



North Dakota Geological Survey

Determination of Activation Energy and Frequency Factor for Samples of the Bakken Formation (Miss.–Dev.): Williston Basin, ND

By

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Abstract

Six samples of shale from the Bakken (Miss.-Dev.) Formation were analyzed using LECO TOC, Rock Eval 6 and multiple heating rate pyrolysis. The results indicate that within a single well penetrating thermally immature source rock, the frequency factor and activation energy vary in a log-linear fashion. Another sample from a similarly immature core produced almost identical kinetic parameters. The only sample that did not cluster along the linear trend was taken from a well situated within the most thermally mature portion of the basin. These results suggest that subtle variations in kerogen composition are responsible for the observed covariance in the activation energy and natural logarithm of the frequency factor. These results also suggest that changes in the kinetic parameters caused by thermal maturation result in higher activation energies and smaller frequency factors that are conspicuously different than the kinetic parameters obtained from the less mature sample set.

Introduction

The question of the role that the reaction kinetics involved in the degradation of kerogen into petroleum products is central to petroleum systems.

Magoon and Beaumont (1999) define a “petroleum system” as:

“a pod of active source rock and all genetically related oil and gas accumulations. It includes all of the geologic elements and processes that are essential if an oil and gas accumulation is to exist”.

The essential geologic elements involve rocks that act as petroleum sources, reservoirs, seals and overburden. The processes include trap formation and those involved in hydrocarbon generation, migration, and accumulation. A petroleum system forms when the location and timing of the essential geologic elements and processes result in petroleum accumulations. At the core of every petroleum system there is a source rock that consists of organic matter that originated in a near surface environment, was modified into kerogen during burial and when subjected to sufficient heat degrades into petroleum (oil, gas, or some combination). The purpose of this investigation is to present experimental data collected from the Bakken Formation that may be used to determine the kinetic properties of this formation with the expectation that these results will better constrain the relationship between formation temperature and current oil generation rates.

One of the most important questions that impact the interpretation of maturation indicators such as T_{max} is whether the natural variation in kerogen composition is present in the source rocks. This is significant because, under the same thermal stress, different kerogen compositions decompose into petroleum at different rates. Therefore if compositional variations are minimal, as suggested by Waples et al. (2010), then the intrinsic compositionally dependent parameters that control reaction rates (activation energy and frequency factor)

should be narrowly defined within a given well and vary significantly between wells that have much different thermal histories. Waples et al. argue there is not enough variation in kerogen composition within the Bakken Formation to affect the frequency factor. They advance this idea with the claim that the frequency factor is essentially constant for the formation as a whole and that variations in activation energy reflect the degree of organic maturation.

To test this idea this study makes use of activation energy and frequency factor data collected from three wells containing cores taken from the upper and lower Bakken shale. These samples allow for observation of the variation in the activation energy and frequency factor that have matured under the same thermal conditions as well as how these factors change with variations in thermal stress experienced by different wells. The wells were selected based on the availability of core and presumed level of maturation as defined by previously determined values of T_{max} . Individual samples were selected to encompass as large a stratigraphic range as the availability of analyses and core permitted.

The significance of oil generation rates to the formation of the Bakken petroleum system is central to Meissner's (1978) and Price's (1994) ideas that source beds in the Bakken Formation are capable of forming a continuous petroleum accumulations within the almost impermeable beds that lie between and below the two source beds of the Bakken Formation. Because the role of migration and trap formation are largely eliminated in this system, the role of maturation and oil generation becomes the system's defining process. Therefore, concentrating on chemical processes, especially those that control reaction rates, becomes critical in applying the petroleum system concept to this formation.

Chemical reaction rates are usually described in terms of the Arrhenius equation as follows:

Eq. 1

$$k = Ae^{-E_a/RT}$$

Where:

k is the change in the molar mass of the reactant with respect to time

A is a frequency factor describes the number of potential elementary reactions per unit time

E_a is the activation energy that describes the energy barrier that must be exceeded in order for a reaction to occur

R is the gas constant

T is the reaction temperature (°K)

When the reaction in question is first order and occurs under isothermal conditions then the activation energy (E_a) and frequency factor can be obtained from a plot of natural log of the reaction rate ($\ln k$) versus inverse temperature varies ($1/T$) where k is the reaction rate

(mass/time) and temperature (T) in degrees K. However, the activation energy and frequency factor may also be determined from non-isothermal experiments as long as the temperature changes at a constant rate. Kissinger (1958) found an approximate solution for the Arrhenius equation under these conditions. In his solution, Kissinger shows that the temperature that corresponds with the maximum reaction rate (T_p) shifts (Fig. 1) with the heating rate (β) in accordance with the activation energy (E_a) and frequency factor (A) as follows:

Eq. 2

$$\ln (\beta/T_p^2) = \ln (AR/E_a) - E_a/R T_p$$

Where:

E_a = Activation Energy (kJ/mole)

R = Gas Constant (.008314) kJ/mol-°K

A = Frequency factor (min⁻¹)

T_p = Temperature that causes maximum reaction rates (°K)

β = Heating Rate (°K/min)

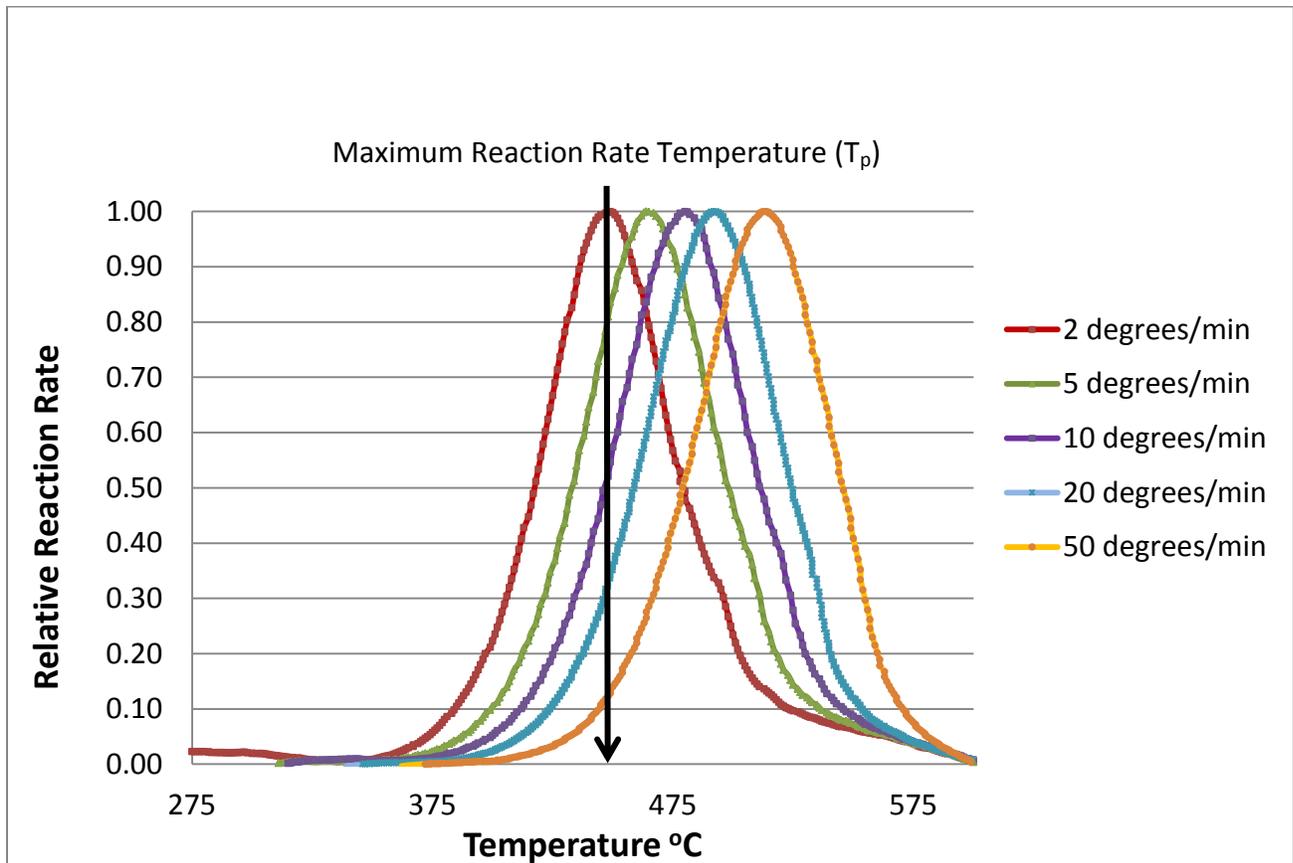


Figure 1. Pyrograms illustrating the shift to higher maximum reaction rate temperatures (T_p) as the heating rate (β) increases. The pyrograms are from a sample of the Bakken Formation collected from the Federal DG-1 (see Table 1).

Activation energies were determined for samples of core taken from the Federal DG-1, Dobrinski 18-44 and N&D 1-05-H (Fig. 3). These three wells are believed to represent the two extremes of maturation present in the Bakken Formation based on the availability of core and previously determined T_{max} values. The Dobrinski 18-44 and N&D 1-05-H wells represent the least mature end and the Federal DG-1 the most mature. A total of four samples were collected from the N&D 1-05-H in order to evaluate the potential variation in activation energy that exists within the Bakken Formation at a single location. A single sample from the Federal DG-1 was collected in order to examine the potential change in activation energy that occurs during maturation. The activation energies for these samples are summarized in Table 1.

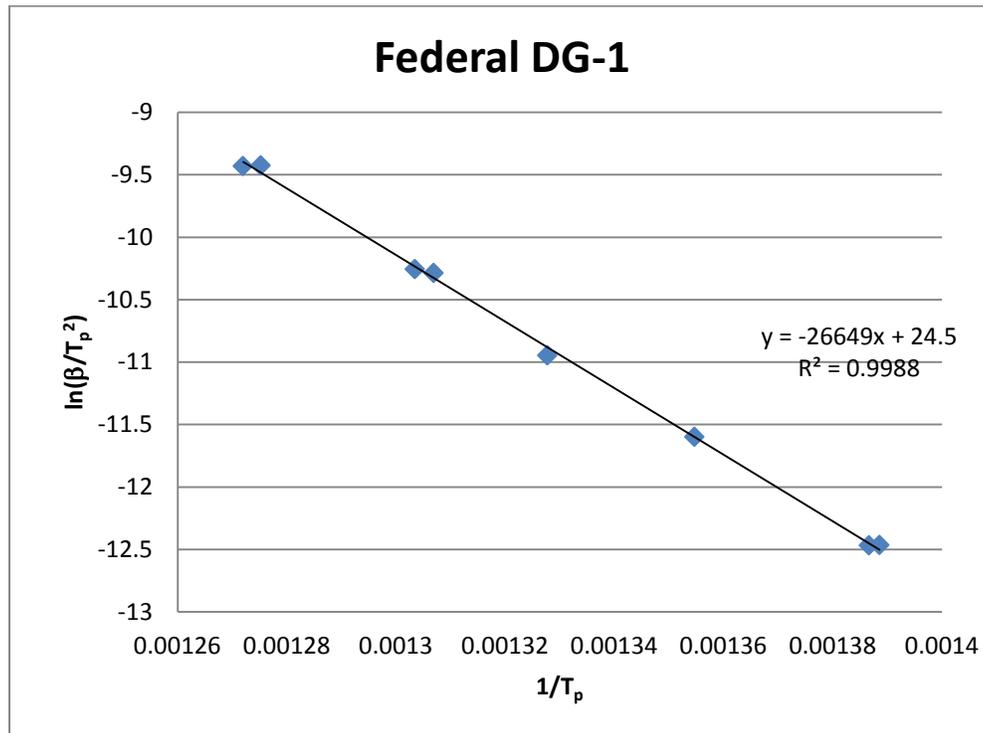


Figure 2. Peak reaction rate temperatures (T_p) and corresponding heating rates (β) plotted in accordance with the Kissinger Equation (Eq. 2). The slope and intercept of a linear regression finds the activation energy (E_a) and frequency factor (A). In this example, the activation energy is 222 kJ/mole and the frequency factor is $1.2 \times 10^{15} \text{ min}^{-1}$.

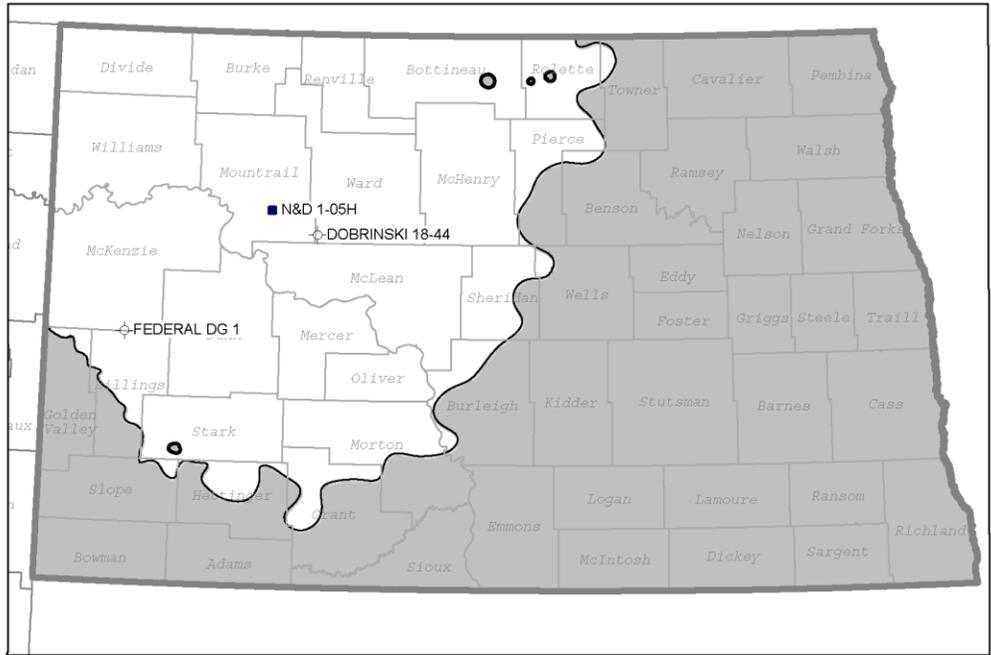


Figure 3. Index Map showing the sampled wells for this report. Shaded portion of the map represents areas in which the Bakken Formation is absent.

Methods:

All of the samples used in this study are from core (see appendix for logs and sample locations). Approximately five grams of material were collected and shipped to Weatherford Labs for analysis. Following crushing, analyses included the determination of the total organic carbon (TOC) by the LECO method along with measurements of T_{max} , the amount of free hydrocarbons (S_1), reactive kerogen (S_2) organic oxygen compounds (S_3) present in each sample. T_{max} , S_1 , S_2 and S_3 and the derived values for hydrogen index (HI), oxygen index (OI) and production index (PI) were determined using the Rock Eval 6 method (see Table 1).

The determination of the activation energy (E_a) and frequency factor (A) were accomplished using heating rates that increased 2, 5, 10, 20 and 50 degrees C/min. An additional heating rate and peak temperature was obtained from the Rock Eval pyrolysis used to find T_{max} . The data supplied by Weatherford included measurements of the relative amount of hydrocarbons generated by the decomposition of kerogen at temperatures above that needed to vaporize free hydrocarbons (see Fig. 1 for an example). The peak reaction temperature (T_p) for each heating rate was obtained using a polynomial interpolation of the recorded pairs of temperature and hydrocarbon mass obtained during pyrolysis. These data are included in the spreadsheet labeled Kinetic Data.xlsx (included with the CD) and are plotted using the Kissinger method (see Appendix for graphs). Linear regression of these plots supplies the slope and

intercept which allows for the determination of E_a and A from the following:

$$\begin{aligned} \text{Slope} &= -E_a / R \\ &\text{and} \\ \text{Intercept} &= \ln (AR/E_a) \end{aligned}$$

$$\text{where } R = .008314 \text{ kJ/mole}^{-\circ}\text{K}$$

Results:

All of the sample analyses exhibit a strong linear correlation ($r^2 > 0.99$) when plotted as $\ln(\beta/T_p^2)$ versus $1/T_p$. Consequently, reasonable estimates of activation energy (E_a) and frequency factor (A) are possible (see appendix and attached files for graphical and tabular data). The samples from the N&D 1-05 H yielded activation energies that increased with depth from 209 kJ/M to 220 kJ/M (Table 1). Frequency factors also increase with depth. This variation in activation energy and corresponding frequency factor represents a tenfold difference in the Arrhenius reaction rate at 100°C (Eq. 1). The sample from the Dobrinski 18-44, sampled near the base of the lower Bakken at another marginally mature location, provided an activation energy and frequency factor that was very similar to the sample from near the base of the lower shale in the N&D 1-05 H. Activation energy when plotted against the natural log of the frequency factor for the four samples from the N&D 1-05 H exhibits a good linear relationship that suggests an interdependence between these two kinetic parameters (Fig. 4). The only sample that cannot be reasonably associated with this line is from the significantly more mature Federal DG-). Even though the activation energy measured in the Federal DG-1 is high, it is probably not high enough to unambiguously differentiate it from similar activation energies present in the less mature N&D 1-05 H. It is only the combination of relatively high activation energy and low frequency factor that clearly separates this more mature sample from the other samples from the less mature portions of the Bakken.

Conclusions:

The data collected during the course of this study show that there is a systematic variation in activation energy and frequency factor within samples that have been subjected to the same burial and thermal stresses. One sample collected from a well with the same level of immaturity exhibited very similar kinetic parameters. The sample from the most mature portion of the basin exhibited a conspicuously different pair of kinetic parameters that separates it from the less mature samples. These results suggest that variations in source rock composition may be evident in the covariance between frequency factor and activation energy. Variations in composition caused by maturation result in kinetic parameters that do not vary in

accordance with the kinetic trends present in the immature samples. If so, then one should expect a sample suite collected from a mature source rock near the basin center to also have a covarying set of activation energies and frequency factors that are different from the immature source rocks presented here.

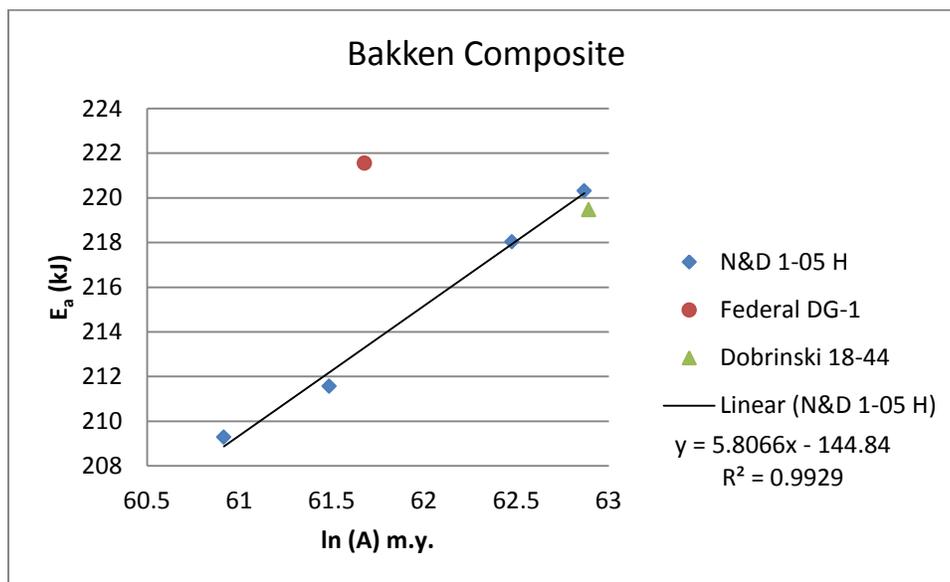


Figure 4. The distribution of activation energies and frequency factors for samples of the Bakken Formation. The linear trend is drawn through the kinetic data from the N&D 1-05 H. The apparent covariance in kinetic parameters probably represents variations in kerogen composition.

Table 1. Rock Eval 6 and Kissinger method kinetics results for samples of the Bakken Formation.

Sample ID	WELL NAME	Core Depth (ft.)	S ₁ mg Oil g sample	S ₂ mg HC g sample	S ₃ mg OC g sample	T _{MAX} (°C)	LECO TOC (wt %)	HI $\frac{100 \times S_2}{\text{TOC}}$	OI $\frac{100 \times S_3}{\text{TOC}}$	PI $\frac{S_1}{(S_1+S_2)}$	E _a kJ/M	A min
8177-1	Dobrinski 18-44	8666	2.03	23.19	1.15	424	7.83	296	15	0.080	219.50	3.92E+15
9569-1	Federal DG-1	10932	4.21	11.94	0.58	456	9.85	121	6	0.261	221.56	1.16E+15
16532-1	N&D 1-05 H	9410.5	9.33	101.83	1.50	430	17.03	598	9	0.084	209.29	5.43E+14
16532-2	N&D 1-05 H	9426	8.41	67.64	0.71	428	11.57	584	6	0.111	211.58	9.61E+14
16532-3	N&D 1-05 H	9469	11.79	101.70	2.24	426	18.30	556	12	0.104	218.04	2.58E+15
16532-4	N&D 1-05 H	9482.5	11.41	54.82	0.65	430	10.70	512	6	0.172	220.31	3.82E+15

References:

Kissinger, H. E., 1957, Reaction Kinetics in Differential Thermal Analysis: Analytical Chemistry, v. 29, p 1702-1706.

Magoon, L.B., and Beaumont, E.A., 1999, Petroleum system, in Beaumont, E.A. and Foster, N.H., eds., Exploring for oil and gas traps: American Association of Petroleum Geologists Treatise of Petroleum Geology, Chap. 3, p. 3.1-3.34.

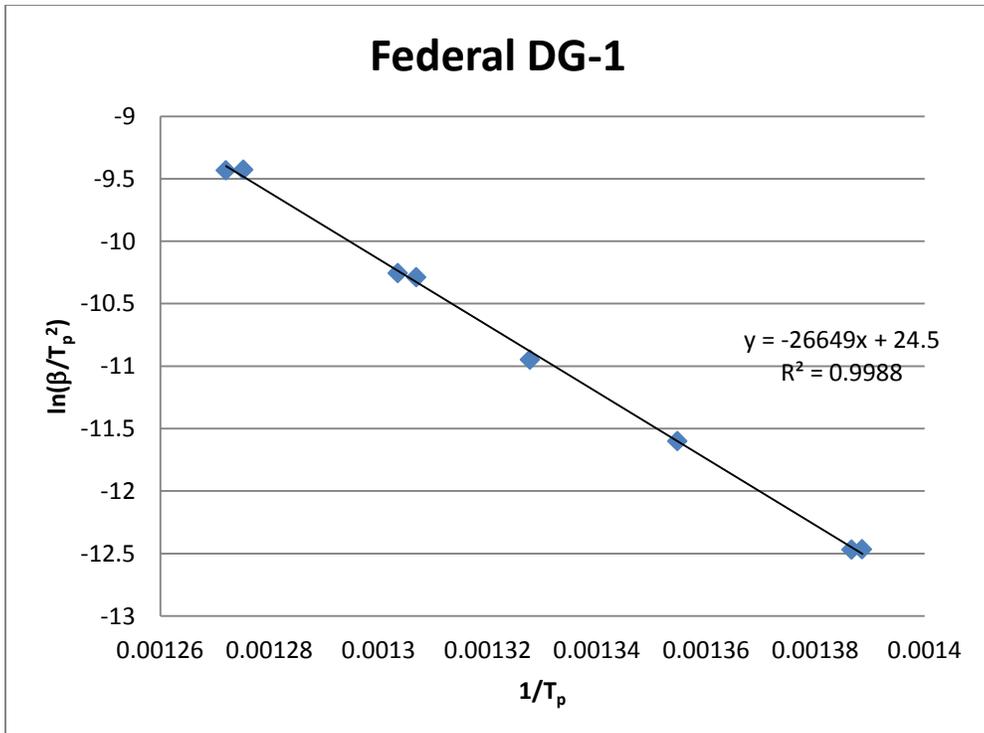
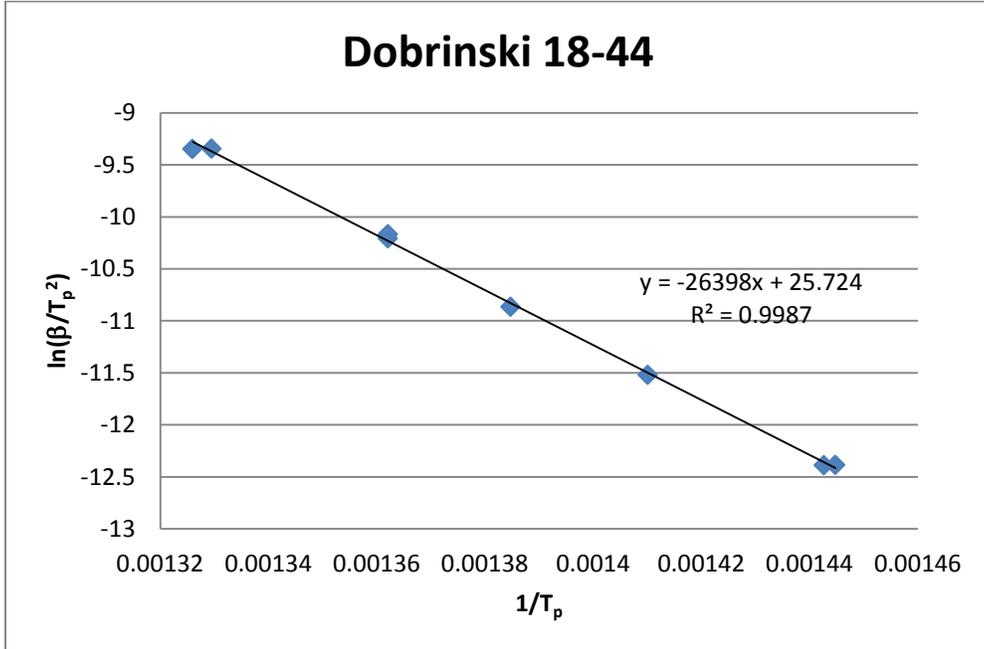
Meissner, F.F., 1978, Petroleum geology of the Bakken Formation Williston Basin, North Dakota and Montana, *in* D. Rehg, ed., 1978 Williston Basin Symposium: Montana Geological Society, Billings, Montana, p. 207-227.

Price, L.C. and LeFever, J.A., 1994, Dysfunctionalism in the Williston Basin: The mid-Madison/Bakken petroleum system: Bulletin of Canadian Petroleum Geology, v. 42, no. 2, p. 187-218.

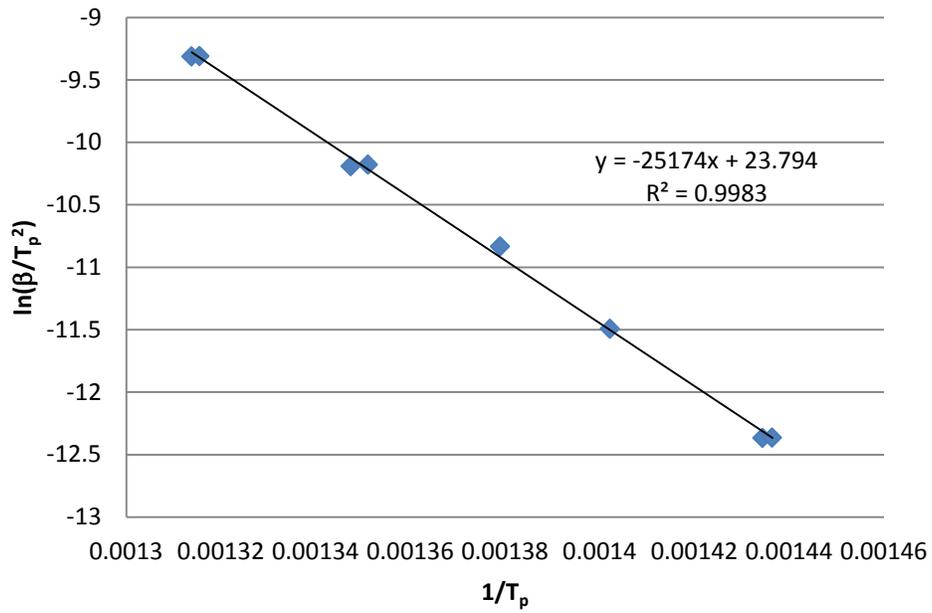
Waples, D. W., Leonard, J. E., Robert Coskey, R., Safwat, S., Nagdy, R., 2010, A New Method for Obtaining Personalized Kinetics from Archived Rock-Eval Data, Applied to the Bakken Formation, Williston Basin: AAPG Search and Discovery, Article #90108©2010 AAPG International Convention and Exhibition, September 12-15, 2010 Calgary, Alberta, Canada

Appendix I

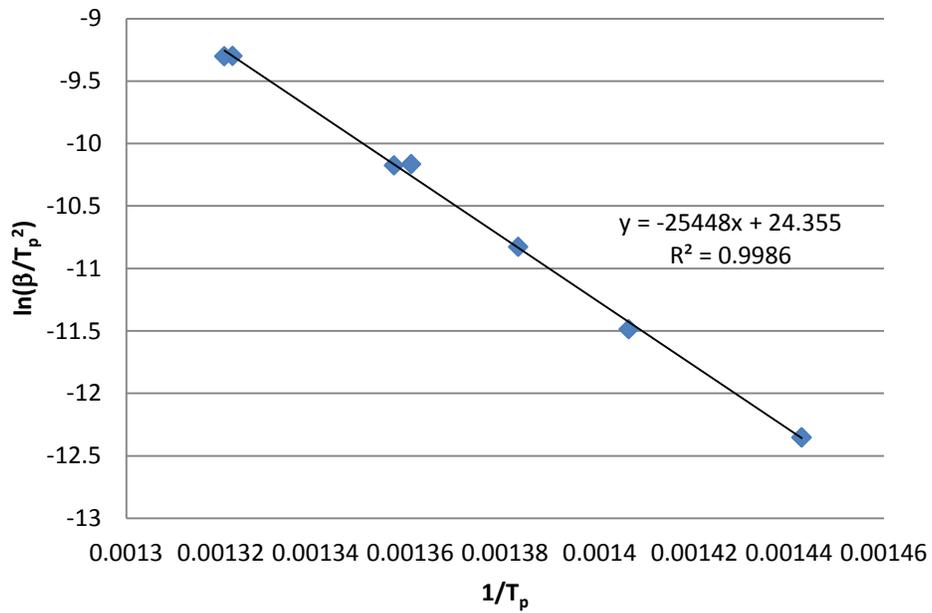
Kissinger Plots for the wells posted in Figure 3 and results tabulated in Table 1.



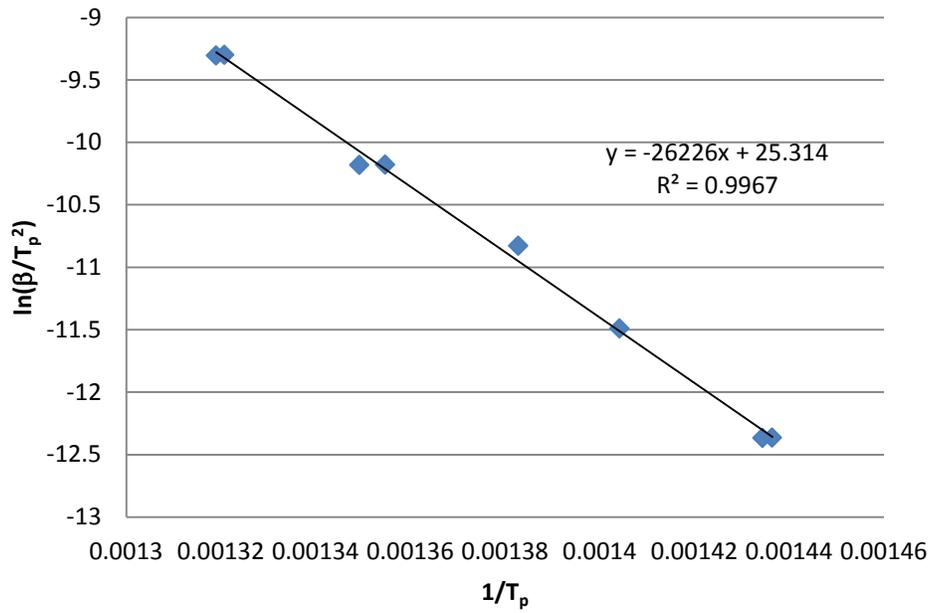
N&D 1-05H 9410



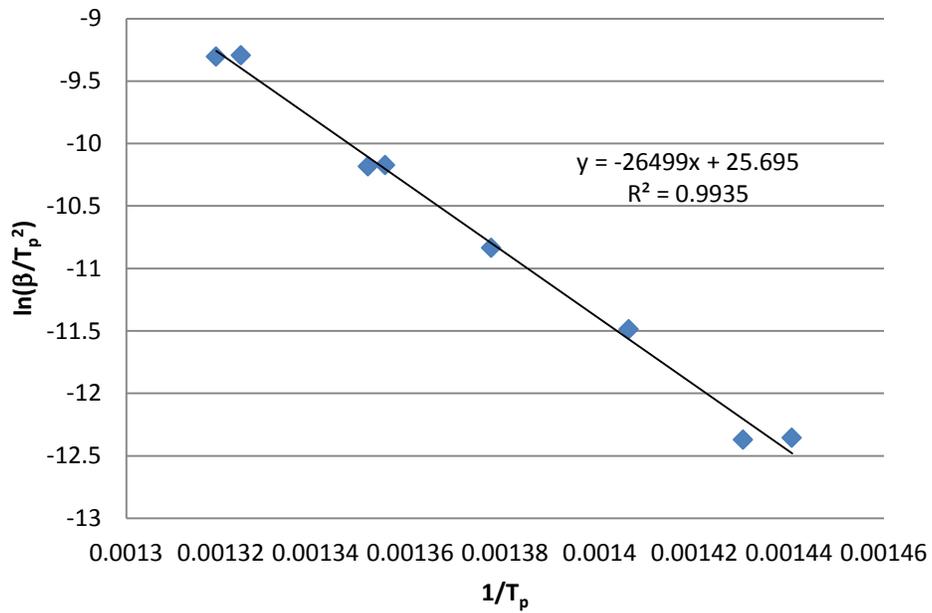
N&D 1-05H 9426



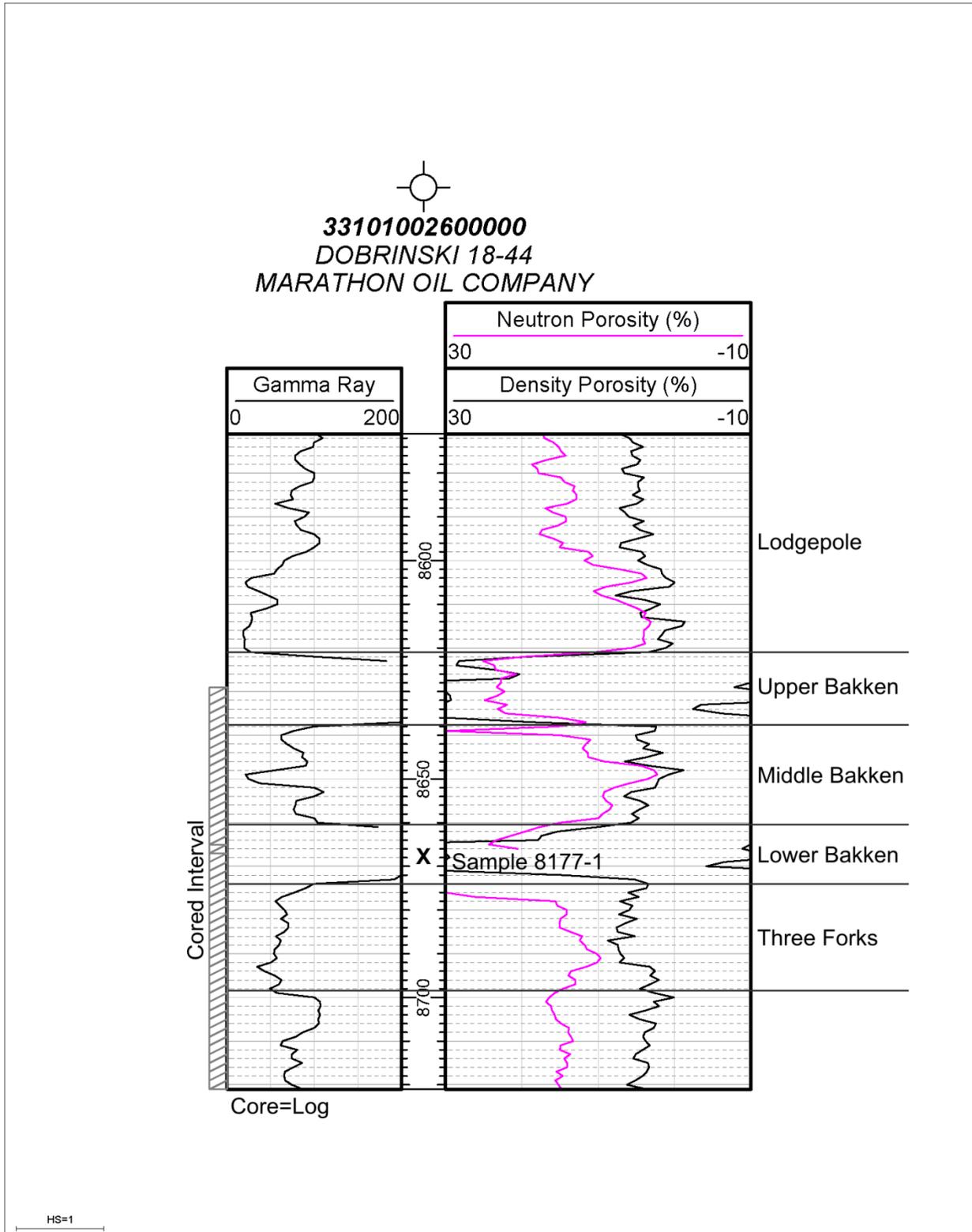
N&D 1-05H 9469



N&D 1-05H 9482

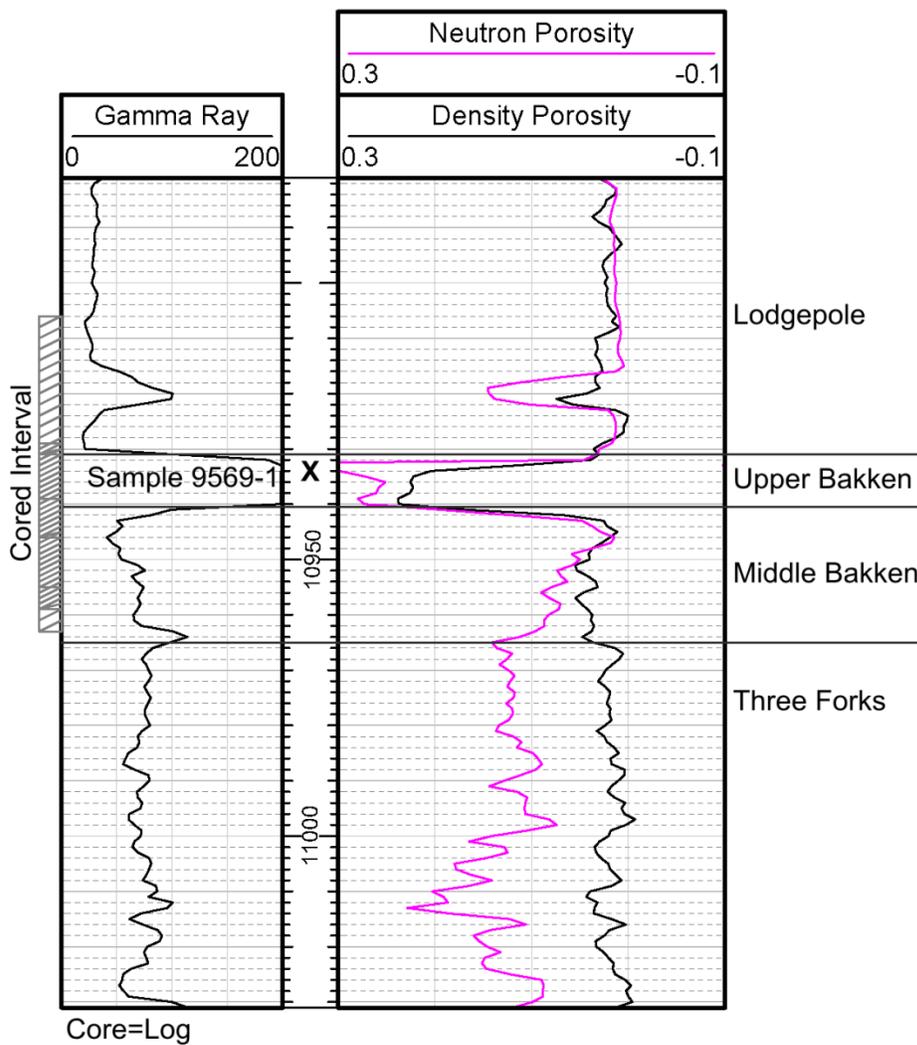


Appendix II – Neutron-Density Porosity Logs showing sample locations.





33053015360000
FEDERAL DG 1
CITIES SERVICE OIL CO.



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33061005210000
 N&D 1-05H
 EOG RESOURCES, INC.

