper Bakken Shale; LBS: Lower Bakken Shale.

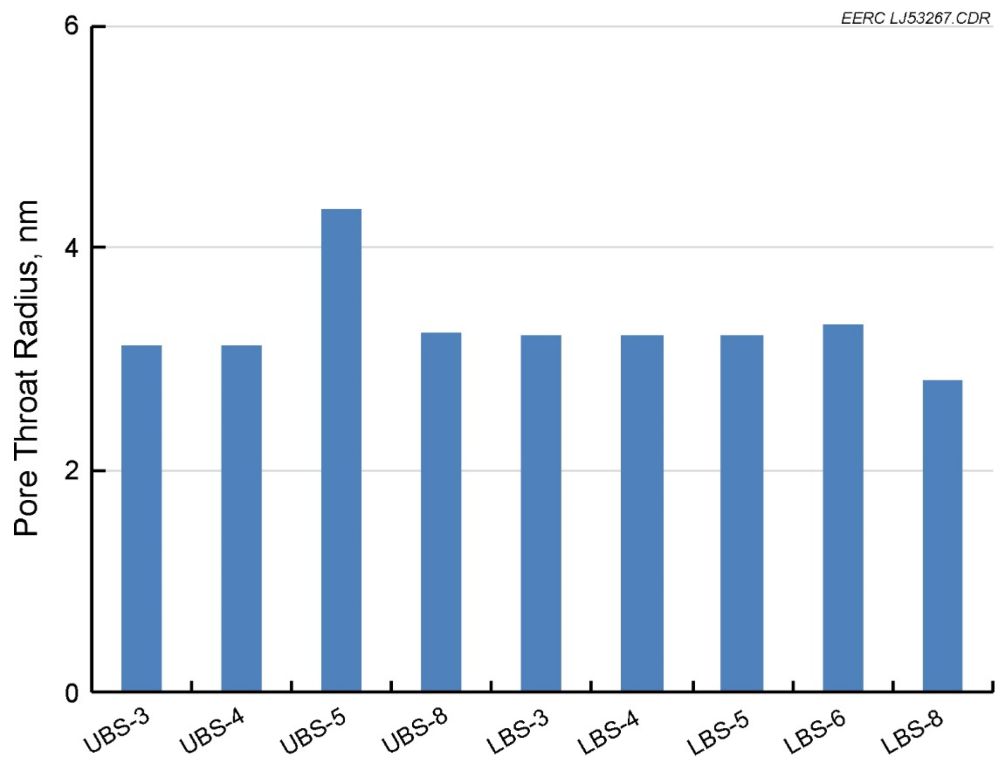

Figure 10. Mean pore throat radius in Bakken shale samples.

Sediment Chemical Analysis – Rock-Eval

TOC content was measured for the twenty shale core samples; the results clearly showed considerable TOC (10–15 wt%) in most of the shale samples, as shown in Figure 11. Although kerogen is the source to generate oil and gas underground, hydrocarbons are difficult to mobilize from the organic matter directly using conventional methods. Rock-Eval pyrolysis is the most widely used pyrolysis technique to characterize organic matter in the rock. In the measuring process, a rock sample is placed in a vessel and heated progressively to a high temperature under an inert atmosphere. When the temperature reaches a certain level, kerogen is pyrolyzed and combusted, and then the amount of released hydrocarbons and CO_2 is measured.[49-52]

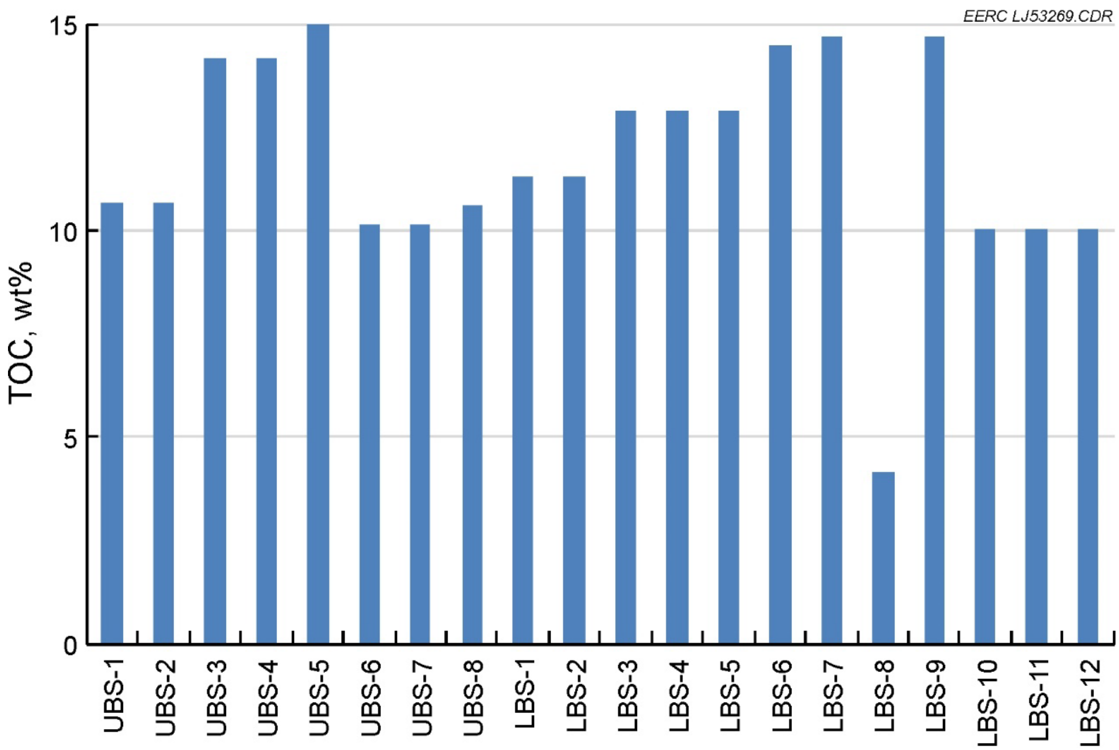

Figure 11. TOC in Upper and Lower Bakken shale samples.

Figure 12 shows the typical cycles during a Rock-Eval pyrolysis analysis.[37, 49] Several technical indicators are used in the Rock-Eval pyrolysis to describe the kerogen properties. T_{max} is the temperature at which maximum release of hydrocarbons from cracking of kerogen during pyrolysis analysis is possible; it is measured at the peak of S_2. S_1 is the peak measuring the quantity of free hydrocarbons (including oil and gas) existing in the rock and which are volatilized below 300°C. S_2 is the peak giving the amount of hydrocarbon-type compounds produced by the cracking of the organic matter when the temperature increases to 650°C (this value varies depending on the sample measured). This peak shows the quantity of hydrocarbons that could be produced in the rock; therefore, this important parameter estimates the ability of the source rock to generate hydrocarbons. S_3 is the peak showing the quantity of CO_2 produced from pyrolysis of the organic matter during the temperature lowering stage. PI is the productivity index, which can be calculated as $PI = S_1/(S_1 + S_2)$. Since PI usually increases with depth, it can be used to characterize the evolution level of the organic matter and divide zones with high or low amounts of hydrocarbons. Other indexes such as hydrogen index $HI = S_2/TOC*100$, oxygen index $OI = S_3/TOC*100$, and the ratio of S_2/S_3 can also be used to determine the type of organic matter in the rock. S_1 and S_2 are usually measured in mg hydrocarbon/g rock; S_3 is measured in mg CO_2/g rock. The important geochemical and geologic characteristics of the Bakken shales could be identified by mapping these parameters.[33,37,52]

With crossplots of pyrolysis parameters such as HI vs. OI and TOC vs. S_2, etc., the kerogen type in the Bakken shales has been divided.[33] In general, Type II marine oil-prone kerogen is the major kerogen in the Bakken shales, and it is distributed across most of the formation. Type I kerogen also appears locally, and some shallow Bakken shales have mixed Type II/III kerogen as well. Previous studies showed that the values of S_2, HI, and TOC decrease when the burial depth increases, which indicates the maturation of Bakken shales with the increase of formation depth. In this study, over 180 shale samples were collected from the Upper and Lower Bakken shale intervals (11,040–11,060 ft and 11,100–11,120 ft) of Well A (shown as the yellow star in Figure 7) to analyze the source rock maturity in the most productive area of the formation. Figure 13 shows the zonation of source rock maturity based on the crossplot of PI vs. T_{max}. The figure indicates that there is still a considerable portion of immature kerogen in the source rock even though the shales are deeply buried. For the mature kerogen, most of it falls into the region of the oil generation window and part of it falls into the wet-gas generation window. The finding matches the surface production very well: oil is generally light, a considerable amount of gas is produced with oil from most of the Bakken wells, and the gas is usually quite wet as shown in Figure 14 (less than 85% methane in the produced gas).[13,53-54] The composition of the produced gas (60 mol% methane, 14 mol% ethane, 9 mol% propane, and 9 mol% heavier hydrocarbon components [C4+]) makes the wet gas have liquidlike flow behavior in the reservoir when pressure is greater than 5000 psi and temperature is greater than 200°F.

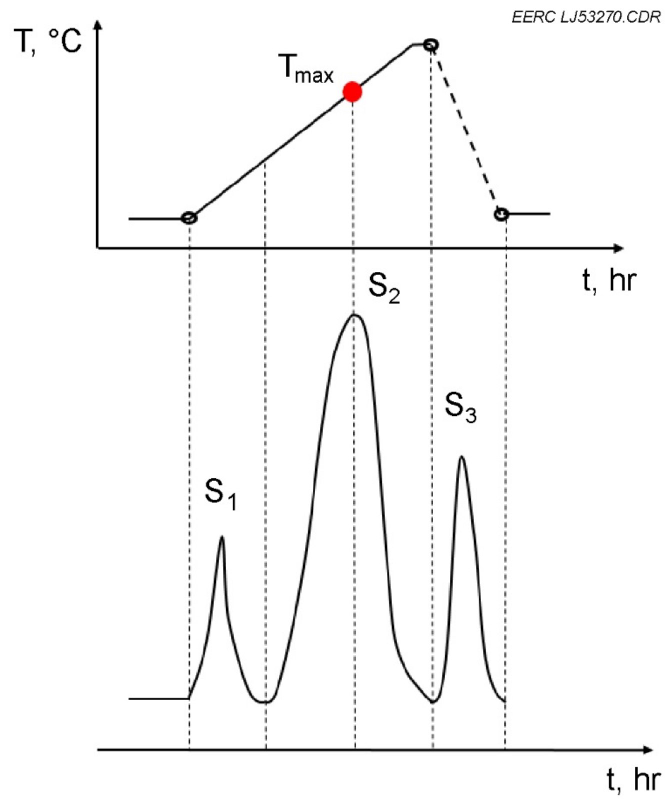

Figure 12. Schematic of the cycles during Rock-Eval pyrolysis analysis.

Supercritical CO_2 Extraction of Oil from Bakken Shales

Supercritical CO_2 has been effective for extracting hydrocarbons (up to C20+) from conventional reservoirs, where CO_2 can effectively reduce oil viscosity, increase oil mobility, and expulse oil from the pore space by volumetric expansion.[22-23] Recent laboratory experiments demonstrate that supercritical CO_2 interacts with the oil associated with unconventional tight rocks, solvating the oil so that it can be extracted at reservoir temperature and pressure.[28] In the present study, hydrocarbons were extracted from the shale samples with CO_2 under typical Bakken reservoir conditions (e.g., 5000 psi and 230°F).[10] Figure 15 shows a schematic of the experimental setup for extracting hydrocarbon from Bakken shales. In contrast to conventional core flooding experiments, each core sample (1.1-cm diameter and approximately 4 cm in length, shown as Item 5 in Figure 15) was put loosely inside the extraction vessel (Item 6 with 1.5-cm diameter and 5.7 cm in length), which was placed into an ISCO Model SFX-210 supercritical extractor thermostatically controlled at 230°F. The pressure throughout the entire system was maintained at 5000 psi by an ISCO model 260D syringe pump operated in the constant pressure mode.

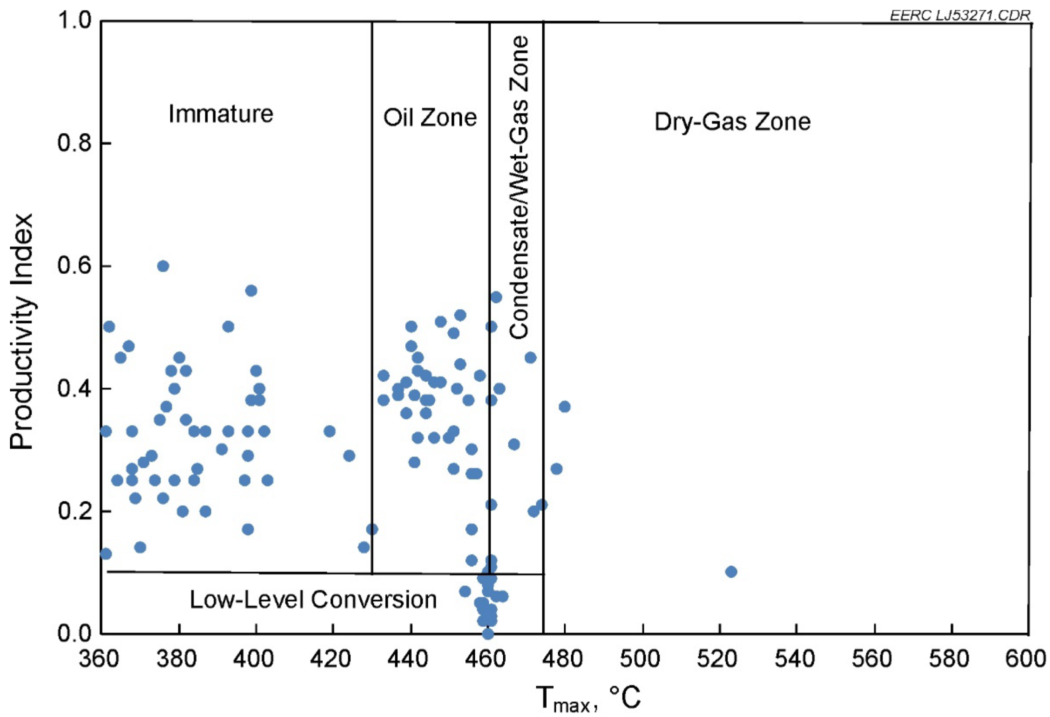

Figure 13. Source rock maturity of Bakken shales collected from Well A.

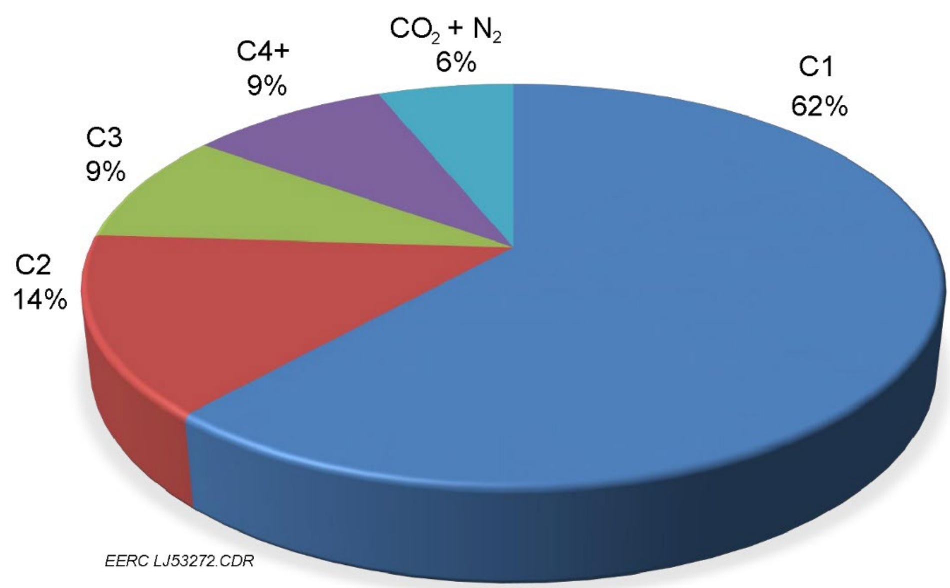

Figure 14. Produced gas composition and content found in Bakken wells in North Dakota.[54]

Hydrocarbons that were recovered were collected by opening the outlet control valve (8) at certain intervals (hourly for the first 7 hours of exposure and an additional exposure up to 24 hours). The flow rate of CO_2 was controlled at 1.5 mL/min by the flow restrictor (9), and about two cell void volumes (ca. 15 mL total) of CO_2 were purged into 15 mL of methylene chloride to collect the hydrocarbons recovered during each exposure time. Following the 24-hour CO_2 exposure, the rock sample was crushed to a fine powder and extracted with the aid of sonication three times in 20 mL methylene chloride to recover the remaining hydrocarbons. Percent recoveries are defined as the quantity of crude oil hydrocarbons found in the CO_2 extracts in comparison to the total oil hydrocarbons extracted by both CO_2 and methylene chloride.

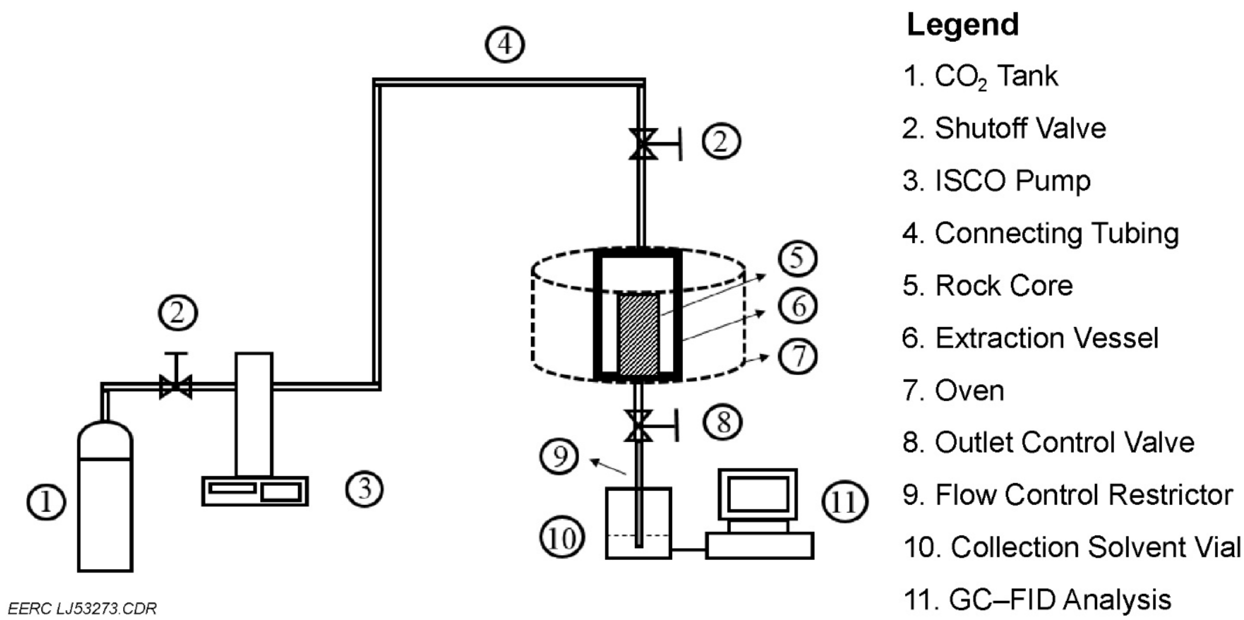

Figure 15. Schematic of experimental setup for extracting hydrocarbon from Bakken shales (GC–FID is gas chromatography–flame ionization detection).[10]

Results and Discussion

Results from 20 samples showed supercritical CO_2 enables extraction of a considerable portion of hydrocarbons (15%–65%) from Bakken shales. Figures 16 and 17 show the oil recovered from the Upper and Lower Bakken shale cores within 24 hours, respectively. Basically, the oil recovery performance was similar in both Upper and Lower Bakken shales: the majority of the oil was recovered in the first 7 hours, and most samples had overall recoveries less than 60%. Compared to the CO_2 extraction results in the tight cores from Middle Bakken and Three Forks, the oil recovery in the shale samples is more widely distributed. Several factors may contribute to the oil recovery results in the shales.

According to Figure 13, around 40% of the kerogen samples belong to the immature category, which means the hydrocarbons have not yet transformed into oil, so there is little liquid oil in the kerogen pores.[33] Although oil could be obtained by heating the rock in situ or at the surface to mature the kerogen, it is difficult to extract oil out of the immature kerogen under the typical reservoir conditions in the Bakken. Therefore, if most of the kerogen in a core sample is immature, then not much oil can be extracted from it.

Figure 9 shows that the pores are small ($r_{35} \leq 5$ nm) in the shale samples. A considerable part of the hydrocarbon molecules exist in an adsorbed state in these nanometer-scale pores, and the volume of oil-filled pores occupied by free fluid is less than 40% based on molecular dynamics simulation using the Bakken's petrophysical properties.[48] Figure 18 shows a schematic of oil and gas distribution in a kerogen pore where the movable oil and gas are recoverable in the extraction process while the adsorbed oil may stay in the pore. The oil layer adsorbed on the pore wall also makes the kerogen more oil-wet, which was demonstrated by various wettability studies of Bakken rocks.[55-56] The percentage of adsorbed oil decreases with increasing pore size. Kerogen also has more complex pore structure than nonorganic matter, and the pore throat radii in kerogen are usually tiny ($r \leq 4$ nm), as shown in Figure 10. Such tiny pore throat sizes induce high capillary pressure between phases when oil, gas, and water coexist in the core. The smaller the pore throat size, the more difficult it is to overcome capillary resistance between phases. These mechanisms make it difficult to recover oil from the shales using conventional methods.[10,55]

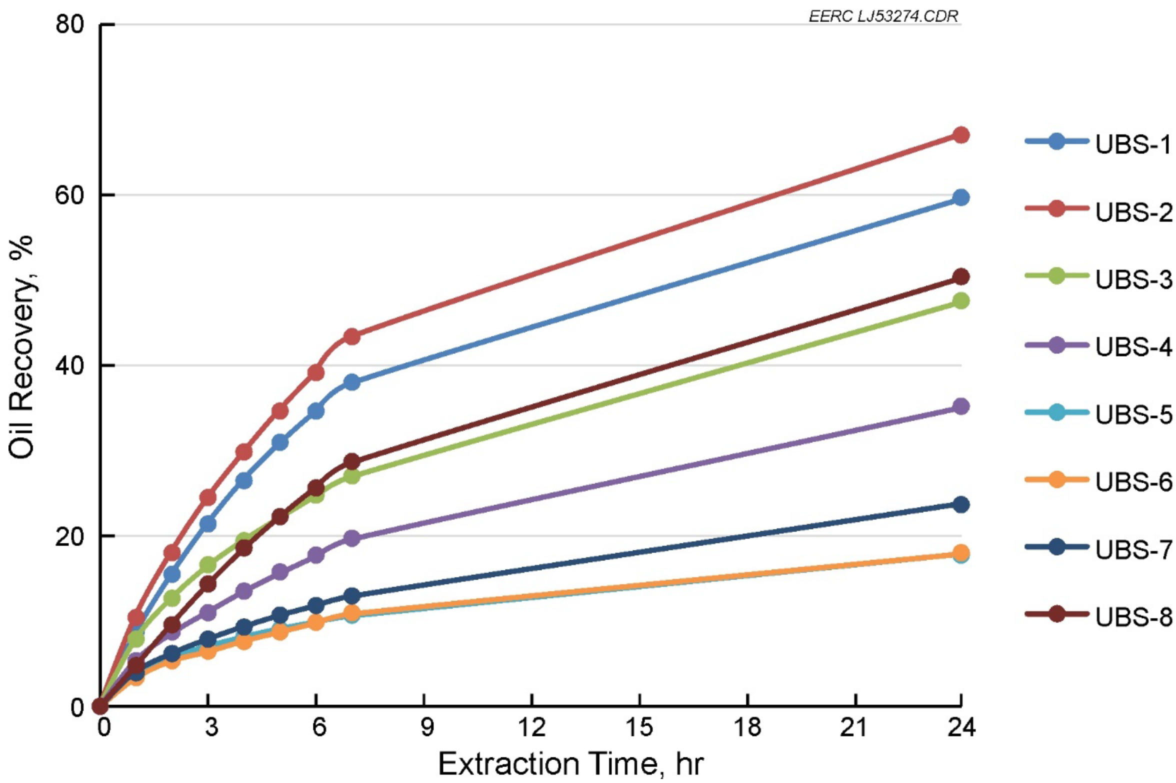

Figure 16. Oil recovery from the Upper Bakken cores.

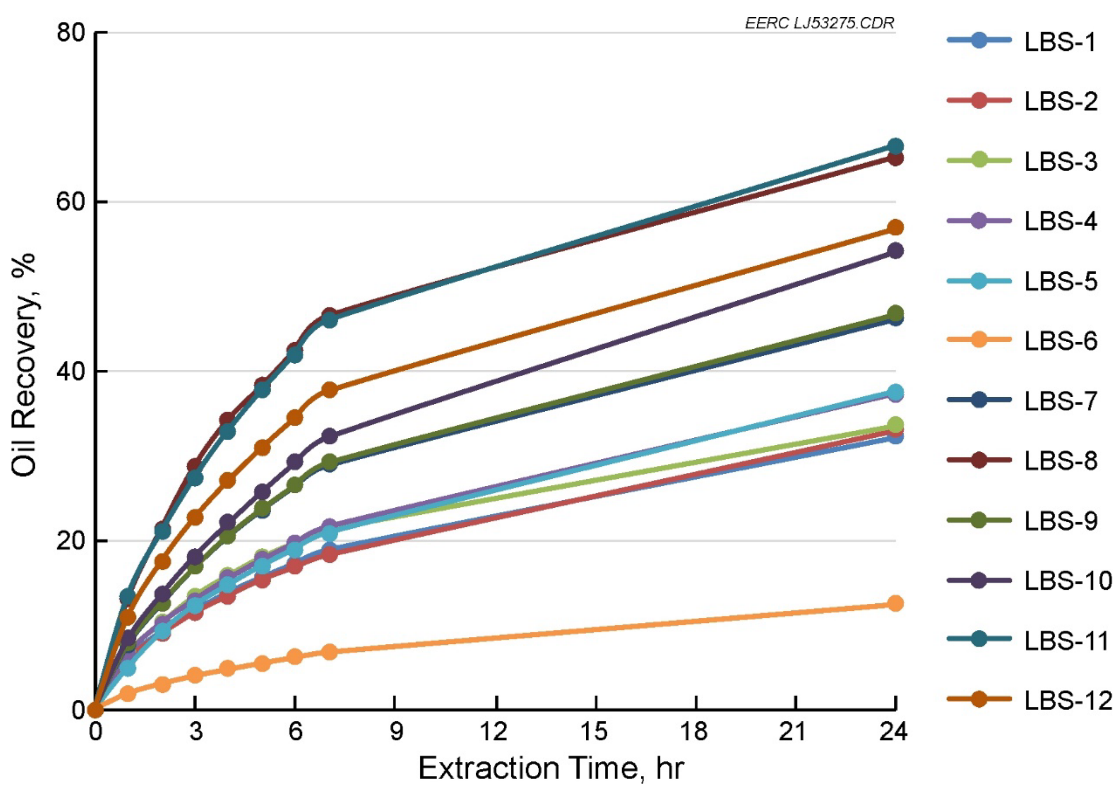

Figure 17. Oil recovery from the Lower Bakken cores.

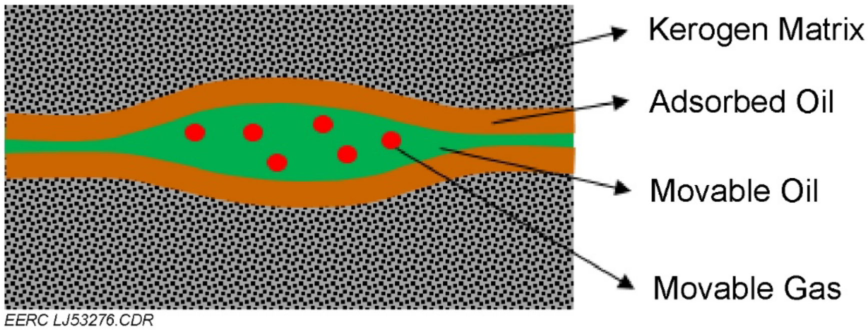

Figure 18. Schematic of oil and gas distribution in kerogen.

Supercritical CO_2 is able to reduce or even eliminate the interfacial tension between oil and gas under Bakken reservoir conditions. Minimum miscibility pressure (MMP) tests showed that interfacial tension between oil and CO_2 can be removed when pressure is above 2500 psi at 230°F, which means the capillary effect is minimized in the experiments under reservoir conditions (i.e., 5000 psi and 230°F).[41] Therefore, CO_2 is able to push the oil through the pore throats when the pressure gradient is greater than the frictional resistance in the pores. Pressure–volume–temperature (PVT) tests showed that the Bakken oil swells with CO_2 and the swelling factor increases from 1.0 to 1.5 when the CO_2 mole fraction increases from 0 to 0.5 in the oil. The volumetric expansion could effectively expel part of the oil from the pore space when there is a high concentration of CO_2 in the oil. The results may be used to improve modeling and forecasting the effects of CO_2 EOR and improve our knowledge of mechanisms controlling CO_2 storage. Such information could be used to suggest possible approaches for increasing ultimate recovery and storing CO_2 in some areas of the Bakken Formation.

Conclusions

Overall production performance in the BPS was reviewed based on drilling and production data from the past decade. Results showed that production is declining in the two main non-shale units, with a generally low oil recovery factor. We extended the study area to the two shale units—Upper and Lower Bakken shales—which serve as the source rock for the Bakken reservoirs. A series of experiments were conducted to investigate shale properties and the possibility of extracting oil out of it using supercritical CO_2. Based on the experimental results, the following conclusions have been drawn:

1. Both core samples and well logs indicate that there is significant hydrocarbon saturation in the Upper and Lower Bakken shale members; however, not many wells are producing in these units, and the oil transport behavior in the shales has not been fully investigated.
2. Six primary mineralogical components were detected in the shale samples through XRD analysis, which showed that quartz and illite are the major components in the matrix of Bakken shales, accounting for 67% of total matrix weight.
3. High-pressure mercury injection tests showed that the mean radii of pore and pore throat are less than 5 and 4 nm, respectively, in both the Upper and Lower Bakken samples. Such tiny pore sizes yield high capillary pressure and make fluid flow difficult in the reservoir.
4. TOC content was measured, and kerogen was characterized by Rock-Eval/TOC pyrolysis, which indicated that TOC is 10–15 wt% in the shales and a considerable portion of the kerogen is immature. The Rock-Eval results align well with the composition of the produced fluids.
5. Supercritical CO_2 extraction was conducted on 20 shale samples under typical Bakken reservoir conditions (e.g., 5000 psi and 230°F). Results showed that supercritical CO_2 is able to extract a considerable portion (15%–65%) of the hydrocarbons from the Bakken shales within 24 hours.

Nomenclature

BPS	Bakken petroleum system	PI	productivity index
EERC	Energy & Environmental Research Center	PVT	pressure, volume, temperature
EOR	enhanced oil recovery	S_h	hydrocarbon saturation, fraction
FESEM	field emission scanning electron microscopy	S_w	water saturation, fraction
GC–FID	gas chromatography–flame ionization detection	T_{max}	maximum temperature, °C
HI	hydrogen index	TOC	total organic carbon
LBS	Lower Bakken shale	UBS	Upper Bakken shale
MMP	minimum miscibility pressure	XRD	x-ray diffraction
OI	oxygen index		

Acknowledgment

The authors thank Marathon Oil and the North Dakota Geological Survey for providing the samples used in these investigations. Financial support from the U.S. Department of Energy National Energy Technology Laboratory, Marathon Oil, Hess Corporation, Continental Resources, ExxonMobil-XTO, and the North Dakota Industrial Commission through the North Dakota Oil and Gas Research Council and the Lignite Energy Council is gratefully acknowledged. Additional support to the program was provided by Kinder Morgan, Computer Modelling Group, Schlumberger, and Baker Hughes. The authors also appreciate Dr. Yinghui Li (InPetro Technologies), and Dr. Basak Kurtoglu (Citi), and Ron Ness (North Dakota Petroleum Council) for their helpful discussions on EOR technologies with respect to unconventional reservoirs.

References

1. Chaudhary, A.S., Ehlig-Economides, C.A., and Wattenbarger, R.A., 2011, Shale oil production performance from a stimulated reservoir volume, *in* Proceedings of SPE Annual Technical Conference and Exhibition: SPE-147596, Denver, Colorado, October 30 – November 2.
2. Clarkson, C.R., Jensen, J.L., and Blasingame, T.A., 2011, Reservoir engineering for unconventional gas reservoirs—what do we have to consider?, *in* Proceedings of SPE North American Unconventional Gas Conference and Exhibition: SPE 145080, the Woodlands, Texas, June 14–16.
3. Alfi, M., Yan, B., Cao, Y., An, C., Wang, Y., He, J., and Killough, J., 2014, How to improve our understanding of gas and oil production mechanisms in liquid-rich shale, *in* Proceedings of SPE Annual Technical Conference and Exhibition: SPE 170953, Amsterdam, The Netherlands, October 27–29.
4. Jin, L., Pu, H., Wang, Y., and Li, Y., 2015, The consideration of pore size distribution in organic-rich unconventional formations may increase oil production and reserve by 25%, eagle ford case study, *in* Proceedings of the Unconventional Resources Technology Conference: URTeC-2148314, San Antonio, Texas, July 20–22, 2015.
5. Agalliu, I., Smith, C., Tavallali, M., Rao, M., Adams, S., Montero, A., Levesque, L., Coughlin, C., Yang, D., and Gallagher, S., 2016, CO_2 EOR Potential in North Dakota—challenges, policy solutions, and contribution to economy and environment, 2016, IHS Energy consulting report, June.
6. Jin, L., Hawthorne, S., Sorensen, J., Kurz, B., Pekot, L., Smith, S., Bosshart, N., Azenkeng, A., Gorecki, C., and Harju, J., 2016, A systematic investigation of gas-based improved oil recovery technologies for the Bakken tight oil formation, *in* Proceedings of the Unconventional Resources Technology Conference: URTeC-2433692, San Antonio, Texas, August 1–3.
7. Gaswirth, S.B., Marra, K.R., Cook, T.A., Charpentier, R.R., Gautier, D.L., Higley, D.K., Klett, T.R., Lewan, M.D., Lillis, P.G., Schenk, C.J., Tennyson, M.E., and Whidden, K.J., 2013, Assessment of undiscovered oil resources in the Bakken and Three Forks Formation, Williston Basin Province, Montana, North Dakota, and South Dakota: USGS National Assessment of Oil and Gas Fact Sheet, U.S. Geological Survey.
8. Ran, B., and Kelkar, M., 2015, Fracture stages optimization in Bakken Shale Formation, *in* Proceedings of the Unconventional Resources Technology Conference: URTeC 2154796, San Antonio, TX, July 20–22.
9. Kurtoglu, B., and Kazemi, H., 2012, Evaluation of Bakken performance using coreflooding, well testing, and reservoir simulation, *in* Proceedings of the SPE Annual Technical Conference and Exhibition: SPE 155655, San Antonio, Texas, October 8–10.
10. Jin, L., Sorensen, J.A., Hawthorne, S.B., Smith, S.A., Pekot, L.J., Bosshart, N.W., Burton-Kelly, M.E., Miller, D.J., Grabanski, C.B., Gorecki, C.D., Steadman, E.N., and Harju, J.A., 2016, Improving oil recovery by use of

carbon dioxide in the Bakken unconventional system—a laboratory investigation: SPE Reservoir Evaluation & Engineering-Reservoir Engineering, December.

11. Nojabaei, B., Johns, R.T., and Chu, L., 2013, Effect of capillary pressure on phase behavior in tight rocks and shales: SPE Reservoir Evaluation & Engineering, v. 16, no. 3, p. 281–289.
12. Kurtoglu, B., Raski, F., Salman, A., and Kazemi, H., 2013, Evaluating long term flow regimes in unconventional oil reservoirs with diverse completion technology, *in* Proceedings of the SPE Unconventional Resources Conference: SPE 167145, Canada, Calgary, Alberta, November 5–7.
13. Jin, L., Hawthorne, S., Sorensen, J., Pekot, L., Bosshart, N., Gorecki, C., Steadman, E., and Harju, J., 2017, Utilization of produced gas for improved oil recovery and reduced emissions from the Bakken Formation, *in* Proceedings of the SPE Health, Safety, Security, Environment & Social Responsibility Conference: SPE-184414, North America, New Orleans, Louisiana, April 18–20.
14. Khoshghadam, M., Khanal, A., and Lee. W.J., 2015, Numerical study of impact of nano-pores on gas-oil ratio and production mechanisms in liquid-rich shale oil reservoirs, *in* Proceedings of the Unconventional Resources Technology Conference: SPE 178577, San Antonio, Texas, July 20–22.
15. Jones, R.S., 2016, Producing gas-oil ratio behavior of tight oil reservoirs, *in* Proceedings of the Unconventional Resources Technology Conference: URTeC 2460396, San Antonio, Texas, August 1–3.
16. Ozkan, S., Kurtoglu, B., and Ozkan, E., 2012, Long-term economic viability of production from unconventional liquids-rich reservoirs—the case of Bakken Field: SPE EM, v. 4, no. 4, October.
17. Afonja, G., Hugher, R.H., Nagineni, V.G.R., and Jin, L., 2012, Simulation study for optimizing injected surfactant volume in a miscible carbon dioxide flood, *in* Proceedings of SPETT Energy Conference and Exhibition: SPE 158220, Port-of-Spain, Trinidad, June 11–13.
18. Jin, L., Wojtanowicz, A.K., and Hughes, R.G., 2010, An analytical model for water coning control installation in reservoirs with bottomwater: Journal of Canadian Petroleum Technology, v. 49, no. 5, May.
19. Alvarado, V., and Manrique, E., 2010, Enhanced oil recovery—an update review: Energies, 2010.
20. Jin, L., and Wojtanowicz, A.K., 2010, Performance analysis of wells with downhole water loop installation for water coning control: Journal of Canadian Petroleum Technology, v. 49, no. 6.
21. Jin, L., and Wojtanowicz, A.K., 2011, Analytical assessment of water-free production in oil wells with downhole water loop for coning control, *in* Proceedings of SPE Production and Operations Symposium: SPE 141470, Oklahoma City, Oklahoma, March 27–29.
22. Moritis, G., 2006, EOR survey: Oil and Gas Journal, v. 104, no. 15.
23. Jin, L., 2016, Impact of CO_2 impurity on MMP and oil recovery performance of the Bell Creek Oil Field, *in* Proceedings of the 13th International Conference on Greenhouse Gas Control Technologies: GHGT-13, Lausanne, Switzerland, November 14–18.
24. Aryana, S.A., Barclay, C., and Liu, S., 2014, North cross devonian unit—a mature continuous CO_2 flood beyond 200% HCPV injection, *in* Proceedings of the SPE Annual Technical Conference and Exhibition: SPE 170653, Amsterdam, The Netherlands, October.
25. Hawthorne, S.B., Gorecki, C.D., Sorensen, J.A., Miller, D.J., Harju, J.A., and Melzer, L.S., 2014, Hydrocarbon mobilization mechanisms using CO_2 in an unconventional oil play: Energy Procedia, v. 63.
26. Sorensen, J.A., Hawthorne, S.B., Jin, L., Kurz, B.A., Bosshart, N.W., Smith, S.A., Gorecki, C.D., Steadman, E.N., and Harju, J.A., 2016, Laboratory characterization and modeling to examine CO_2 storage and enhanced oil recovery in an unconventional tight oil formation, *in* Proceedings of the 13th International Conference on Greenhouse Gas Control Technologies: GHGT-13, Lausanne, Switzerland, November 14–18.
27. Kurtoglu, B., Salman, A., and Kazemi, H., 2015, Production forecasting using flow back data, *in* Proceedings of the SPE Middle East Unconventional Resources Conference and Exhibition: SPE 172922, Muscat, Oman, January 26–28.
28. Hawthorne, S.B., Jin, L., Kurz, B.A., Miller, D.J., Grabanski, C.B., Sorensen, J.A., Pekot, L.J., Bosshart, N.W., Smith, S.A., Burton-Kelly, M.E., Heebink, L.V., Gorecki, C.D., Steadman, E.N., and Harju, J.A., 2017, Integrating petrographic and petrophysical analyses with CO_2 permeation and oil extraction and recovery in the Bakken Tight Oil Formation, *in* Proceedings of the SPE Canada Unconventional Resources Conference: Calgary, Alberta, February 15–16.
29. Webster, R.L., 1984, Petroleum source rocks and stratigraphy of the Bakken Formation in North Dakota: Rocky Mountain Association of Geologists, Denver, Colorado.
30. Sonnonberg, S.A., Jin, H., and Sarg, J.F., 2011, Bakken mudrocks of the Williston Basin, world class source rocks: AAPG, Search and Discovery, 80171.

31. Pollastro, R.M., Roberts, L.N.R., and Cook, T.A., 2013, Geologic assessment of technically recoverable oil in the Devonian and Mississippian Bakken Formation: U.S. Geological Survey Digital Data Series DDS–69–W, Reston, Virginia.
32. Jin, H., and Sonnonberg, S.A., 2013, Characterization for source rock potential of the Bakken Shales in the Williston Basin, North Dakota and Montana, *in* Proceedings of Unconventional Resources Technology Conference: URTeC 1581243, Denver, Colorado.
33. Jin, H., 2014, Source rock potential of the Bakken Shales in the Williston Basin, North Dakota and Montana [Ph.D. dissertation]: Colorado School of Mines, Golden, Colorado.
34. Harbor, R.L., 2011, Facies characterization and stratigraphic architecture of organic-rich mudrocks, upper cretaceous Eagle Ford Formation, South Texas [M.S. Thesis]: University of Texas at Austin, Austin, Texas.
35. Kovscek, A.R., Tang, G.Q., and Vega, B., 2008, Experimental investigation of oil recovery from siliceous shale by CO_2 injection, *in* Proceedings of the SPE Annual Technical Conference and Exhibition: SPE 115679, Denver, Colorado, September 21–24.
36. Tovar, F.D., Eide, O., Graue, A., and Schechter, D.S., 2014, Experimental investigation of enhanced recovery in unconventional liquid reservoirs using CO_2—a look ahead to the future of unconventional EOR, *in* Proceedings of the SPE Unconventional Resources Conference: SPE 169022, The Woodlands, Texas, April 1–3.
37. Simenson, A.L., Sonnenberg, S.A., and Cluff, R.M., 2011, Depositional facies and petrophysical analysis of the Bakken Formation, Parshall Field and Surrounding Area, Mountrail County, North Dakota: Rocky Mountain Association of Geologists.
38. Pitman, J.K., Price, L.C., and LeFever, J.A., 2001, Diagenesis and fracture development in the Bakken Formation, Williston Basin—implications for reservoir quality in the middle member: U.S. Geological Survey Professional Paper 1653, U.S. Department of the Interior U.S. Geological Survey, November.
39. Schmoker, J.W., and Hester, T.C., 1983, Organic carbon in the Bakken Formation, United States Portion of Williston Basin: AAPG Bulletin, v. 67, no. 12.
40. Schmoker, J.W., and Hester, T.C., 1990, Formation resistivity as an indicator of oil generation—Bakken Formation of North Dakota and Woodford Shale of Oklahoma: The Log Analyst, v. 31, no. 1.
41. Hawthorne, S.B., Miller, D.J., Jin, L., and Gorecki, C.D., 2016, Rapid and simple capillary-rise/vanishing interfacial tension method to determine crude oil minimum miscibility pressure—pure and mixed CO_2, methane, and ethane: Energy & Fuels.
42. Williams, J.A., 1974, Characterization of oil types in Williston Basin: AAPG Bulletin, v. 58, no. 7.
43. Ozkan, E., Raghavan, R.S., and Apaydin, O.G., 2010, Modeling of fluid transfer from shale matrix to fracture network, *in* Proceedings of the SPE Annual Technical Conference and Exhibition: SPE 134830, September 19–22, Florence, Italy.
44. Josh, M., Esteban, L., Delle Piane, C., Sarout, J., Dewhurst, D.N., and Clennell, M.B., 2012, Laboratory characterisation of shale properties: Journal of Petroleum Science and Engineering, p. 88–89.
45. Kazil, T., Li, Y., Jin, L., and Wu, X., 2015, How typical langmuir isotherm curves underestimate OGIP and production by 20%, a Barnett case study, *in* Proceedings of Southwest Section AAPG Annual Convention: Wichita Falls, Texas, April 11–14, AAPG Search and Discovery Article #90214.
46. Jin, L., and Wojtanowicz, A.K., 2014, Progression of injectivity damage with oily waste water in linear flow: Petroleum Science, v. 11.
47. Du, L., and Chu, L., 2012, Understanding anomalous phase behavior in unconventional oil reservoirs, *in* Proceedings of the SPE Canadian Unconventional Resources Conference: SPE 161830, Calgary, Alberta, October 30 – November 1.
48. Wang, S., Feng, Q., Javadpour, F., Xia, T., and Li, Z., 2015, Oil adsorption in shale nanopores and its effect on recoverable oil-in-place: International Journal of Coal Geology, v. 147–148.
49. Tissot, B.P., and Welte, D.H., 1984, Petroleum formation and occurrence, 2d ed.: Springer Verlag, Heidelberg.
50. Jarvie, D.M., and Johnson, M.S., 2008, Maturity and organofacies assessment of Bakken shale—implications for new areas for exploration and production: AAPG Rocky Mountain Section, July 9–11, Search and Discovery Article #90092.
51. Kuila, U., 2013, Measurement and interpretation of porosity and pore-size distribution in Mudrocks—the hole story of shales [Ph.D. Dissertation of Colorado School of Mines]: Golden, Colorado.
52. Aderoju, T.E., and Bend, S.L., 2013, A rock-eval evaluation of the Bakken formation in southern Saskatchewan: Saskatchewan Geological Survey, Summary of Investigations, v.1, Sask. Ministry of the Economy.

53. Schmatko, T., Hervet, H., and Leger, L., 2005, Friction and slip at simple fluid–solid interfaces—the roles of the molecular shape and the solid–liquid interaction: Physical Review Letters, v. 94.
54. Wocken, C.A., Stevens, B.G., Almlie, J.C., and Schlasner, S.M., 2012, End-use technology study—an assessment of alternative uses for associated gas: North Dakota Industrial Commission and U.S. Department of Energy report, Energy & Environmental Research Center, November.
55. Wang, D., Butler, R., Zhang, J., and Seright, R., 2012, Wettability survey in Bakken shale with surfactant-formulation imbibition: SPE Reservoir Evaluation & Engineering, v. 15, no. 6.
56. Alvarez, J.O., and Schechter, D.S., 2016, Altering wettability in Bakken shale by surfactant additives and potential of improving oil recovery during injection of completion fluids, *in* Proceedings of the SPE Improved Oil Recovery Conference: SPE-179688, Tulsa, Oklahoma, April 11–13.