PS Bakken Oil-Generation Kinetics by Hydrous Pyrolysis and its Testing in 1-D Model*

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Abstract

The lower and upper Bakken shales are world-class source rocks in the Williston Basin, sourcing reservoirs in the Bakken, upper Three Forks, and lower Lodgepole formations, which comprise the economically significant Bakken Petroleum System (BPS). A good understanding of the thermal-burial history of Bakken shales, with oil-generation kinetics as the key thermal dynamic parameter, is essential to achieve realistic charge history, which closely relates to Bakken oil presence in reservoirs of BPS across the Williston Basin. 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. 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 1.25×1027m.y.-1 for an oil-generation reaction. These kinetic parameters were tested in a well-constrained 1D 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 suggests 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.

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Background

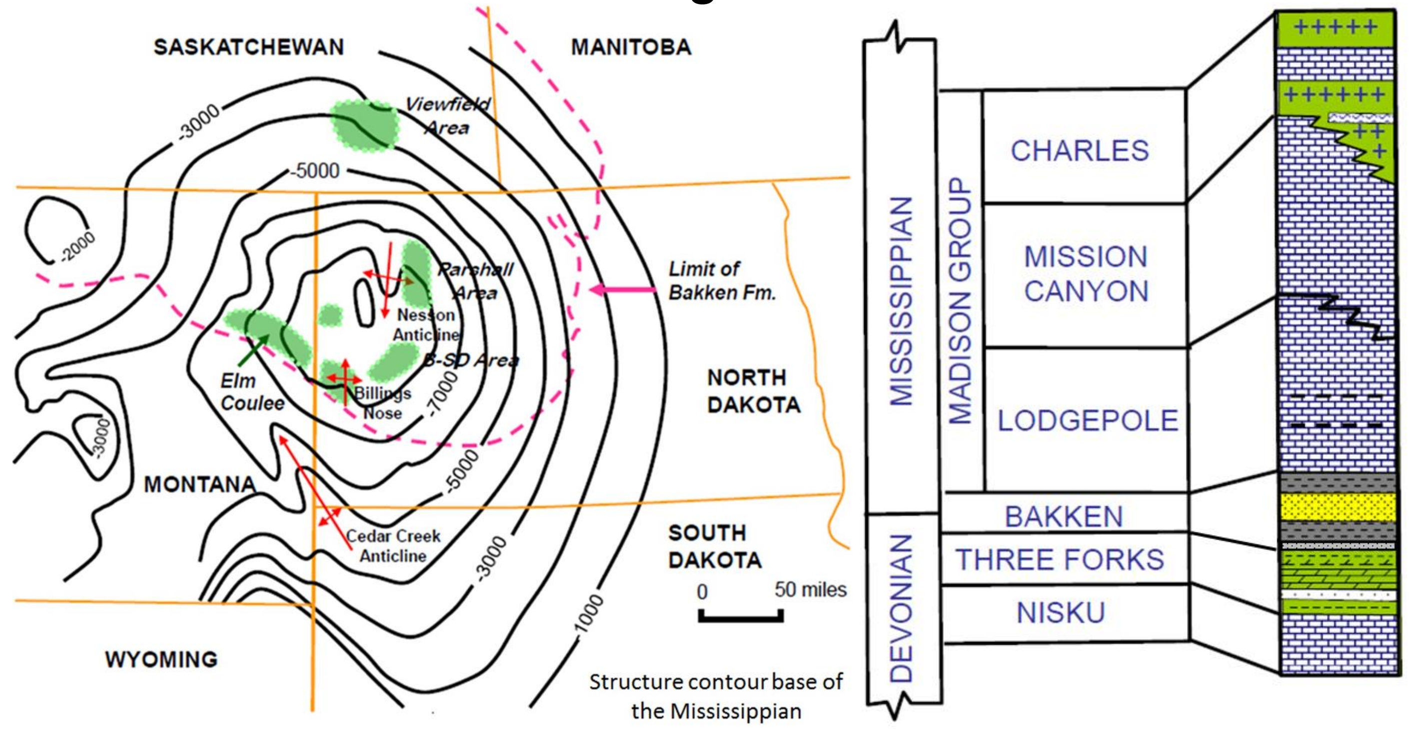


Figure 1.L Location map of the Williston Basin with major structures and oil fields in the basin (From Sonnenberg and Pramudito, 2009). Figure 1.R Generalized stratigraphic column for the Bakken Petroleum System in the Williston Basin. The lower and upper Bakken shales are world class source rocks in the Williston Basin, sourcing reservoirs in the Bakken, upper Three Forks, and lower Lodgepole formations, which comprise the economically significant Bakken Petroleum System (BPS).

Objectives

Bakken oil presence in reservoirs of BPS across the Williston Basin closely relates to realistic charge history (the timing and extent of Bakken oil generation and expulsion), which is controlled by the thermal-burial history of Bakken shales and oil-generation kinetics of kerogens. The thermal-burial history of BPS is constructed by integration of the stratigraphy, lithologies, thermal conductivity, surface temperatures, and heat flow in Williston Basin. Bakken oil-generation kinetics (frequency factor and activation energy) was derived from series of hydrous pyrolysis (HP) experiments in this study and applied to the thermal-burial history of BPS to determine timing and extent of oil generation from Bakken shales. The reasonable extrapolation from the short-time experimental process at high temperatures in lab setting to the geologic process with long periods of reactions at low temperatures in natural systems (Hunt et al., 1991) is typically accomplished by the way of the Arrhenius equation (left part), which is also combined with first-order rate function (right part):

$$f(\varepsilon) = \{A_0 \exp[-E_a/RK]\}\ t = k_T\, t = \ln[1/(1-X)],$$

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 = the fraction of expelled oil at a specific temperature (expelled oil yield / maximum oil yield).

Methods

Hydrous pyrolysis (HP) 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). All HP experiments were conducted at the USGS Organic Geochemical Laboratories, Lakewood, CO. 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. Major steps and procedures to conduct HP experiments were described by Lewan (1985 and 1993), and 200g composite sample and 400 distilled water were used in each of temperature- (300, 320, 340, 350, 355, 360, and 365°C for 72h) and time-series (different durations at 300, 320, 340, and 350°C) of HP experiments.

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_0) [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

a Atomic ratios based on elemental analyses.
b Mean random suppressed vitrinite reflectance based on limited number of measurements on solid bitumen (a.k.a. suppressed vitrinite) by Mark Pawlewicz (USGS).
c Soxhlet bitumen extraction.
d Total organic carbon content.
e SRA bulk geochemistry analysis: HI= mg S2/g TOC, OI= mg S3/g TOC, and PI=S1/(S1+S2).

Results

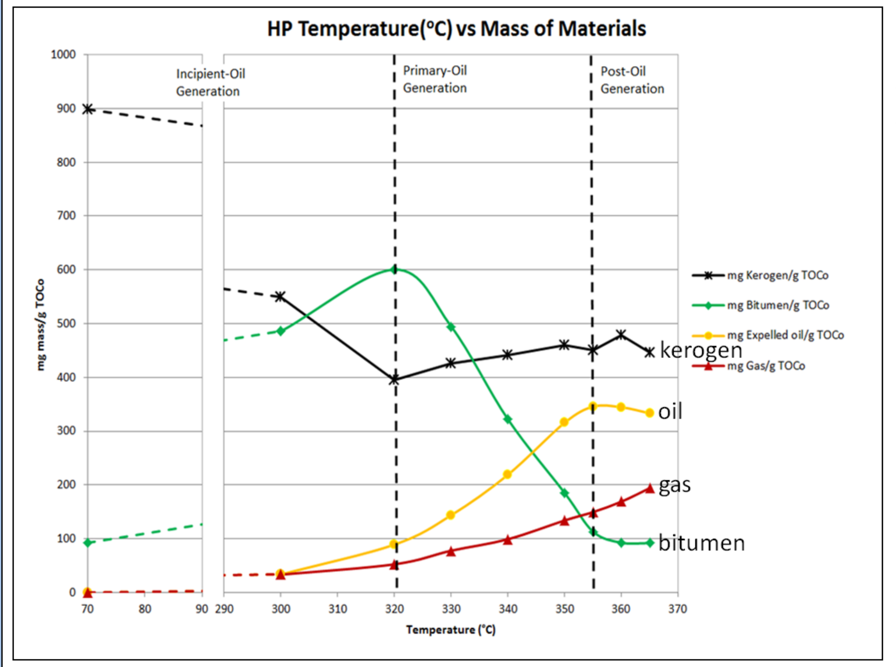
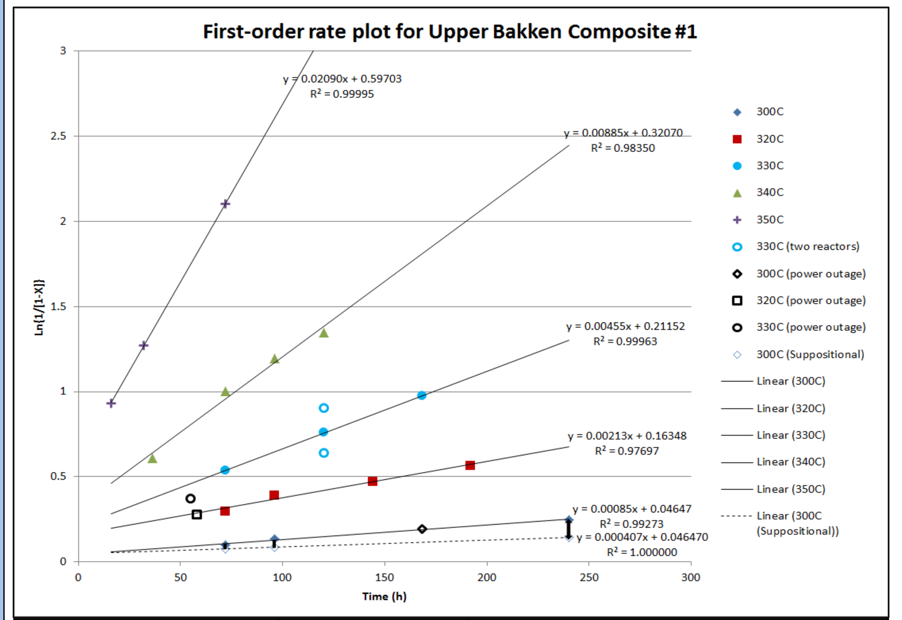
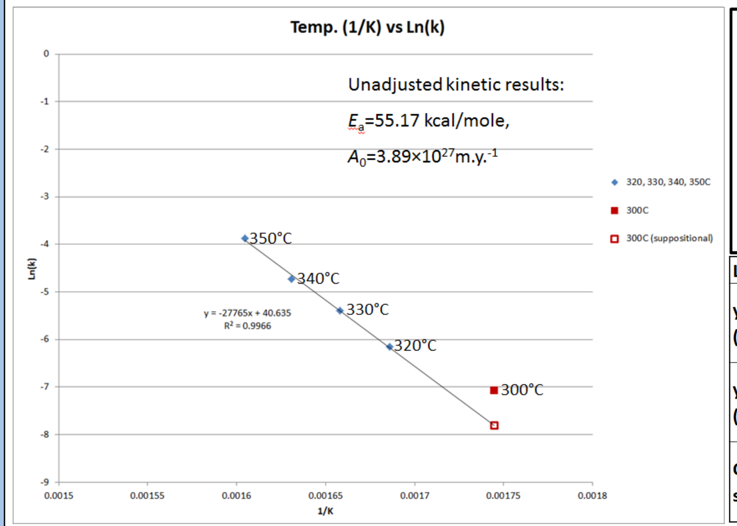


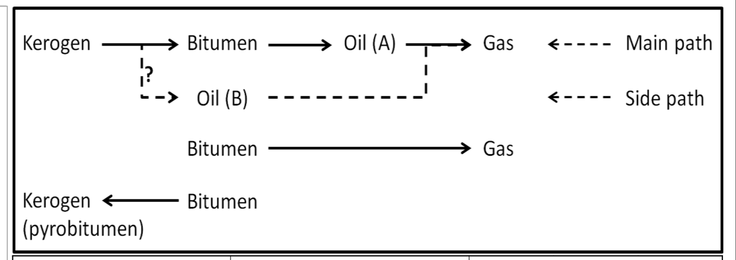
Figure 2. Numerical yields of four organic phases (kerogen, bitumen, oil and gas) with experiment temperatures (maturity) for the 72h temperature-series HP experiments. Kerogen content drops to its minimum at 320°C and then gradually increases due to pyrobitumen forming. Intense bitumen generation ranges from 300 to 320°C, and then reaches to its minimum level from 355°C. From 320 to 350°C is a main zone of immiscible oil generation, with maximum yield (17.8g per 200g sample) at 355°C. The gas is slowly being generated, with a steady increase during the whole bitumen and oil generation. This study supports the concept of Lewan (1994) that bitumen is a product-precursor for immiscible oil.



HP Temperature		Rate constant		Zero-time Intercept		
Celcius (°C)	1/K (Kelvin)	k(/h)	Ln (k)	Ln [1/(1-X)]	Transformation Ratio (X)	Oil Yield (g)
350	0.001605	0.02090	-3.868	0.59703	0.4496	8.0021
340	0.001631	0.00885	-4.727	0.32070	0.2744	4.8836
330	0.001658	0.00455	-5.393	0.21152	0.1906	3.3935
320	0.001686	0.00213	-6.152	0.16348	0.1508	2.6845
300	0.001745	0.00085	-7.070	0.04647	0.0454	0.8082

Figure 3. First-order rate plot of Ln{1/[1-X]} vs. Time(h) for immiscible oil generation from composite sample in the time-series HP and the linearity of each time-series HP implies the pseudo first-order petroleum generation. The regression slope values are the first-order rate constant, k. Table 2. Summary of experiment temperatures, rate constants, and associated zero-time intercepts. Zero-time intercepts increase with experimental temperatures, because some oils are generated during the warm-up periods of experiments. However, the zero-time intercepts are unexpectedly high, probably due to three hypothesis: (1) marginal maturity of upper Bakken composite sample; (2) low activation energy (10 to 20 kcal/mole) for conversion of kerogen to bitumen; (3) *in-situ* oil or early-generated oil during early maturation of kerogen.





Linear regression equation	Parameters	Results		
y=0.000850x+0.04647 (true)	Experiment duration (h)	72	96	240
	X	0.0966	0.1262	0.2204
	True Oil Yield (g)	1.719	2.247	3.923
y=0.000407x+0.04647 (suppositional)	Experiment duration (h)	72	96	240
	X	0.0730	0.0820	0.1342
	Estimated Oil Yield (g)	1.299	1.459	2.389
Comparison (true vs suppositional)	**(True-Estimated) Oil Yield (g)**	0.420	0.788	1.534
	(True-Estimated)/TrueX100%	24.4	35.1	39.1
	(True-Estimated)/17.8X100%	2.4	4.4	8.6

Figure 4. Arrhenius plot of the rate constants determined from the time-series HP experiments for Upper Bakken Comp. #1 shale, and 300ºC rate constant (red square) is apparently off the main trend, which physically suggests generation of more immiscible oil in the 300ºC time-series HP experiment, and the suppositional rate constant for 300ºC is extrapolated from the linear regression relationship from rates of higher temperatures (>=320ºC, mainly bitumen to oil generation process). Diagram 1 suggests this extra oil (Oil_B) may get directly generated from kerogen, apart from the main oil (Oil_A) generation from bitumen. Table 3 shows the comparison between suppositional and true oil yields for 300ºC time-series HP experiments, and maximum yield difference after the longest duration (240h) was calculated at 1.534g (about 8.6% of 17.8 maximum oil yield) as extra early-generated oil during initial kerogen maturation. Because derivation of the bitumen to oil conversion kinetics is the main objective, an adjustment for the kinetic model was conducted by subtraction of 1.534g from oil yields of all temperatures- and time-series HP experiments to eliminate the Oil(B) influence on Oil(A) generated from bitumen during the main oil window.

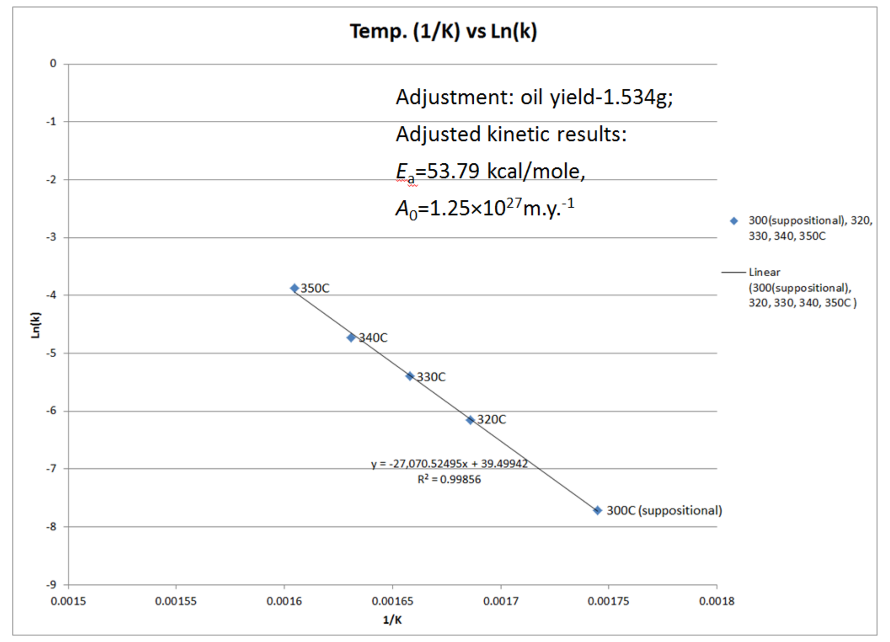


Figure 5. Arrhenius plot of the adjusted rate constants. The five rate constant points present a nearly linear Arrhenius relationship. The slope value of this linear Arrhenius regression equation allows calculation of new E_a (53.79 kcal/mole), which is lower than its unadjusted counterpart (55.17 kcal/mole, Fig. 4). The A_0 associated with this adjusted activation energy is calculated at 1.25×10^{27}m.y.$^{-1}$, which is also lower than its unadjusted counterpart (3.89×10^{27}m.y.$^{-1}$, Fig. 4). Open-system kinetics of the same sample was measured by Source Rock Analyzer in Weatherford lab as follow: E_a=54 kcal/mole, A_0=4.89×10^{27}m.y.$^{-1}$.

1D Model Testing

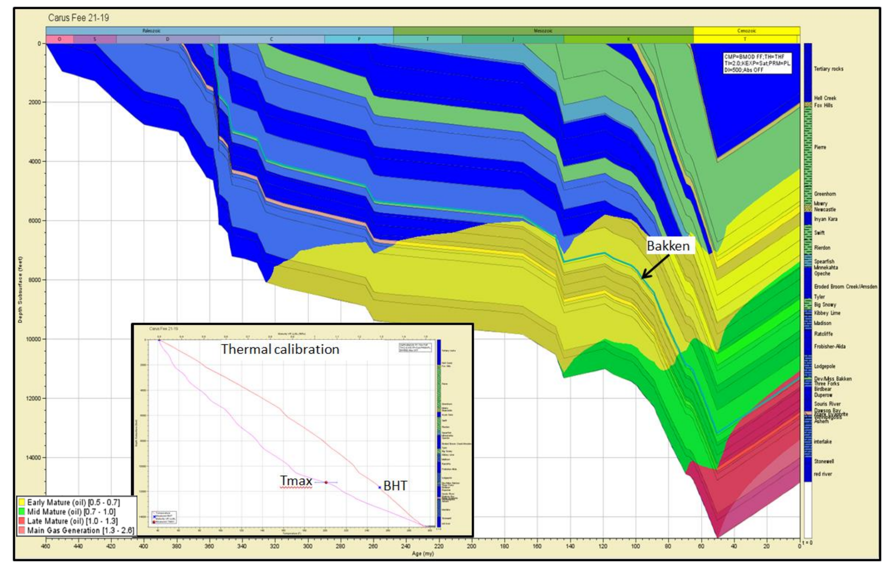


Figure 6. The kinetic parameters for immiscible oil generation in this study were applied to a model in the Williston Basin using the BasinMod2011. The Carus Fee 21-19 well (W102.9640235, N47.5426488) was chosen for basin modeling analysis, because its information about the depositional history, corrected bottom hole temperature (BHT), and the inferred transformation ratio (TR) of Bakken shale is available. After thermal calibration of Tmax and corrected BHT , the maturity windows were modeled for the Carus Fee 21-19 well and displayed with the burial history.

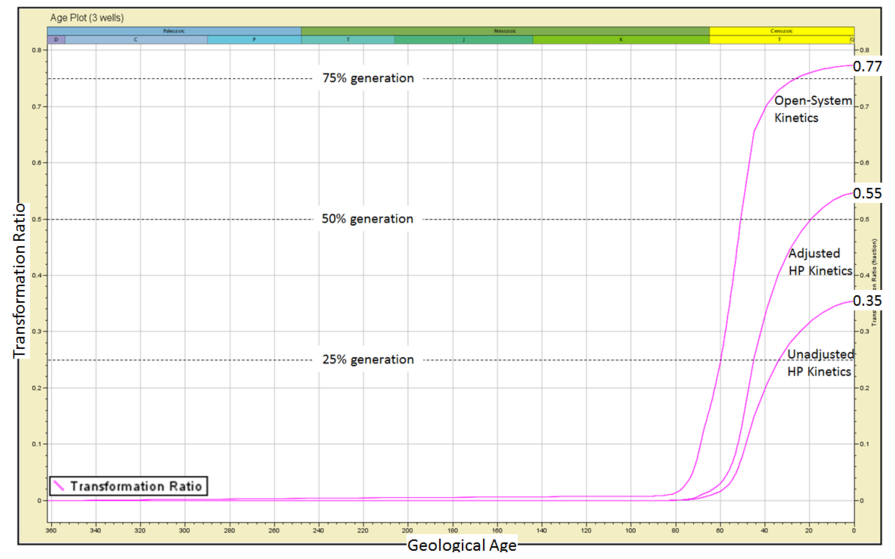


Figure 7. Kinetics from two analytical methods (the adjusted and unadjusted kinetics from HP and open-system kinetics from SRA) was applied to the calibrated thermal-burial history model of the Carus Fee 21-19 well. The transformation ratios for oil generation within Bakken shales through geologic time was simulated based on the three kinetic values, and their TR modeling outcomes are shown in Fig. 7. Lewan et al., (2013) indicated that HI of upper Bakken shale is also a good proxy for kerogen atomic H/C ratio, which can be directly related to the amount of immiscible oil generated and expelled from a source rock based on hydrous pyrolysis (shown in left part of Table 4). 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 (Table 5). So, based on the correlative relationship between TR and HI of Lewan's study, the present-day TR for the Carus Fee 21-19 well was estimated at 0.535.

Table 4

	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

Table 5

Wells	Formation	Depth Interval (ft)	Averaged TOC (wt.%)	Averaged HI (mg HC/g OC)	Averaged PI	Averaged Tmax (°C)	Tmax difference (°)	Corrected Tmax (°C)
Carus Fee 21-19	UBS	11291-11303	10.9	166	0.30	450.5	5.5	456.0
Deadwood Canyon 43-28	LBS	10147-10188	13.6	400	0.12	438.8	9.4	448.2
N&D 1-05H	UBS	9411-9427	11.1	468	0.10	431.7	0.8	432.5
Dobrinski 18-44	UBS	8629-8637	13.2	460	0.07	419.9	N/A	

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. Based on the suggested threshold values of Lewan et al. (2013) and the established relationship between pyrolysis HI and Tmax parameters, an integrated threshold scheme was made for Bakken shales and shown in Table 4.

Application

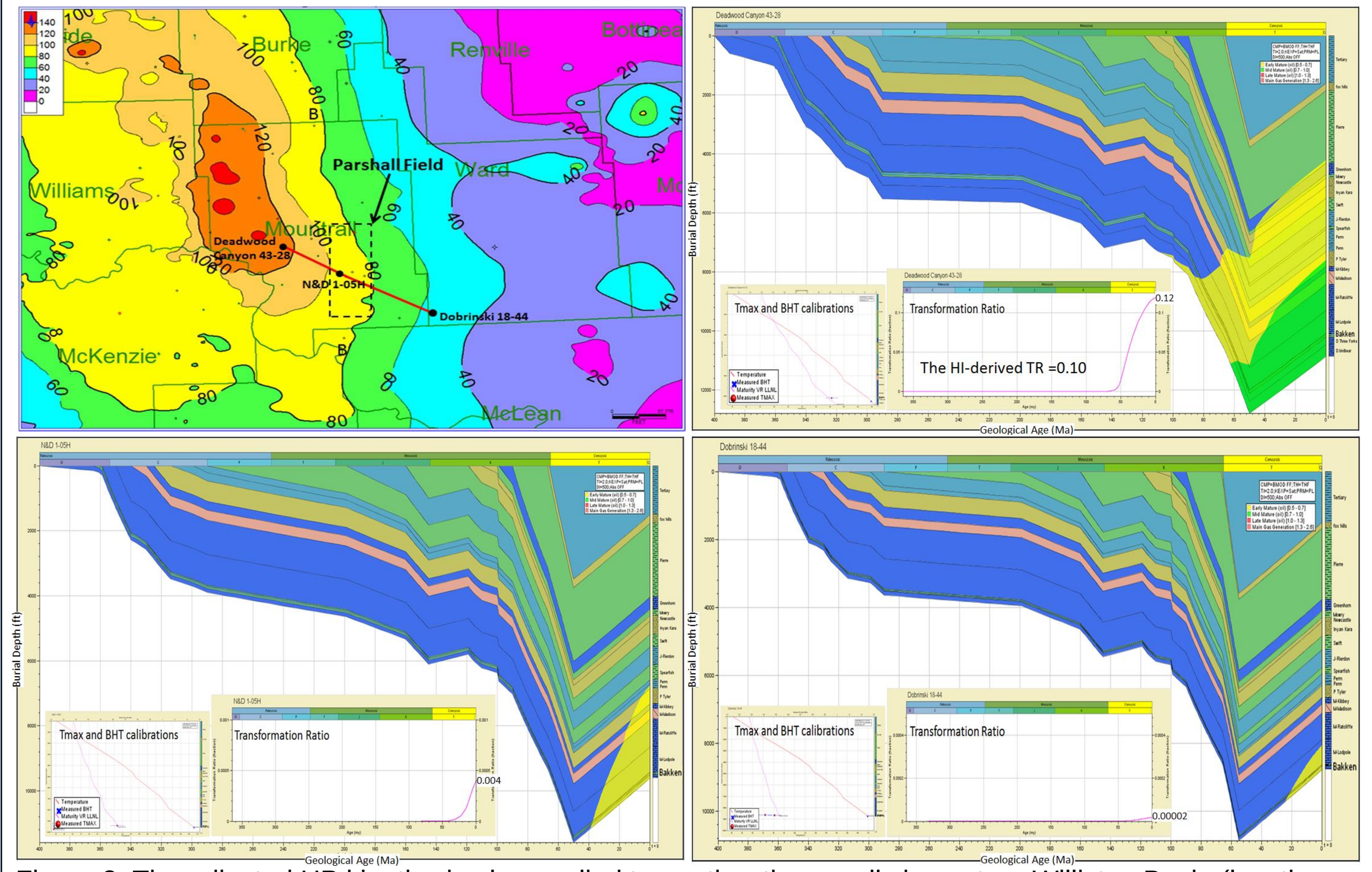


Figure 8. The adjusted HP kinetics is also applied to another three wells in eastern Williston Basin (locations shown in Figure 6.12): the Deadwood Canyon 43-28 (west of the Parshall Field), N&D 1-05H (in the Parshall Field), and Dobrinski 18-44 well (east of the Parshall Field), to simulate their extent of oil generation (transformation ratio, TR). TR = 0.12 at Deadwood Canyon 43-28, TR = 0.004 at N&D 1-05H, and TR = 0.00002 at Dobrinski 18-44.

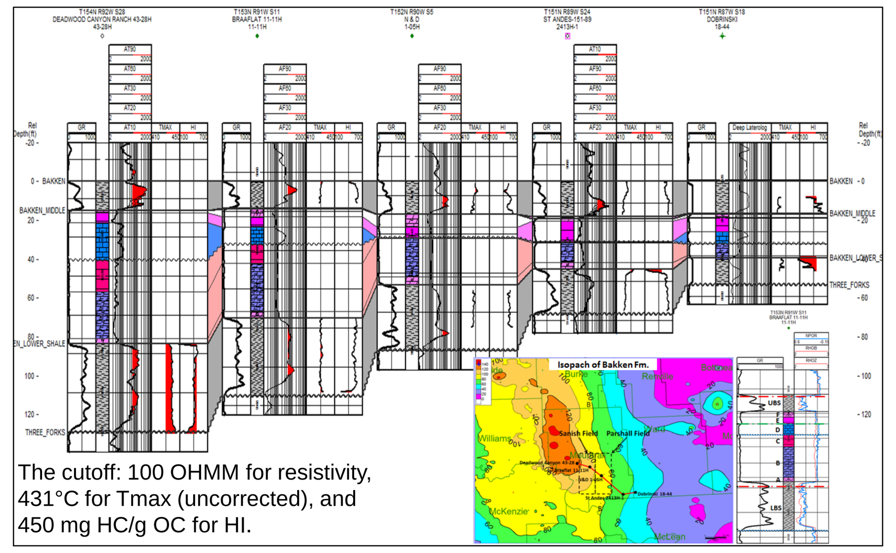


Figure 9 illustrates a west-east cross-section through the Parshall field. A nice correlation between the Resistivity log and maturity parameters (Tmax and HI). The Tmax, resistivity, and HI logs at the N&D well indicate that Bakken shales in this area are immature with very minimal extent of oil generation, but significant amount of oil resources are discovered in this area. So, most of the produced oil was probably migrated from west to the Parshall/Sanish area with more mature Bakken shales expelling significant amounts of oil, which can short-laterally migrate through mid-Bakken to the Parshall Field.

Conclusions

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. 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 suggests 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.

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