Oil-Generation Kinetics for Oil-Prone Bakken Shales and its Implication

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Abstract

The marine oil-prone lower and upper Bakken shales are world class source rocks in the Williston Basin, which are a significant element for the Bakken Petroleum System (BPS) and sourcing reservoirs in the middle Bakken, upper Three Forks, and lower Lodgepole formations. A good understanding of the thermal-burial history of Bakken shales is essential to achieve realistic charge history, which closely relates to Bakken oil presence in reservoirs of BPS across the Williston Basin. The oil-generation kinetics is one of the most important thermal dynamic parameters. The maturation of immature Bakken shales under a hydrous closed-system setting was implemented by the method of hydrous pyrolysis (HP) in a temperature- and time-series of order. This method provides a conceivable analogue for natural oil generation and expulsion. The derived kinetics for Bakken shales includes activation energy at 53.79 kcal/mole and frequency factor at 1.25×10^{27}m.y.$^{-1}$ for an oil-generation reaction. These kinetic parameters were tested in a well constrained 1-D thermal-burial history model. The modeled extent of oil generation correlates well with transformation ratios of Bakken shales from independent analysis. The HP oil-generation kinetics were also applied to other thermal-burial histories in the basin, and further modeling results indicate very minimal oil generation from Bakken shales in the Parshall Field and early oil generation in the Sanish Field. This agrees with measured thermal maturity indices and transformation ratios determined by atomic H/C ratios of isolated kerogens for those areas. The discovery of significant oil reserves in the Parshall/Sanish area implicates that, instead of charging from in-situ Bakken shales, the majority of discovered oil may have been laterally migrated from more mature down-dip Bakken shales adjacent to the Parshall/Sanish area.

Introduction

The lower and upper Bakken shales of the Bakken Formation, one of the world-class marine oil-prone source rocks, were deposited from the Late Devonian to Early Mississippian in the Williston Basin, which is an intra-cratonic sedimentary basin (Figure 1). The Nesson, Cedar Creek and Billings anticlines are major structures in the basin. Bakken Formation is a relatively thin but a laterally persistent unit in the central, deeper parts of the Williston Basin (Meissner, 1978; Gerhard et al., 1990; Pitman et al., 2001; Sonnenberg et al., 2011; Jin et al., 2012; Jin and Sonnenberg, 2013;). The Figure 2 shows four members of the Bakken Formation: in an ascending order, the Pronghorn calcareous siltstone member, lower Bakken siliceous organic-rich shale member, middle Bakken dolomitic siltstone and sandstone member, and upper Bakken shale member lithologically identical with the lower shale (LeFever et al., 2011; Jin et al., 2015; Xu et al., 2016).

A good understanding of the thermal-burial history of Bakken shales is essential to achieve realistic charge history, which closely relates to Bakken oil presence in reservoirs of BPS across the Williston Basin. The thermal-burial history of BPS can be constructed by integration of the stratigraphy, lithologies, thermal conductivity, surface temperatures, and heat flow in Williston Basin. The intrinsic oil-generation kinetics (frequency factor and activation energy) of kerogen is one of the most important thermal dynamical parameters for source rocks, and it actively impacts petroleum generation and expulsion during the thermal and burial history. But the reliable oil-generation

kinetics is difficult to acquire due to requirements of intensive experiments, so normally a kinetic analogue from similar shales from other basins are often applied, however, resulting in many unexpected uncertainties. However, in this study, Bakken oil-generation kinetics was derived from series of hydrous pyrolysis (HP) experiments.
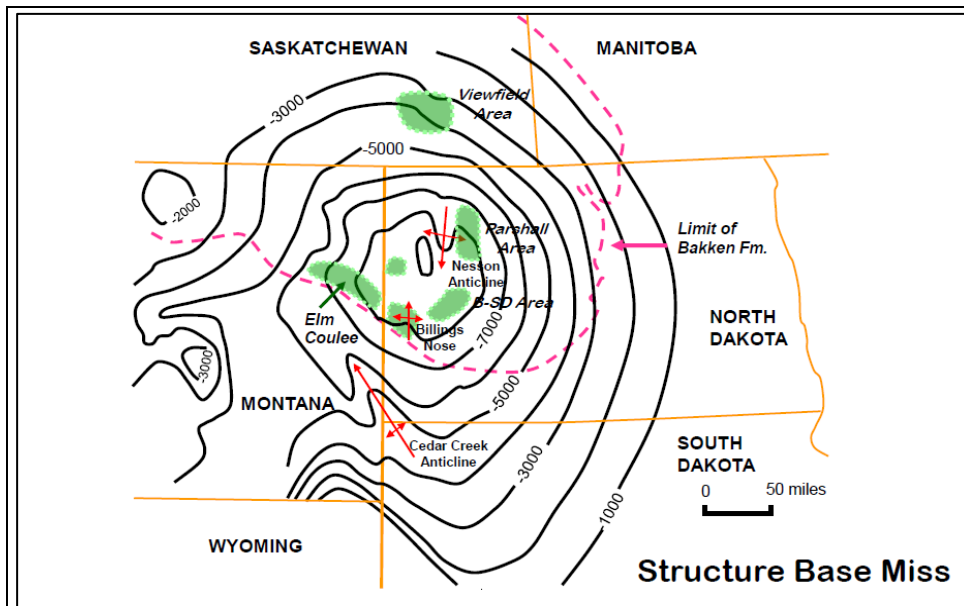

Figure 1. Location map of the Williston Basin with structure contour (interval = 1000ft) at the base of Mississippian (From Sonnenberg and Pramudito, 2009; modified from Webster, 1984). The dashed line on the map indicates the limit of the Bakken Formation. Green dotted boxes show the locations of major oil fields or areas in the basin.
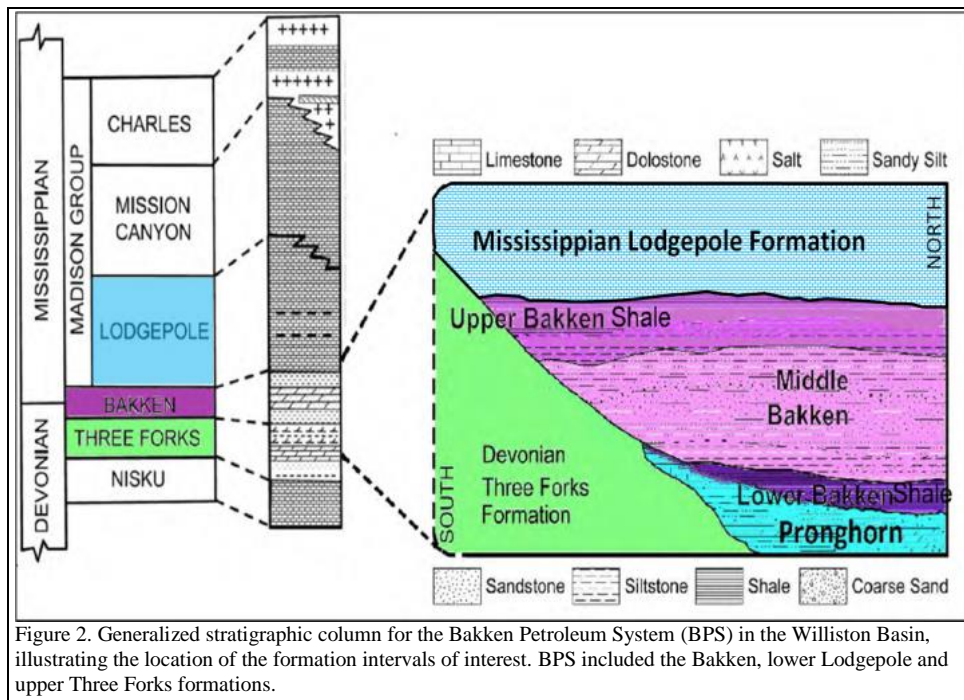
Figure 2. Generalized stratigraphic column for the Bakken Petroleum System (BPS) in the Williston Basin, illustrating the location of the formation intervals of interest. BPS included the Bakken, lower Lodgepole and upper Three Forks formations.

After derivation of oil-generation kinetics, the numerical thermal simulation of Bakken shales through the thermal-burial history was built based on reasonable extrapolation from the short-time experimental process at high temperatures in lab setting to the geologic processes with long periods of reactions at low temperatures in natural

systems, and it can provide essential information about timing and extent of oil generation from Bakken shales. This thermal simulation is typically accomplished by the way of the Arrhenius equation (left part of Equation 1), which is also combined with first-order rate function (right part of Equation 1) (Hunt et al., 1991):

$$f(\varepsilon) = \{A_0 \exp\,[-\,E_a/RK)]\}\,t = k_T\,t = Ln[1/(1-X_T)] \qquad \textbf{Equation (1)}$$

where $f(\varepsilon)$ = the extent of oil generation; A_0 = frequency factor; E_a = activation energy; R = ideal-gas constant; K = absolute temperature; t = heating time; k_T = rate constant at a specific temperature; X_T = the fraction of expelled oil at a specific temperature (expelled oil yield / maximum oil yield). The thermal-burial history can determine time and temperature values in natural systems, and laboratory pyrolysis methods can determine the kinetic parameters, E_a and A_0.

Methods

Hydrous pyrolysis has been shown to be a particularly useful analogue to simulate the petroleum generation, migration and expulsion processes in source rocks, which are conceivably same as those in nature, with expelled oil compositionally similar to natural crude oils (Winters et al., 1983; Lewan, 1994; Jin, 2014; Jin et al., 2016). Determining the kinetics for oil generation by HP requires 5 to 10 kg of a homogeneous thermally-immature sample. Therefore, totally10 kg immature Bakken shales were collected from Saskatchewan Subsurface Laboratory and homogenized as composited sample for HP experiments, and the characteristics of original "Upper Bakken Composite #1" sample is summarized in Table 1. This composite upper Bakken sample is rich in immature (416.8°C Tmax and 0.53 %R_o) marine oil-prone (Type II kerogen) organic matters with high hydrocarbon generation potential (1.12 H/C ratio and 560 HI). However, this composite upper Bakken sample still potentially contains a small amount of bitumen or moveable hydrocarbon (higher than expected bitumen content of 92mg/g TOC_o, higher than expected PI of 0.08, and lower than expected H/C ratio of 1.12), which are probably generated during very early maturation and stay *in-situ* in source rocks. However, these Bakken shale samples collected are the most immature samples capable to collect in Canada.

All HP experiments were conducted at the USGS Organic Geochemical Laboratories, Lakewood, CO. Based upon the definition (Lewan et al., 1979; Lewan, 1985), hydrous pyrolysis refers to the thermal decomposition of organic compounds in the presence of liquid water at subcritical temperatures (<374°C) in a closed reactor. Based on previous experiences and the prerequisite that at least 10g maximum yield of free oil should be acquired from the HP experiment at the optimized condition, the sample weight for each HP experiment was estimated and controlled to be 200g, Based on calculation, the weight of added distilled water into the reactor for HP experiments was decided to be 400g. The added rock and distilled water would take up 84.8% of HP reactor volume at the highest experimental temperature (365°C). Multiple temperature-series (at 300, 320, 340, 350, 355, 360, and 365°C for 72h) and time-series (with different durations at 300, 320, 340, and 350°C) of HP experiments were conducted, and major steps and procedures to conduct HP experiments were described in more details by Jin (2014).

Table 1. Summary table for geochemical characteristics for isolated kerogen and whole rock

Composite Sample ID	Kerogen				Whole Rock					
	Type	H/C [a]	S_{org}/C [a]	Suppressed %R_o [b]	Bitumen content (mg bitumen /g TOC_o) [c]	TOC (wt.%) [d]	HI [e]	OI [e]	PI [e]	Tmax (°C)
Upper Bakken Composite #1	II	1.12	0.011	0.53	92	25.74	560	4.5	0.08	416.8

Results and discussion 1: Yields of Organic Phases

In total, four kinds of organic phases were involved in the petroleum generation from immature upper Bakken composite samples: kerogen, bitumen, immiscible oil, and gas. Two organic phases were directly obtained from the temperature- and time-series HP experiments: (1) total immiscible oil from recovered free and equipment-rinsed oil and (2) hydrocarbon gas generated in association with immiscible oil. Bitumen, extracted by organic solvents from

the recovered rock chips, is the third organic phase. The fourth organic phase is the residual kerogen, the content of which in the recovered rock chips is indirectly determined by Source Rock Analyzer (SRA) after HP experiments.

Numerical yields of four organic phases were acquired after the 72h temperature-series HP experiments, and the cross-plotting of quantitative yields of organic phases with experiment temperatures is shown in Figure 3. In the cross-plot, the non-zero data points at 70°C (estimated from its burial depths of ~5000ft) represent original kerogen and in-situ bitumen contents in the unheated composite sample, respectively. Kerogen content drops from the beginning and reaches its minimum value at 320°C, and then it starts gradually increasing as the HP experiment temperature increases. Simultaneously, there is a significant trend of early intense bitumen generation from 300 to 320°C (representing the incipient-oil generation window), and at 320°C, the bitumen content reaches its maximum value. Subsequently, it dramatically decreases as the yield of immiscible oil is rapidly increasing from 320 to 355°C (representing the primary-oil generation window). At 355°C, the bitumen content almost decreases down to its minimum level and then is stabilizing, and the yield of immiscible oil reaches its maximum. The hydrocarbon gas was slowly generated with a steady increase during the whole course of bitumen and oil generation. These observations support the concept of Lewan (1994) that bitumen cracked from kerogen is a product-precursor for immiscible oil, because of the close inverse relationship between bitumen and expelled hydrocarbon (oil and gas) contents.
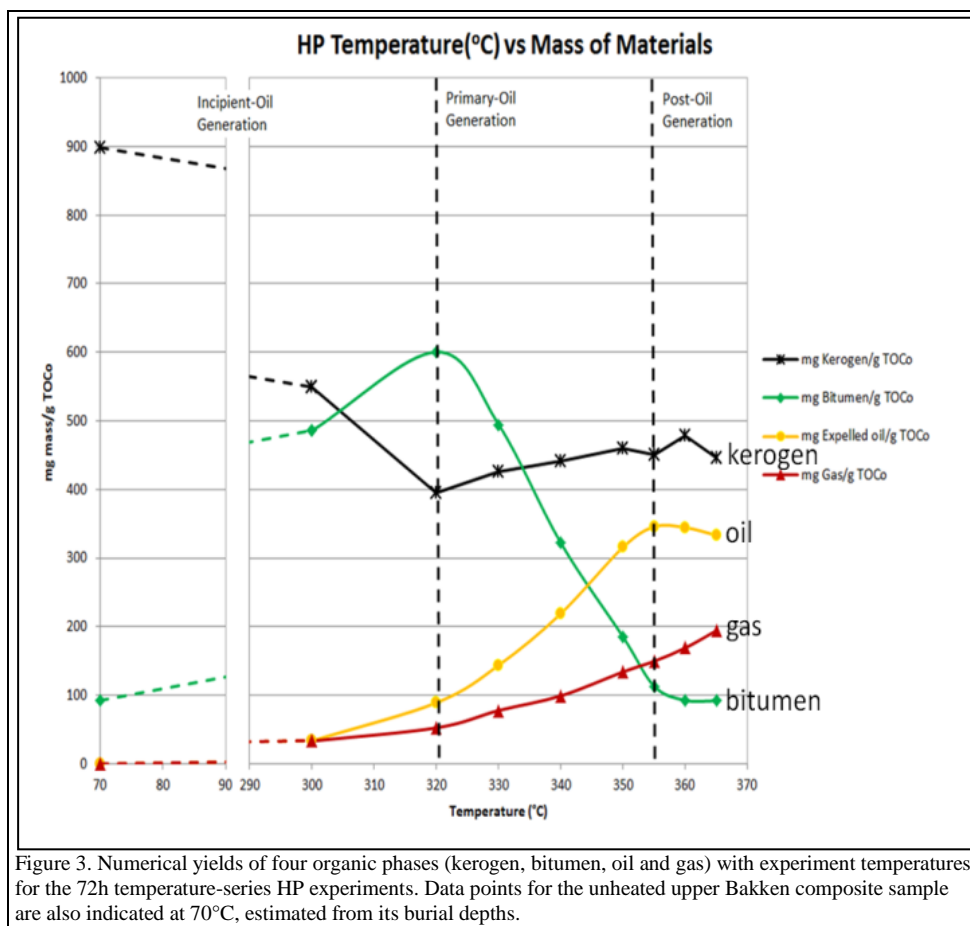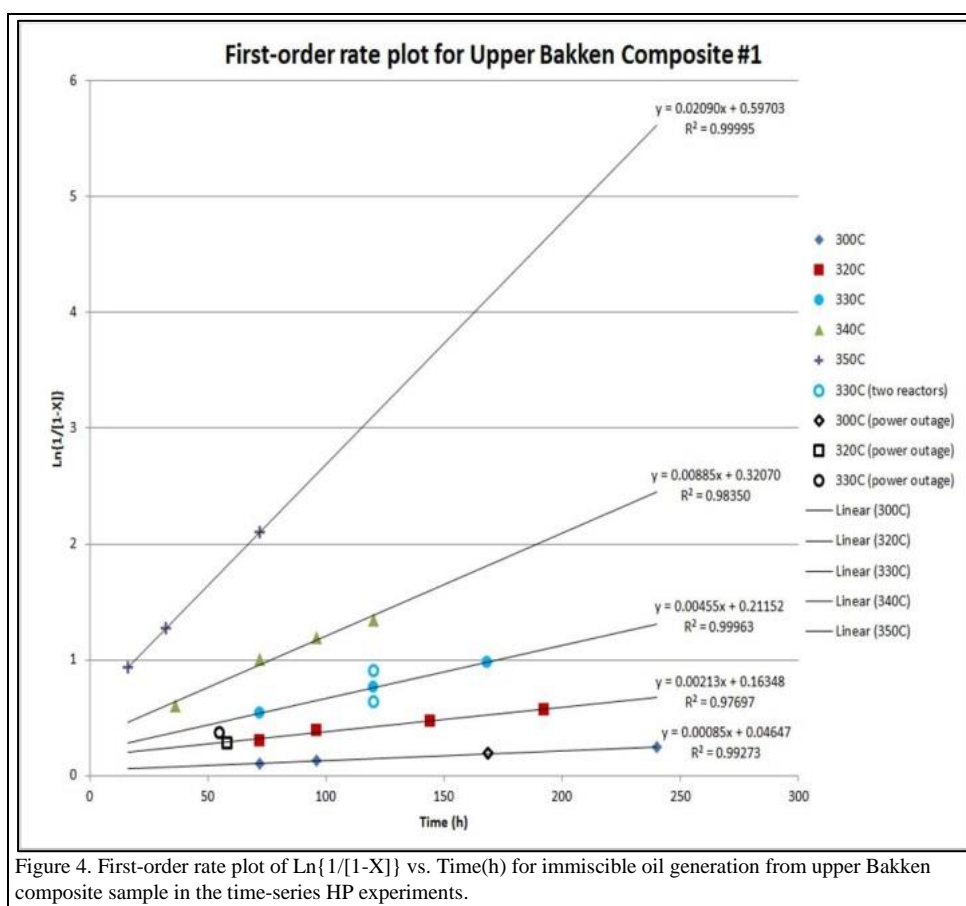

Figure 3. Numerical yields of four organic phases (kerogen, bitumen, oil and gas) with experiment temperatures for the 72h temperature-series HP experiments. Data points for the unheated upper Bakken composite sample are also indicated at 70°C, estimated from its burial depths.

In addition, after the maximum yield (17.8g) of immiscible oil at 355°C, there is no dramatic decrease of immiscible oil yield in the temperature range from 355°C to 365°C, which corresponds to high level of thermal maturity for the heated upper Bakken composite sample. This is also due to the fact the experiment temperature conditions in this study were primarily for oil generation examination and resulted thermal maturity of heated upper Bakken composite sample in HP experiments was lower than thermal maturity for intense thermal cracking of oil to gas. So, thermal cracking of immiscible oil did not significantly occur in HP experiments, and no significant decrease in oil

content was observed from the HP experiments, even the one with the highest experiment temperature (365°C, equivalent to the highest thermal maturity level).

Results and discussion 2: Derivation of Bakken Kinetics

For derivation of Bakken Kinetics, the transformation ratios (X = expelled oil yield/maximum oil yield) were used first to calculate the extent of expelled oil generation ($f(\varepsilon)$) by using the first-order function shown as follows: $f(\varepsilon)=Ln(1/(1-X))$. The first-order rate plot of Ln (1/(1-X)) vs experiment time (hours) for upper Bakken composite sample is shown in Figure 4. Oil yield results of the HP experiments with power outage are not included for the derivation of rate constants but shown as a reference. For duplicate HP experiment conductions at the thermal condition of 330 °C/120h, an averaged oil yield value and its associated Ln (1/(1-X)) were used for rate constant acquisition. The experiment temperatures, rate constants and correlation coefficients, and zero-time intercepts for the upper Bakken composite sample at five temperatures are summarized in Table 2. As shown in Figure 4, linearity of the time-series HP experiments (at 300, 320, 330, 340, and 350°C), with R^2 values close to 1, effectively implies that the pseudo first-order reaction occur in the heated upper Bakken composite sample in HP experiments at these temperatures.

Figure 4. First-order rate plot of Ln{1/[1-X]} vs. Time(h) for immiscible oil generation from upper Bakken composite sample in the time-series HP experiments.

Zero-time intercepts of these linear relationships are positive values. They increase with experimental temperatures, probably because of some oil generation during the a ~1h heat-up period from room temperature and a ~20h cool-down times back to the room temperature. During the warm-up and cool-down times, some little amount of oil may be generated and expelled from upper Bakken composite sample, and this effect was enhanced because of increased thermal conditions at higher experiment temperatures and the increasing positive intercepts. However, the zero-time intercepts are unexpectedly high, probably due to three hypotheses: (1) marginal maturity of upper Bakken composite sample with more *in-situ* bitumens to start with; (2) low activation energy (10~20 kcal/mole) for

conversion of kerogen to bitumen; (3) *in-situ* oil or early-generated oil during early maturation of kerogen. More details related to high Zero-time intercepts are discussed by Jin (2014).

Table 2. Summary table with experiment temperatures, rate constants, and associated intercepts derived from the first-order rate plot for the times-series HP experiments

HP Temperature		Rate constant			Intercept			
Celcius (°C)	1/K (Kelvin)	k(/h)	Ln (k)	Correlation Coefficient (R^2)	Zero-time intercept (Ln [1/(1-X)])	Ln(zero-time intercept)	Transformation Ratio (X)	Oil Yield (g)
350	0.001605	0.02090	-3.868	0.99995	0.59703	-0.5158	0.4496	8.0021
340	0.001631	0.00885	-4.727	0.98350	0.32070	-1.1372	0.2744	4.8836
330	0.001658	0.00455	-5.393	0.99794	0.21152	-1.5534	0.1906	3.3935
320	0.001686	0.00213	-6.152	0.97697	0.16348	-1.8111	0.1508	2.6845
300	0.001745	0.00085	-7.070	0.99273	0.04647	-3.0689	0.0454	0.8082

The Arrhenius plot was made by cross-plotting the natural logarithm of derived rate constants (ln(k)) with the reciprocal of their absolute experimental temperature (1/K) and shown in Figure 5. Bakken oil generation kinetics (the activation energy, E_a, and frequency factor, A_0) can be obtained from the slope and intercept values of the regressed linear relationship. The 300°C rate constant (red square) is apparently off the main trend based on rate constants at higher temperatures (blue diamonds), indicating that slightly more immiscible oil generation may occur in the 300 °C time-series HP experiment of upper Bakken composite sample. Apart from the 300°C rate constant point, the remaining rate constant points present a well-established linearity (Figure 5). So, the 300°C rate constant point was excluded from the linear Arrhenius relationship for derivation of unadjusted E_a and A_0. As a result, the activation energy (E_a) was calculated at 55.17 kcal/mole, and the frequency factor (A_0) at 3.89×10^{27} m.y.$^{-1}$.
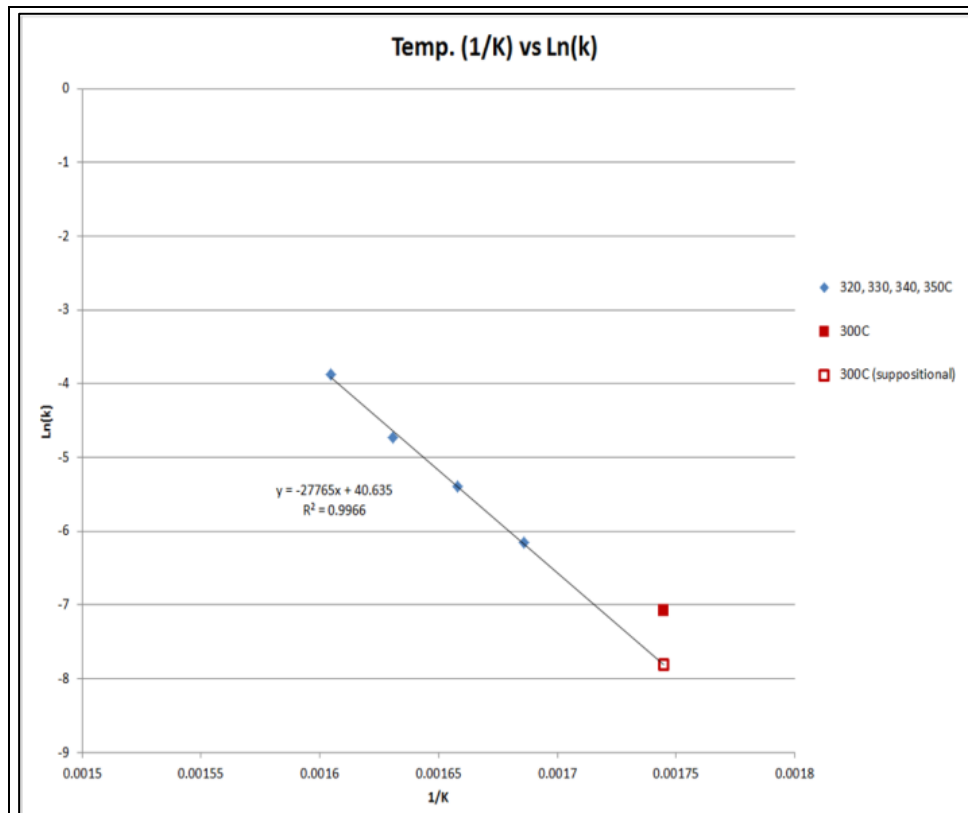

Figure 5. Arrhenius plot of the rate constants determined from the time-series HP experiments for Upper Bakken Comp. #1 shale and the suppositional rate constant for 300°C extrapolated from the linear regression relationship.

Adjustment of kinetic model for the upper Bakken composite sample by appropriate correction seems necessary to capture low temperature (300 ºC) reactions. By extrapolation from the main trend, the suppositional 300ºC rate constant can be estimated (red hollow square with rate constant k calculated at 0.000407) and used to establish a linear rate constant equation in the first-order rate plot. The intercept value (0.04647) of the linear regression equation for the 300ºC time-series HP experiment in Figure 4 was still used to derive the suppositional linear rate constant equation, which is expressed as y=0.000407x+0.04647 (Figure 6). Based on this suppositional linear equation, the extent of oil generation (Ln[1/(1-X)]) for the 300 ºC HP experiments with different periods (72h, 96h, and 240h) were estimated and shown as hollow symbols for 300 ºC suppositional in Figure 6. The dashed regression line through these data points reproduced the utilized suppositional equation.
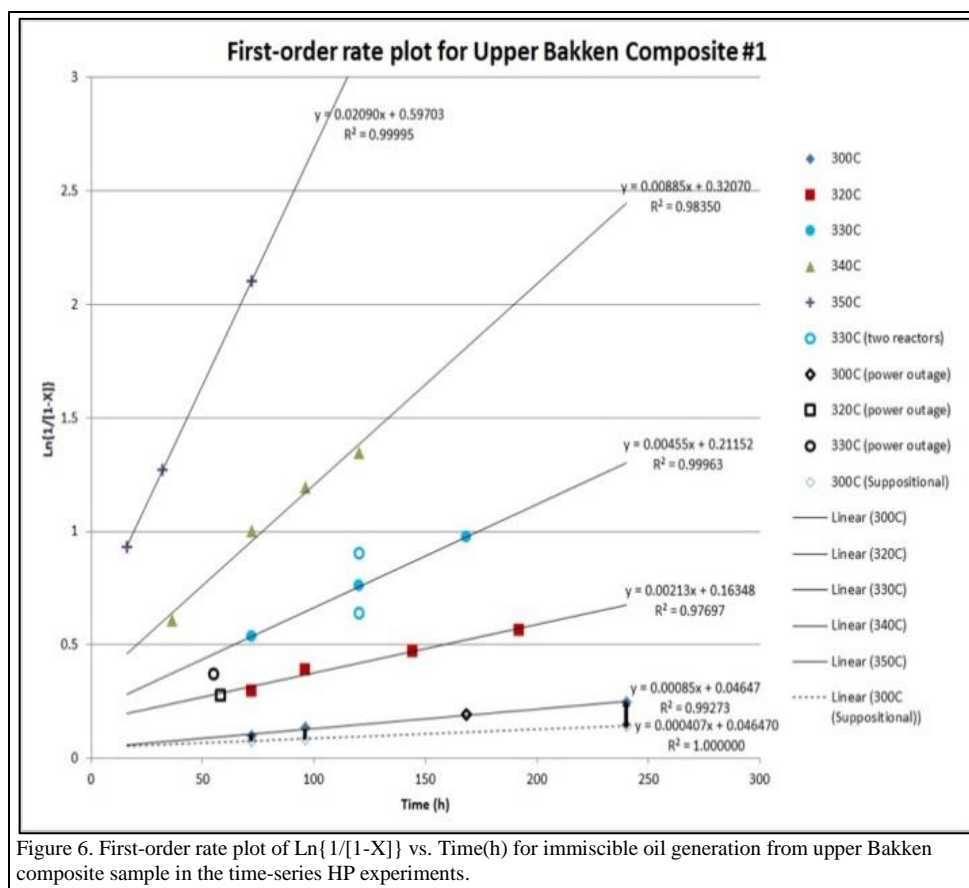

Figure 6. First-order rate plot of Ln{1/[1-X]} vs. Time(h) for immiscible oil generation from upper Bakken composite sample in the time-series HP experiments.

The suppositional rate constant value (0.000407) may mainly correspond to the pseudo-first-order reaction from bitumen to immiscible oil in the 300ºC time-series HP experiments, since it is extrapolated from the main trend of the high temperature time-series HP experiments, in which the pseudo-first-order reaction from bitumen to immiscible oil is intensively occurring (immiscible oil increase in the Figure 3). But there is a 0.000443 gap (0.00085 minus 0.000407) between the suppositional and true rate constant values, suggesting enhanced rate constant by another potential source of oil for the 300ºC time-series HP experiments. After calculations, maximum yield of this extra oil from 240h HP experiment for the 300ºC time-series equals to 8.6% of the maximum oil yield, 1.534g. This is probably because the actual petroleum generation processes are more complex than generalized previous concept, and the modified interrelationships between various organic phases are proposed in Figure 7.

The Main Path (Oil A, Figure 7) represents the previously generalized concept of the consecutive irreversible pseudo-first-order reactions between four organic phases (Engler, 1913; Hubbard and Robinson, 1950), and new proposed side path may contribute extra immiscible oil (Oil B) observed in the 300ºC time-series HP experiments, which is probably generated directly from kerogen. So, oil yields in the 300ºC time-series of HP experiments consist

of two components: the generation of Oil (A) associated with the rate constant at 0.000407, that of Oil (B) at 0.000443, and rate constant of all Oil (A) and Oil (B) together equaling to 0.00085.
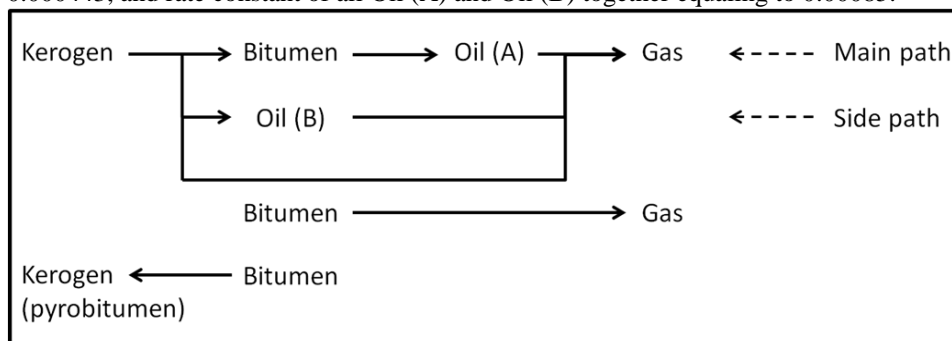

Figure 7. Proposed interrelationships between various organic phases (modified from Engler, 1913; Hubbard and Robinson, 1950).

The derivation of Bakken kinetics based on the oil generation during the main oil window is probably the more important focus in this study. Due to longer duration (240h) 300ºC time-series HP experiment and up to 80% completion of maximum bitumen generation, 1.534g could be considered as the maximum yield of Oil (B) directly generated from kerogen during early maturation of upper Bakken composite sample. An adjustment for the kinetic model for upper Bakken composite sample was conducted by subtraction of 1.534g from oil yields of all temperatures- and time-series HP experiments to represent the main oil window. After subtraction, the adjusted oil yields, transformation ratio, and extent of oil generation (Ln[1/(1-X)]) were recalculated for each temperatures- and time-series HP experiment. Then, the modified first-order rate plot of adjusted (Ln[1/(1-X)]) vs. Time (h) was created and shown in Figure 8. Surprisingly, the derived slope values for time-series HP experiments at higher temperatures ($\geq$320°C) are same as before. A new Arrhenius plot after adjustment was created and shown in Figure 9. The five rate constant points present a near perfect linear Arrhenius relationship, with R^2 up to 0.99856. The slope value of this linear Arrhenius regression equation allows calculation of the adjusted E_a (53.79 kcal/mole). The adjusted A_0 associated with this adjusted activation energy is estimated at 1.25×10^{27} m.y.$^{-1}$.
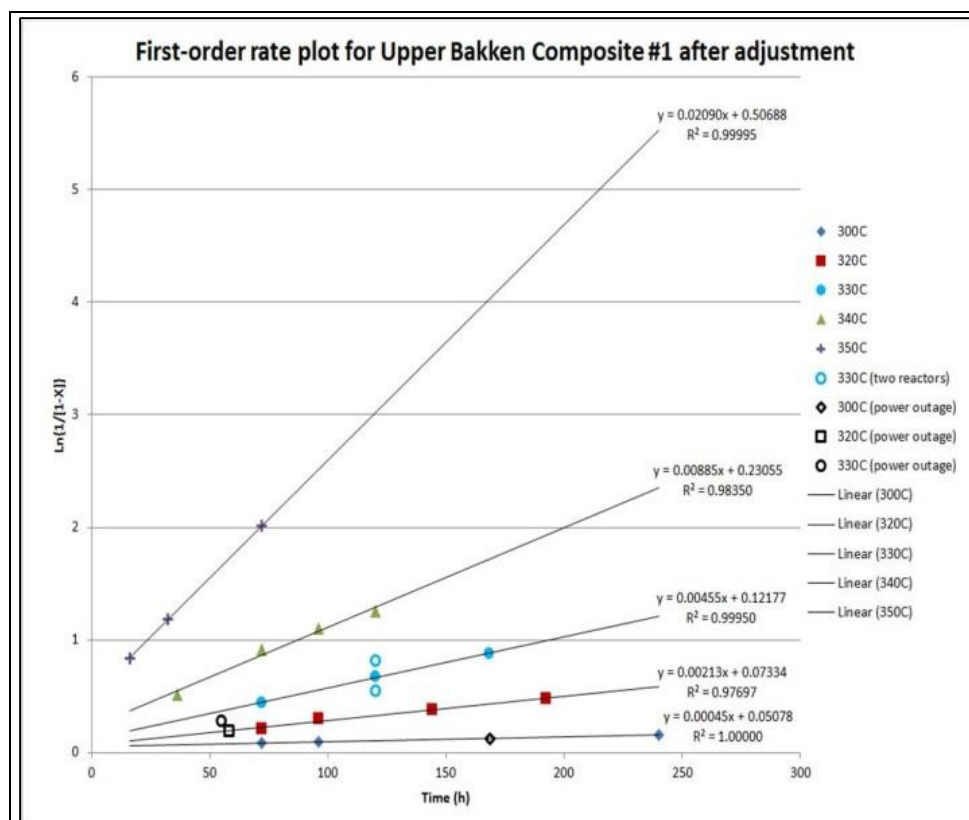

Figure 8. First-order rate plot of adjusted Ln{1/[1-X]} vs. Time(h) for the immiscible oils generated from time-series HP experiments of Upper Bakken Comp. #1 shale.
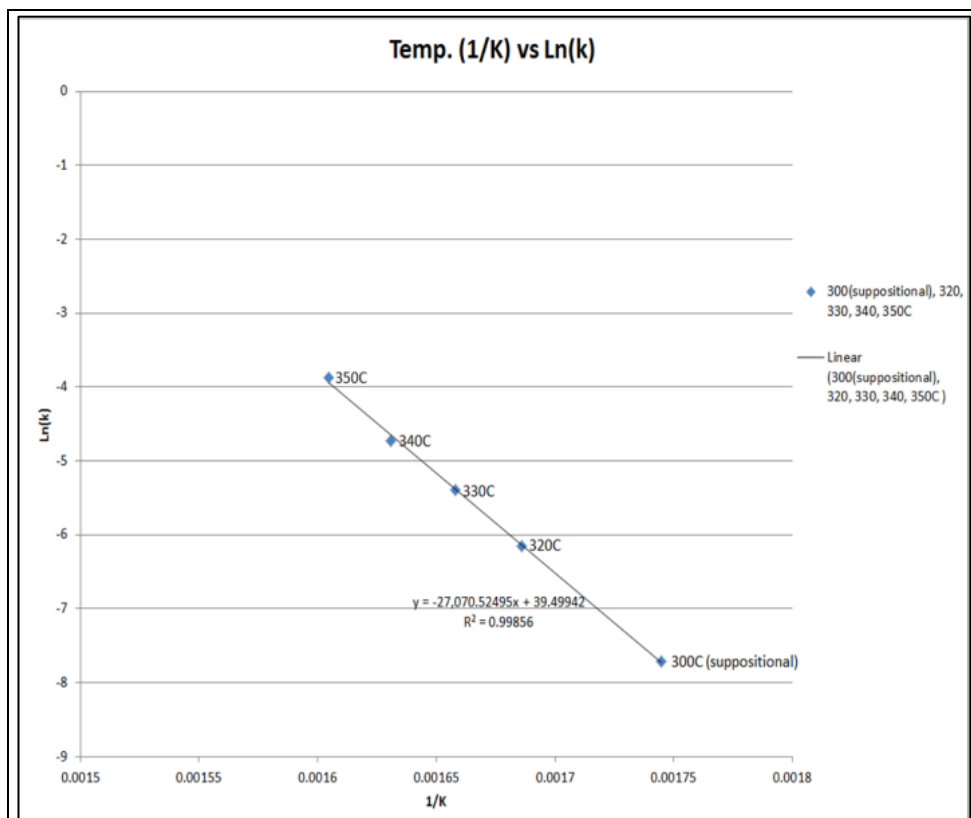
Figure 9. Arrhenius plot of the adjusted rate constants determined from the time-series HP experiments for Upper Bakken Comp. #1 shale. Bakken kinetic can be calculated from the slope value.

Results and discussion 3: Testing and implication of Bakken Kinetics

Duplicate aliquots of the upper Bakken Composite sample after bitumen extraction was sent to the Weatherford Laboratory for open-system kinetic analysis. The open-system kinetics for upper Bakken composite sample is summarized as follows: E_a=54 kcal/mole, with 54% of reaction, and A_0= 1.5509×10^{14}sec^{-1} (4.89427×10^{27}m.y.$^{-1}$) in the discrete model. After derivation of kinetic information (the open- system, adjusted HP, and unadjusted HP kinetics) from open-system pyrolysis and hydrous pyrolysis analyses, it is important to conduct the actual modeling to assess their reliability of these kinetics values.

The kinetic parameters for immiscible oil generation obtained in this study were applied to a model of the Williston Basin using the BasinMod2011 (Platte River Associates, Boulder). The Carus Fee 21-19 well (W102.9640235, N47.5426488) was chosen for basin modeling analysis, because the information about the depositional history, corrected bottom hole temperature (BHT), and the inferred transformation ratio of Bakken shale in this well is available. The burial history was established for the Carus Fee 21-19 well based on its depositional history and shown in Figure 10.

The transformation ratios for oil generation within Bakken shales through geologic time can be simulated based on the three sets of kinetic values, and their individual variations are shown in Figure 11. It is an apparent indication from Figure 11 that the simulation based on the open-system kinetics yields the earliest timing of initial oil generation (TR>0), as early as 320Ma, whereas those based on adjusted and unadjusted HP kinetics possesses a similar timing of initial oil generation, at about 76Ma. The occurrence order for the main stage of oil generation (corresponding to the TR threshold of 0.25) is the open-system, adjusted HP and unadjusted HP kinetics (Figure 11). From the modeling for extent of oil generation based on the open-system, adjusted and unadjusted HP kinetics, their present-day transformation ratio is 0.77 (in the late oil generation stage), 0.55 (in the main oil generation stage), and 0.35 (in the main oil generation stage), respectively. Determination of the more reasonable and representative

kinetics among these three kinetics values for the actual extent of oil generation in the Bakken Petroleum System is very important.
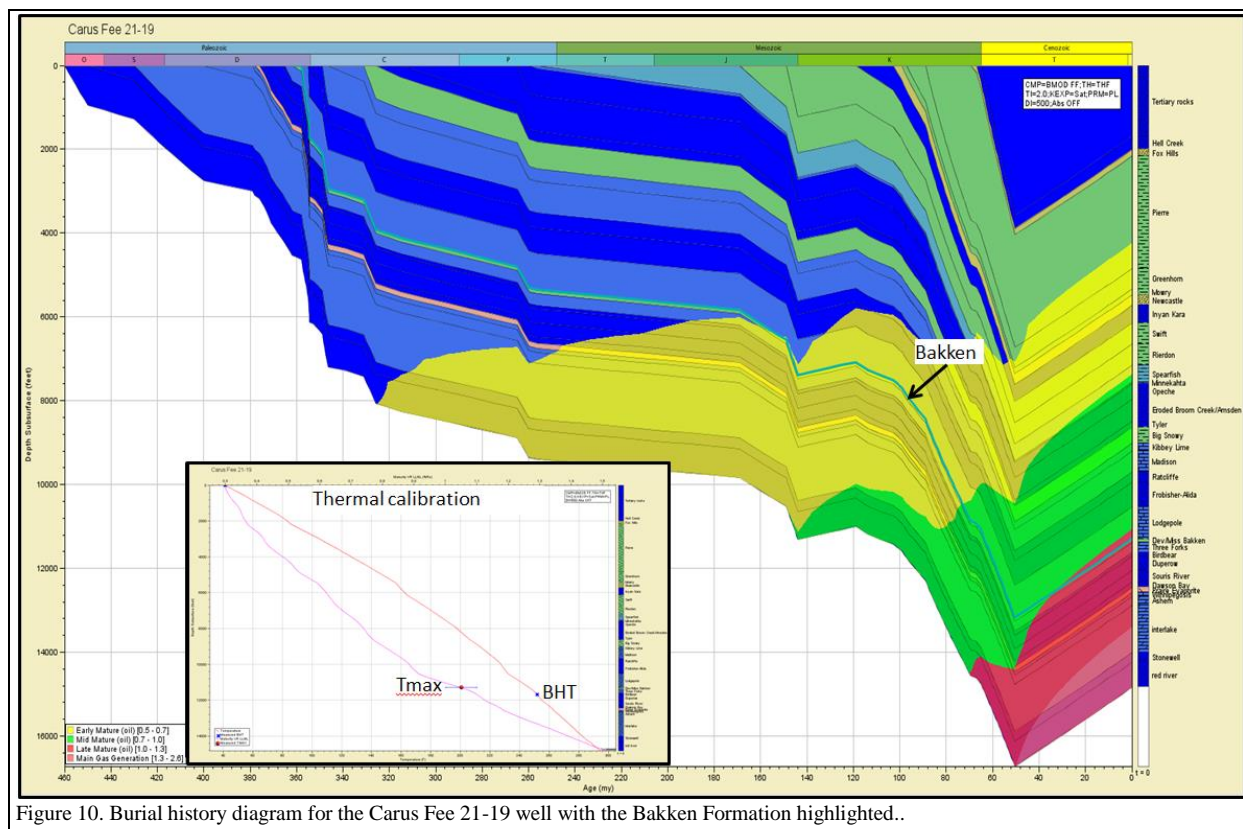

Figure 10. Burial history diagram for the Carus Fee 21-19 well with the Bakken Formation highlighted..

Lewan et al., (2013) indicated that HI of upper Bakken shale is a good proxy for kerogen atomic H/C ratio, which is directly related to the amount of immiscible oil generated and expelled from a source rock based on hydrous pyrolysis. Based on such relationship between HI and atomic H/C ratio in the upper Bakken shale, Lewan et al. (2013) suggested that the onset of oil generation occurred at a HI of 450 mg HC/g OC, although there is no correlative relationship exists between HI and atomic H/C ratio for HI values greater than 450 mg HC/g OC. In addition, based on the relationship between atomic H/C ratios and transformation ratios (TR) for extent of oil generation from HP, the correlative relationship between HI and TR was further established (Table 3). As a result, Lewan et al. (2013) indicated that for upper Bakken shale, a TR of 0.10 occurs at an HI of 400, 0.25 at an HI of 300, 0.47 at an HI of 200, and 0.77 at an HI of 100. The measured HI values for the upper Bakken shale in the Carus Fee 21-19 well is averaged at 166.3 mg HC/g OC. Based on the correlative relationship between TR and HI in the study of Lewan et al. (2013), the present-day TR for the Carus Fee 21-19 well was estimated at 0.535. After comparison, the adjusted HP kinetics provides the best affinity (only 0.015 TR difference) with the TR inferred from HI, whereas those modeled from the open-system kinetics. Accordingly, the modeling results from the adjusted HP kinetics are most correlative with the present-day extent of oil generation from the type II kerogen in Bakken shales. Hence, it is recommended that the adjusted HP kinetics derived from this study can be applied to the Bakken shales for derivation of transformation ratio of oil generation in other areas of the Williston Basin.

The adjusted HP kinetics is also applied to another three wells in eastern Williston Basin (locations shown in Figure 12): the Deadwood Canyon 43-28 (west of the Parshall Field), N&D 1-05H (in the Parshall Field), and Dobrinski 18-44 well (east of the Parshall Field), to simulate their extent of oil generation (transformation ratio). From the simulation results based on the adjusted HP kinetics, the present-day transformation ratio for Bakken shales in the Deadwood Canyon 43-28 well is 0.12 (in the early oil generation stage). The average of measured HI values for the Bakken shales in the Deadwood Canyon 43-28 well was calculated at 399.8 mg HC/g OC. Based on the direct indication of TR from 400 mg HC/g OC of Bakken shales (Lewan et al., 2013), the HI-derived TR for the Deadwood Canyon 43-28 well should be at 0.10. Once again, the modeled TR based on adjusted HP kinetics is

proved to have an affinity with the TR inferred from HI. So, the extent of oil generation in the Deadwood Canyon 43-28 well is about 10 to 12 % of total generation. Similarly, based on the modeling, the Bakken shales in the wells N&D 1-05H are thermally immature and having a TR at about 0.0004 (0.04% of oil generation). The Bakken shales in the Dobrinski 18-44 well are very immature with almost no oil (TR≈0.00002 or 0.002%) generated.
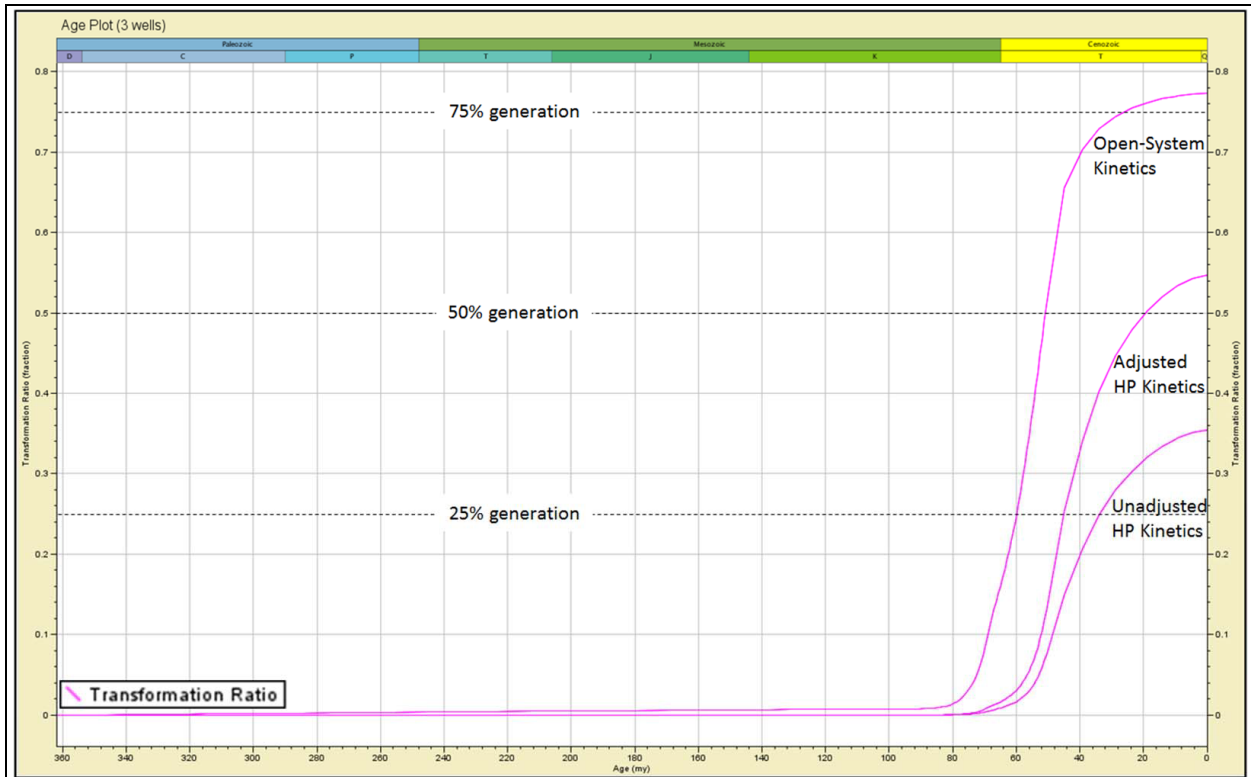

Figure 11. Modeled transformation ratio based on three kinetics for Bakken shales in the BasinMod

Table 3. An integrated threshold scheme was made for Bakken shales. Thresholds of transformation ratios and HI are from Lewan et al. (2013)

	Transformation Ratio (TR)	HI(mg HC/g C)	Measured Tmax (°C)	Extent of oil generation
Thresholds	TR=0	600-450	425-431	No oil generation
	0<TR<0.1	450-400	431-432.5	Incipicient oil generation
	0.1<TR<0.25	400-300	432.5-435	Early oil generation
	0.25<TR<0.47	300-200	435-440	Main oil generation
	0.47<TR<0.77	200-100	440-450	Main oil generation
	0.77<TR	<100	>450	Late oil generation

A west-east cross-section through these three and another two wells is illustrated in the Figure 13. It is indicated from the cross-section that there is a nice correlation between the wireline log (Resistivity) and vertical profiles of geochemical maturity parameters (Tmax and HI). The cutoff for resistivity log is set at 100 OHMM, that for (uncorrected) Tmax log at 431°C, and that for HI log is 450 mg HC/g OC based on the threshold values in Table 3. The resistivity and Tmax maturity results indicate that the upper and lower Bakken shales in Deadwood Canyon 43-28H well are thermally mature, those in Braaflat 11-11H well marginally mature, those in N&D 1-05H and St Andes-151-89 2413H-1wells immature, and those in Dobrinski 18-44 well very immature, which shows correlative results with the modeling results for maturity variation across the Sanish/Parshall area.

In Figure 13, as more basinward, HI is steadily decreasing, and simultaneously, the Tmax and resistivity are increasing due to elevated maturity and higher saturation of oil in shales. The N&D well is located in the Parshall Field. The Tmax, resistivity, and HI logs in this well indicate that Bakken shales in this area are immature with very minimal extent of oil generation, but significant amount of oil resources are discovered in this area. The maturity of Bakken shales in this area is probably not mature enough to generate such enormous amounts of produced oil. So, most of the produced oil was probably migrated from deeper areas, because just west to the Parshall/Sanish area, there are much more mature Bakken shales generating and expelling significant amounts of oil, which can short-laterally migrate to the Parshall Field. Therefore, it is suggested that significant produced oil in the Parshall area may be primarily from deeper parts of basin via short lateral-migration in the mid-Bakken. Moreover, it is suggested from the previous discussions that the maturity is the primary control on Bakken oil generation and expulsion.
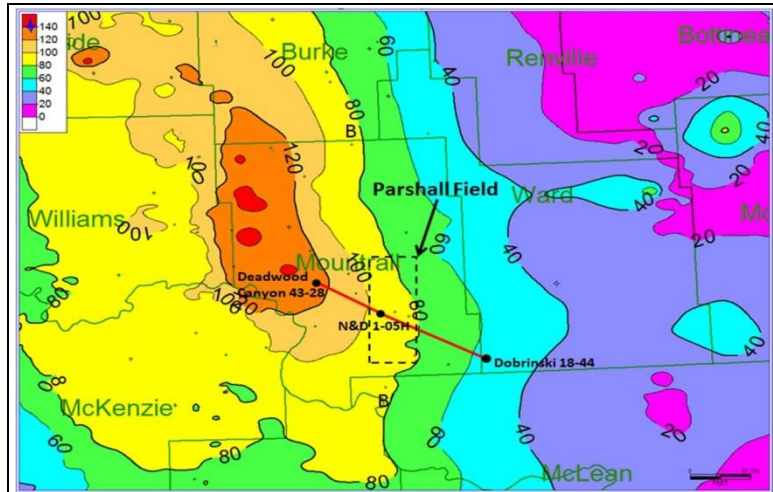

Figure 12. Isopach map of the Bakken Formation in the central and eastern Williston Basin with location of wells for basin modeling application indicated.
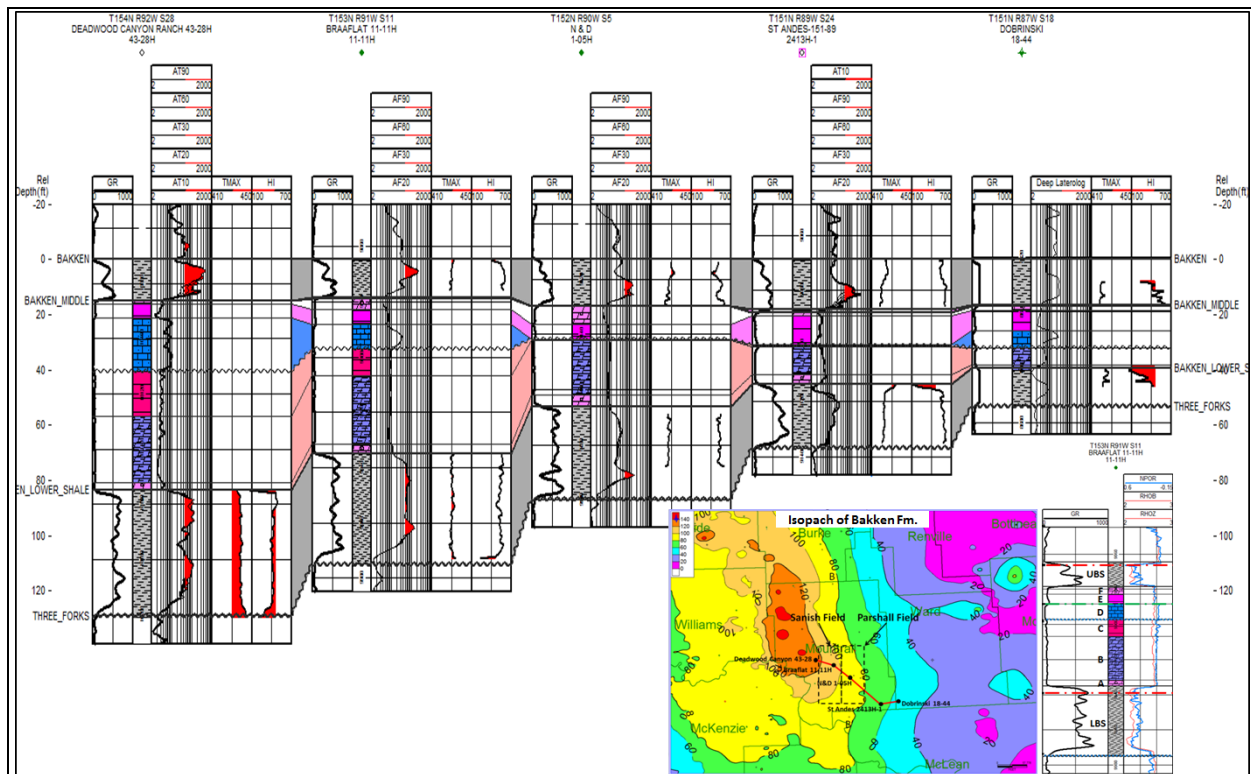

Figure 13. A west to east cross-section through the Parshall Field showing the maturity variation across maturity boundary

Conclusions

Oil-generation kinetics were experimentally derived by the method of hydrous pyrolysis from the immature type II kerogen upper Bakken composite sample collected from Canada. The derived representative oil-generation kinetics for Bakken shales is very important for evaluation of the potential oil reserves within Bakken Petroleum System. As previously suggested by many workers, the concept that bitumen generated from kerogen is the main product-precursor for immiscible oil was reconfirmed by the hydrous pyrolysis experiments in this study. Most of bitumen was significantly generated from kerogen during early maturation (300-320°C experiment temperature), and the following dramatic decrease in bitumen content was paralleled with a steady increase in expelled oil and gas content during the main oil window (320-355°C experiment temperature). Because of the slight maturity of the collected sample, higher zero-time intercept oils were observed from time-series HP experiments, which is probably due to the high relative content of in-situ bitumen in the starting materials. Another factor may be induced by the proposed direct Oil(B) generation from kerogen during early maturation of upper Bakken composite sample in this study. After the whole series of HP experiments, the kinetics (E_a and A_0) of upper Bakken composite sample were calculated and summarized as follow: (E_a= 55.17 kcal/mole and A_0= 3.89×10^{27} m.y.$^{-1}$) for unadjusted kinetics; (E_a= 53.79 kcal/mole and A_0= 1.25×10^{27} m.y.$^{-1}$) for adjusted kinetics, which is reasonable and representative kinetics for Bakken shales after 1D testing and more correlation with other independent results.

The kinetic parameters for immiscible oil generation obtained in this study were applied to the actual thermal-burial history model (the Carus Fee 21-19 well) in the Williston Basin using BasinMod2011. From the modeling based on the open-system, adjusted and unadjusted HP kinetics, their zero-time or present-day transformation ratio (TR) is 0.77 (in the late oil generation stage), 0.55 (in the main oil generation stage), and 0.35 (in the main oil generation stage), respectively. After comparison with the HI-derived TR according to the study of Lewan et al. (2013), the modeling results from the adjusted HP kinetics are most correlative with the present-day extent of oil generation from the type II kerogen Bakken shales. Hence, the adjusted HP kinetics were recommended for estimation of the oil generation from the Bakken shales in other areas of the Williston Basin. The adjusted HP kinetics were applied to three wells in eastern Williston Basin: the Deadwood Canyon 43-28, N&D 1-05H, and Dobrinski 18-44 wells, to simulate their extent of oil generation. The simulation results indicated that the present-day transformation ratio for Bakken shales in the Deadwood Canyon 43-28 well is 0.12, that of the Bakken shales in the N&D 1-05H well is about 0.0004, and that of the Bakken shales in the Dobrinski 18-44 well in only 0.00002, which correlate well with their thermal maturity.

The west-east cross-section through the Parshall Field with Tmax, resistivity, and HI logs shown indicated that Bakken shales in the Parshall area are immature with very minimal extent of oil generation, but significant amount of oil resources are discovered in this area. The maturity of Bakken shales in this area is probably not mature enough to generate enormous amounts of produced oil. So, most of the produced oil was probably migrated from deeper areas, because just west to the Parshall/Sanish area, there are much more mature Bakken shales generating and expelling significant amounts of oil, which then laterally migrated to Parshall Field through the middle Bakken member. Therefore, it is implied that significant produced oil in the Parshall area may be primarily from deeper parts of basin through short lateral-migration in mid-Bakken. It is suggested that the maturity should be the primary control on oil generation and expulsion.

References

Engler, K.O.V., 1913. Die Chemie Und Physik Des Erdols., vol. 1.S. Hirzel, Leipzig.

Gerhard, L. C., S. B. Anderson, and D. W. Fischer, 1990, Petroleum geology of the Williston Basin: *AAPG* Memoir, v. 51, p. 507-559.

Hubbard, A.B., and W.E. Robinson, 1950, A thermal decomposition study of Colorado oil shale: *U.S. Bureau of Mines Report of Investigations* 4744.

Hunt, J.M., M.D. Lewan, J.C. Hennet, 1991, Modeling oil generation with time-temperature index graphs based on the Arrhenius Equation: *AAPG Bulletin*, v. 75, p. 795-807.

Jin, H., M.D. Lewan, and S.A. Sonnenberg, 2016. [PS]Bakken Oil-Generation Kinetics by Hydrous Pyrolysis and its Testing in 1-D Model: *AAPG*, *Search and Discovery*, #41907, Calgary, AB, Canada, 5p.

Jin, H., and S.A. Sonnenberg, 2015. Source Rock Potential and Sequence Stratigraphy of Bakken Shales in the Williston Basin: *Unconventional Resources Technology Conference 2015*, #2169797, San Antonio, TX, USA, 20p.

Jin, H., 2014. Source rock potential of the Bakken shales in the Williston Basin, North Dakota and
     Montana: Doctoral dissertation, Colorado School of Mines, Golden, Colorado, 220 p.

Jin, H., and S.A. Sonnenberg, 2014. Characterization for Source Rock Potential of the Bakken Shales in the
     Williston Basin, North Dakota and Montana: *AAPG, Search and Discovery*, #80356.

Jin, H., and S.A. Sonnenberg, 2013. Characterization for Source Rock Potential of the Bakken Shales in the
     Williston Basin, North Dakota and Montana: *Unconventional Resources Technology Conference 2013*,
     #1581243, Denver, CO, USA, 10p.

Jin, H., S.A. Sonnenberg, and J. F. Sarg, 2012. [PS]Source Rock Potential of the Bakken Shales in the Williston Basin,
     North Dakota and Montana: *AAPG, Search and Discovery*, #20156.

Jin, L., et al. Improving Oil Transportability Using CO2 in the Bakken System - A Laboratorial Investigation. SPE-
     178948, *Proceedings of the SPE International Conference & Exhibition on Formation Damage Control*,
     Lafayette, LA, Feb. 24–26, 2016.

Jin, L., et al. A Systematic Investigation of Gas-based Improved Oil Recovery Technologies for the Bakken Tight
     Oil Formation. URTeC-2433692, *Proceedings of the Unconventional Resources Technology Conference*,
     San Antonio, TX, Aug. 1-3, 2016.

Jin, L. et al. Improving Oil Recovery by Use of Carbon Dioxide in the Bakken Unconventional System: A
     Laboratory Investigation. *SPE Reservoir Evaluation & Engineering-Reservoir Engineering*, Dec. 2016.

LeFever, J. A., R. D. LeFever, and S. H. Nordeng, 2011, Revised nomenclature for the Bakken Formation
     (Mississippi-Devonian), North Dakota: The Bakken-Three Forks Petroleum System In the Williston Basin,
     Rocky Mountain Association of Geologists Publication, p.11-26.

Lewan, M.D., 1985, Evaluation of petroleum generation by hydrous pyrolysis experimentation. *Philosophical
     Transactions of the Royal Society of London*, Series A 315, p. 123-134.

Lewan, M. D., 1994, Assessing Natural Oil Expulsion from Source Rocks by Laboratory Pyrolysis, in L.B. Magoon,
     and W.G. Dow, eds., The petroleum system—from source to trap: *AAPG Memoir 60*, p. 93-117.

Lewan, M.D., K. Marra, P.G. Lillis, D.K. Higley, and S. Gaswirth, 2013, Mapping the Extent and Distribution of Oil
     Formation in the Upper Bakken Formation, Williston Basin: Abs., *AAPG Annual Meeting*, Pittsburgh,
     Pennsylvania, May 19-22, 2013.

Lewan, M.D., J.C. Winters, and J.H. McDonald, 1979, Generation of oil-like pyrolyzates from organic-rich shales:
     Science 203, p. 897-899.

Meissner, F. F., 1978, Petroleum geology of the Bakken Formation, Williston Basin, North Dakota and Montana, in
     D. Rehrig, eds., The economic geology of the Williston Basin: *Proceedings of the Montana Geological
     Society*, 24th Annual Conference, p. 207-227.

Pitman, J. K., L. C. Price, and J. A. LeFever, 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, 17 p.

Sonnenberg, S. A., and A. Pramudito, 2009, Petroleum geology of the giant Elm Coulee Field, Williston Basin:
     AAPG Bulletin, v. 93, no. 9, p. 1127-1153.

Sonnenberg, S. A., H. Jin, and J.F. Sarg, 2011, Bakken Mudrocks of the Williston Basin, World Class Source
     Rocks: *AAPG Annual Convention and Exhibition*, Houston, TX., Poster Session Presentation, *Search and
     Discovery Article # 80171*, April 10-13, 2011,
     http://www.searchanddiscovery.com/documents/2011/80171sonnenberg/ndx_sonnenberg.pdf.

Winters, J. C., J. A. Williams, and M. D. Lewan, 1983, A laboratory study of petroleum generation by hydrous
     pyrolysis, in M. Bjoroy, ed., *Advances in Organic Geochemistry*,1981: New York, John Wiley, p. 524-533.

Xu, J., D.Nandy, and S.A. Sonnenberg,2016, A Petrographic Analysis of the Lower Bakken Shale and the
     Pronghorn Member of the Bakken Formation, Williston Basin, *AAPG Pacific and Rocky Mountain Joint
     Meeting*, October 2-5, 2016, Las Vegas, NV

Xu, J. and S.A. Sonnenberg, 2016, Brittleness and Rock Strength of the Bakken Formation, Williston Basin, North
     Dakota, *Unconventional Resources Technology Conference*, August 1-3 ,2016, San Antonio, TX