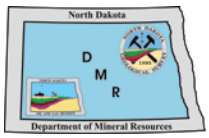

North Dakota Geological Survey

The Compensation Effect from Simulated Programmed Pyrolysis Experiments: A Way to Standardize Source Rock Kinetic Parameters.

By

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Abstract:
The evaluation of source bed oil generation potential is hampered by the lack of absolute precision in the determination of the temperature that corresponds with the maximum rate of hydrocarbon generation during programmed pyrolysis. Numerical simulations show that these temperature errors are capable of inducing significant errors in the determination of the activation energy and frequency factors that define reaction rates. However, the simulations indicate that the errors in activation energy and frequency factor result in an apparent compensation effect that is linear when plotted as activation energy versus natural logarithm of the frequency factor. The slope of the compensation effect is nearly constant and virtually the same as the slope in the compensation effect that is produced by programmed pyrolysis of natural source rocks. These results suggest that a correction can be applied to programmed pyrolysis experiments in which the constant compensation effect slope is used to recalculate the apparent activation energy to a fixed, theoretically reasonable frequency factor.

Introduction:
The use of the Kissinger method in the determination of activation energies and frequency factors is limited by the problem of obtaining precise peak reaction temperature data. The Kissinger method obtains the activation energy and frequency factor from experiments in which reaction temperatures increase at a constant rate. According to Kissinger's derivation of the Arrhenius equation under these conditions the temperature that corresponds with the maximum reaction rate (T_p) changes with heating rate (β) which leads to a solution for the activation energy (E_a) and frequency factor (A) with the following expression:

Eq.1

$$\ln (\beta/T_p^2) = -E_a/R\ (1/T_p) + \ln(A\ R/E_a)$$

Where:

β = Heating rate (^oK/min)
T_p = Peak Reaction Temperature (^oK)
R = Gas Constant (J/^oK-mole)
E_a = Activation energy (J/mole)
A = Frequency factor (1/min.)

This expression produces a line in which the "x" variable is given by ($1/T_p$) and the "y" variable is the natural logarithm of the ratio between the heating rate and the square of the peak reaction temperature (T_p). In theory the determination of the activation energy and frequency factor is simply a matter of conducting several experiments using different heating rates (β), determine the temperature that corresponds with the maximum reaction rate for each heating rate and plotting the temperatures and heating rates as $1/T_p$ versus $\ln(\beta/T_p^2)$. Even though the derivation is correct the method produces widely ranging results that cannot be explained by sample heterogeneity. In many instances the errors associated with this method are themselves linearly distributed when plotted as activation energy (E_a) versus ln(A). The linear relationship is frequently referred to as the "compensation effect". The linear compensation effect has been attributed to measurement errors in T_p which when plotted as (E_a) versus ln(A) results in a linear distribution of data. This linear relationship may be largely an artifact resulting from errors in the measurement of T_p (Nielsen and Dahl, 1991). This article presents the results of a study that tests the appearance of the compensation effect using numerical simulations of the Kissinger equation in which normally distributed random errors in T_p are included. The simulations are designed

to test the idea that small errors in temperature measurements produce a compensation effect similar to those obtained under actual experimental conditions.

Methods:

The simulations involve solving the Kissinger equation for β by assuming constant values for activation energy (E_a), frequency factor (A) and peak reaction temperature (T_p). Once β is found then random error is added to the peak reaction temperature (T_{pe} = T_p+ Error) and the corresponding values for $\ln(\beta/T_{pe}^2)$ and $1/T_{pe}$ are found. The error is obtained with a random number drawn from a normal distribution defined by a mean (μ) equal to the assumed peak reaction temperature ($\mu=T_p$) and a fixed variance (σ^2). Repeating this process, using different peak reaction temperatures and random error, produces values of $\ln(\beta/T_{pe}^2)$ and $1/T_{pe}$. Linear regression of the error bearing data provides the slope and intercept of the resulting trend (Fig. 1). This allows calculation of the apparent activation energy (E_{aa}) and frequency factor (A_a) using Eq.1 as follows:

Eq. 2

$$\text{Slope} = -E_{aa}/R$$
$$\text{Intercept} = A_a R/E_{aa}$$

The simulations shown in Fig. 1 are comparable to experimental methods in which peak reaction rates and the corresponding heating rates are used to solve the Kissinger Equation for E_{aa} and A_a. The experimental method used by the NDGS to determine E_{aa} and A_a for various source rocks in North Dakota typically use five heating rates (2 (2 runs), 5, 10, 20, 50 (2 runs) ^{o}C/min.). The simulations presented here use similar heating rates (2.3 (2 runs), 5.5, 9.4, 20.8, 45.5 (2 runs) ^{o}C/min).

Results:

Even though the assumed activation energy and frequency factor are held constant for all of the simulations, the influence of small random variations in peak reaction temperature resulted in apparent activation energies that ranged almost 8 kJ/mole with apparent frequency factors varying by a factor of more than six. More interestingly the "compensation effect" is clearly evident in the linear trend between the apparent activation energy (E_{aa}) and apparent frequency factor (A_a) in Figure 2. The appearance of a single compensation effect is repeatable for simulations using a single set of kinetic parameters that differ in the level of introduced error. This suggests that errors in peak reaction rate temperatures, as long as they are symmetric about the "true" peak reaction temperature, will produce apparent activation energies (E_{aa}) and apparent frequency factors (A_a) that will be distributed along the same linear trend (Fig. 3). However, the trend of the compensation effect shifts, with changes in the activation energy (Fig. 4) and frequency factor (Fig.5).

The "shift" in the compensation effect is almost entirely in the value of the intercept. Based on 237 simulations using four separate activation energies ranging from 222 to 238 kJ/mole, the slope is almost constant at 5.96 kJ/mole-ln(A) with a standard deviation of 0.076.

The results of the kinetic simulation experiments using the Kissinger equation indicate that for even small random errors in the determination of T_p significantly different values for E_a and A will result. Figure 6 shows how closely the experimental data can be approximated by selected simulations that contain random errors in (σ^2 = 1 ^{o}C) the peak reaction temperature (Fig. 6).

Table 1. Results of four series of simulations that include normally distributed, random errors in temperature. All of these simulations assume E_a = 223 kJ and A= 1 X 10^{14} min^{-1} (ln A = 63.3 $m.y.^{-1}$). The simulations shown used "mean" temperatures of 425 (2 runs), 440, 450, 465, 480 (2 runs) ^{o}C and a variance of 1.0 ^{o}C. These peak temperatures and kinetic parameters are associated with heating rates of 2.3, 5.5, 9.4, 20.8, and 45.5 ^{o}C/min. and are close to those used by the NDIC in the experimental determination of activation energy and frequency factor (2, 5, 10, 20, 50 degrees/min).

r	Slope	Intercept	E_{aa} kJ/mole	A_a Sec^{-1}	$Ln(A_a)$ $m.y.^{-1}$
-1.00	-26979.87	26.40	224.31	7.86E+15	63.59
-1.00	-26265.91	25.38	218.37	2.77E+15	62.55
-1.00	-27356.98	26.89	227.45	1.30E+16	64.09
-1.00	-26056.59	25.06	216.63	2.00E+15	62.22

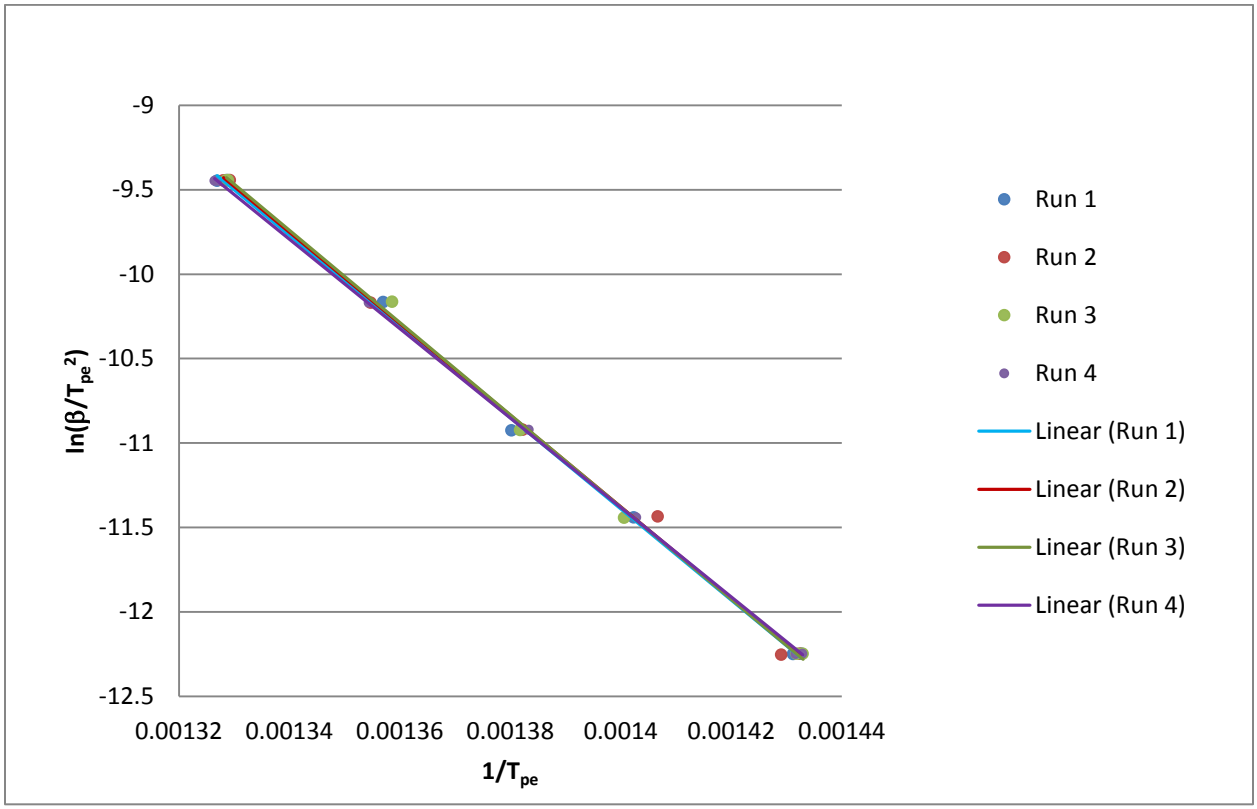

Figure 1. Variation in Kissinger plots for four, simulated, five point pyrolysis listed in Table 1.

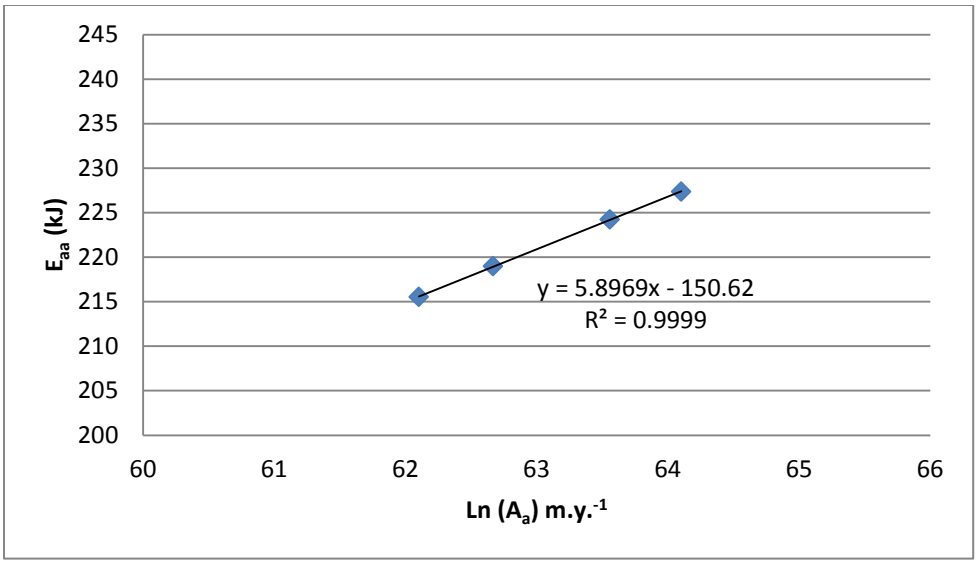

Figure 2. Variation in the apparent activation energy and frequency factor showing a strong linear "compensation effect" that results when T_p includes small random errors (see Table 1).

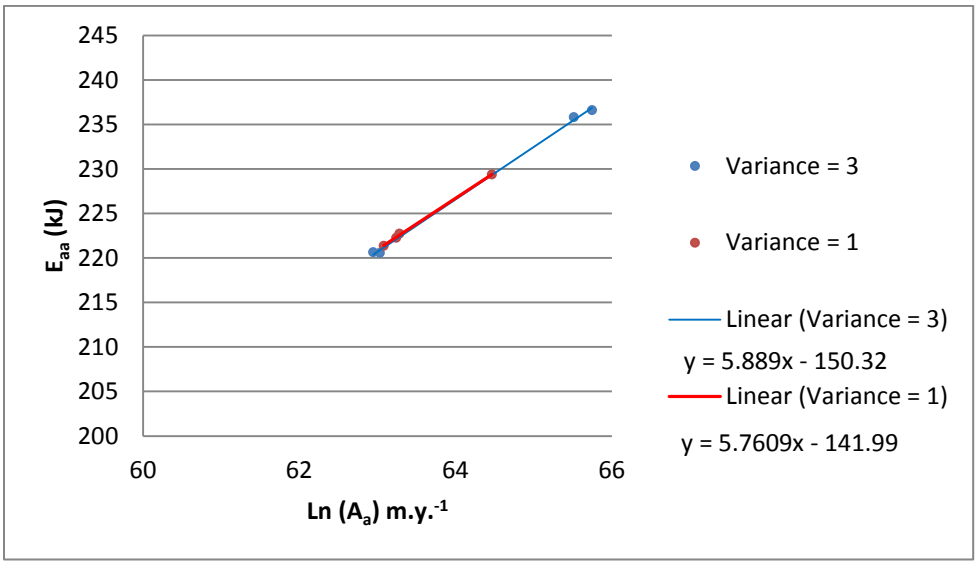

Figure 3. Example showing the compensation effect for two representative sets of simulations in which the error (σ^2) is either 1 or 3 ^{o}C. All other variables are held constant. Regression analysis for both sets of simulations are included.

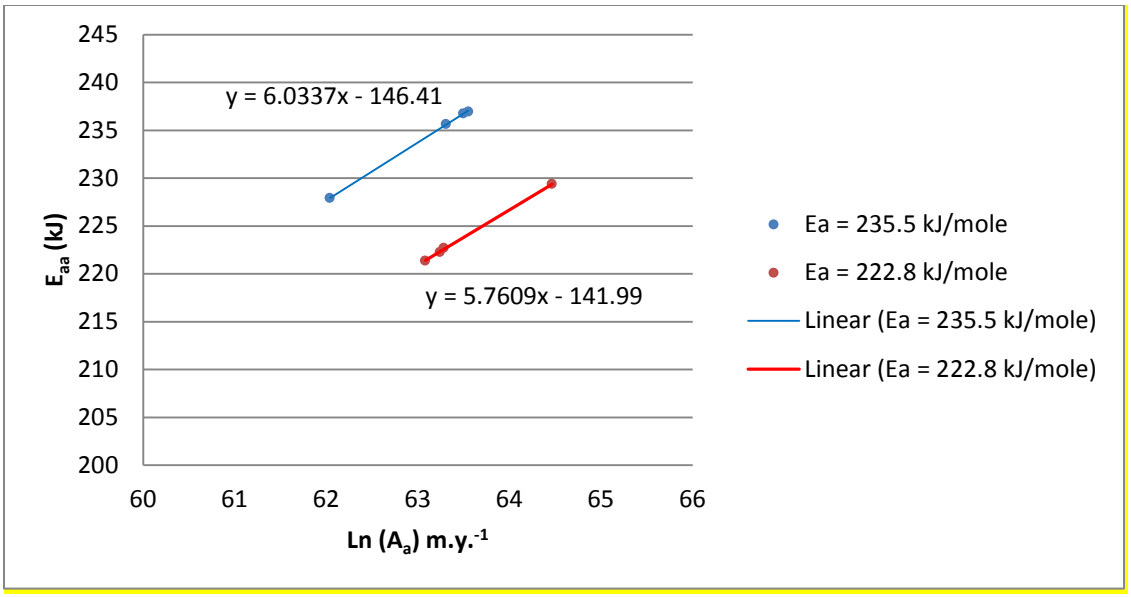

Figure 4. Variation in the apparent activation energy (E_{aa}) and frequency (A_a) factor for simulations that assume that E_a is either 235.5 kJ/mole (blue) or 222.8 kJ/mole (red). Both simulations employ the same error ($\sigma^2 = 1$) and frequency factor (1×10^{14} min^{-1}).

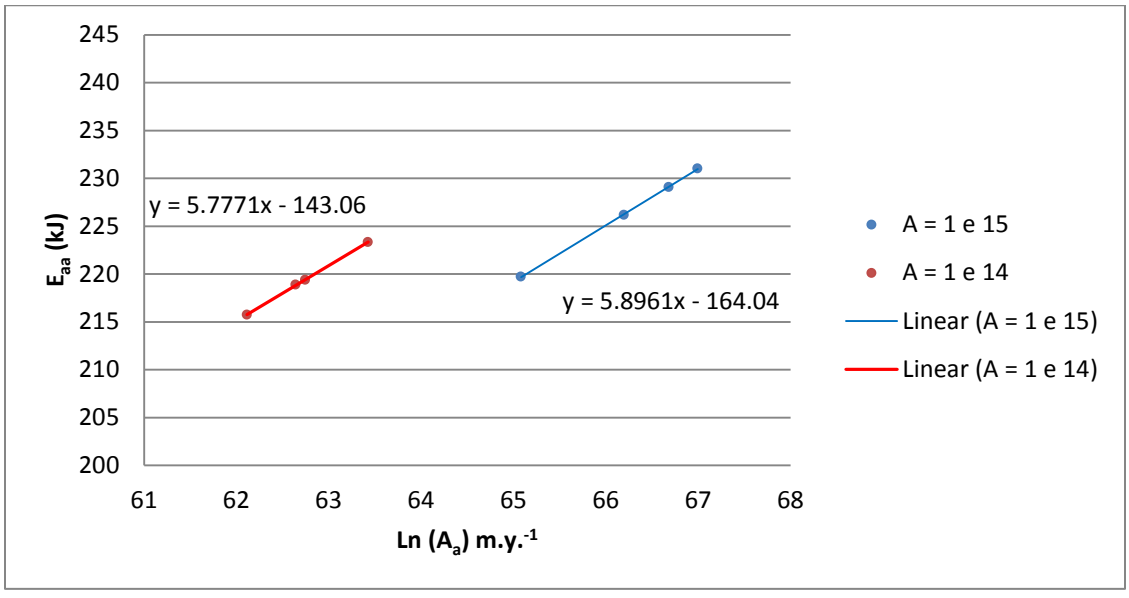

Figure 5. Variation in the apparent activation energy (E_{aa}) and frequency (A_a) factor for simulations that assume that A is either 1×10^{15} (blue) or 1×10^{14} (red). Both simulations employ the same error ($\sigma^2 = 1$) and E_a (222.8 kJ/mole).

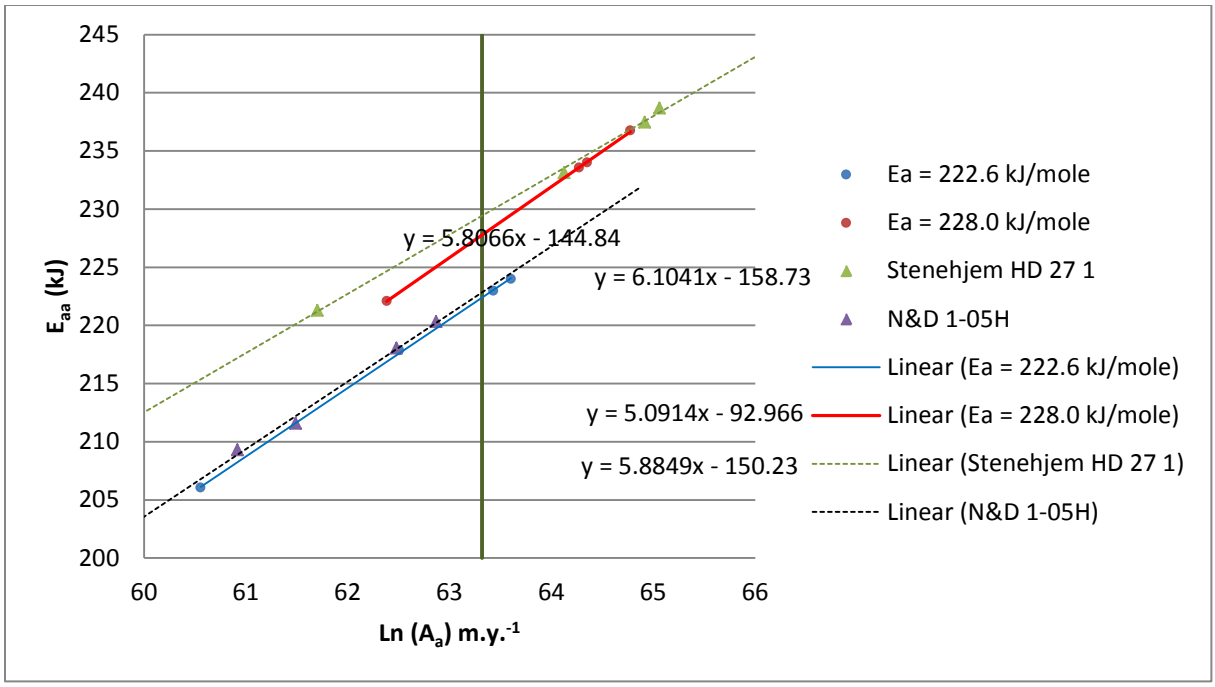

Figure 6. Comparison between two sets of experimentally determined kinetic data from the Bakken Formation and two sets of simulations. The Stenehjem HD 27-1 is situated in near the center of the basin and is considered "mature". The N & D 1-05H is located on the eastern flank of the basin and is considered to be at most "marginally mature". Both simulations used the same range of temperature errors ($\sigma^2 = 1$), frequency factors ($A = 1 \times 10^{14}$) and either a presumed E_a of 222.6 kJ/mole (blue) or 228.0 kJ/mole (red). The vertical line represents the ln(A) that corresponds to 1×10^{14} sec^{-1}.

Discussion:

The simulations suggest a partial solution to this problem. The solution involves accepting the notion that the frequency factor is limited to a relatively small range of values controlled by the entropy of activation. In this treatment the frequency factor relates the increase in reaction entropy that accompanies the increase in "freedom" that occurs when reaction components transition from the ground state to one that is capable of forming a reaction product. This increase in entropy can be expressed as follows (Benson, 1976):

Eq. 3

$$A = C\, e^{(\Delta S/R)}$$

Where:

$C = T\, k_B/h$

T = Temperature (^{o}K)

k_B = Boltzman constant

h = Plank constant

R = Gas constant

ΔS = Entropy of activation

If only simple chemical reactions involving single molecules are considered then the total range of frequency factors should be between 10^{13} and 10^{15} sec.$^{-1}$ (Waples et al.,2010).

Assuming that the frequency factor is constant allows for correcting the experimental data in one of two ways. The first method, appropriate for the situation in which the activation energy is the same for all of the samples, corrects the apparent activation energies by projecting the corresponding regression line to the point that corresponds with the assumed frequency factor (i.e. 1 X 10^{14} $sec.^{-1}$). This in effect reduces the apparent variation in the data that comprise the compensation effect into a single value. This approach is probably adequate for sample sets that generate a compensation effect with a slope that has a value close to the slope of the average, simulated compensation effect (5.96 +/- 0.07).

The second method uses the average slope of the simulated compensation effect to extrapolate a line though the point defined by a measured apparent activation energy and frequency factor and to the point that corresponds with an assumed frequency factor. In some respects this may be a more effective correction in that it does not assume sample homogeneity and does not remove all of the variation that is contained within the data. Furthermore it may be used when there is only one pair of data. This correction can be applied as follows:

Eq. 4

$$E_{ac} = E_{aa} + k_{CE}(A - A_a)$$

Where:

E_{aa} = Apparent activation energy (kJ/mole)
E_{ac} = Corrected activation energy (kJ/mole)
k_{CE} = slope of the "average" compensation effect (5.96 kJ/mole-ln(A m.y.))
A_a = Apparent frequency factor ln(A $m.y.^{-1}$)
A = Presumed frequency factor (ln(A $m.y.^{-1}$)) = 63.319 $m.y.^{-1}$

Therefore in order to recover the underlying activation energy E_a, the corresponding frequency factor (A) can be used in the regression equation developed using the apparent activation energy (E_{aa}) and apparent frequency factor (A_a). In this way, apparent activation energies may be corrected to an assumed frequency factor.

Table 2. Kinetic data for four samples of the N&D 1-05H and Stenehjem HD 27 1 (Kissinger plots and sample locations and logs are in Appendix 1). The apparent activation energies (E_{aa}) and natural logarithm of the frequency factors (ln(A_a $m.y.^{-1}$)) were "corrected" with Eq. 4 (E_{ac}) using a fixed frequency factor of 1 x 10 14 sec^{-1} converted to the equivalent natural logarithm in terms of $m.y.^{-1}$ (ln(A)). T_{max} (^{o}C) from a Rock Eval 6 analysis is included as well.

Well Name	Depth	Formation	ln(A_a)	E_{aa}	E_{ac}	ln(A)	T_{max}
N&D 1-05H	9482	Bakken	62.86792	220.31043	222.99887	63.319	430
N&D 1-05H	9469	Bakken	62.476843	218.04332	223.06257	63.319	426
N&D 1-05H	9426	Bakken	61.487442	211.5774	222.49348	63.319	428
N&D 1-05H	9410	Bakken	60.915765	209.29263	223.61591	63.319	430
Stenehjem HD 27 1	10992	Bakken	65.060303	238.66153	228.28337	63.319	451
Stenehjem HD 27 1	10923	Bakken	64.916238	237.46257	227.94303	63.319	451
Stenehjem HD 27 1	10971	Bakken	64.124863	233.11687	228.31393	63.319	451
Stenehjem HD 27 1	10906	Bakken	61.701548	221.30029	230.9403	63.319	452

Conclusions:

Error associated with measurements of the peak reaction temperature during programmed pyrolysis experiments designed to deliver estimates of activation energy and frequency factor produce erroneous results. Simulations show that small temperature errors are capable of generating a log–linear trend in apparent activation energy and the natural logarithm of the frequency factor. The slope of this linear trend or "compensation effect" is almost constant for both the experimental and simulated data. This constancy in compensation effect slope suggests that the nonisothermal experiments considered may be corrected or standardized by translating the apparent activation energy along a line parallel to the average of the simulated compensation effect slope (5.96) to a point defined by a frequency factor with a constant value of 1×10^{14} sec^{-1}.

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Nielsen, S. B. and Dahl, B., 1991. Confidence limits on kinetic models of primary cracking and implications for the modelling of hydrocarbon generation. *Marine and Petroleum Geology*, **8**, 489-493.

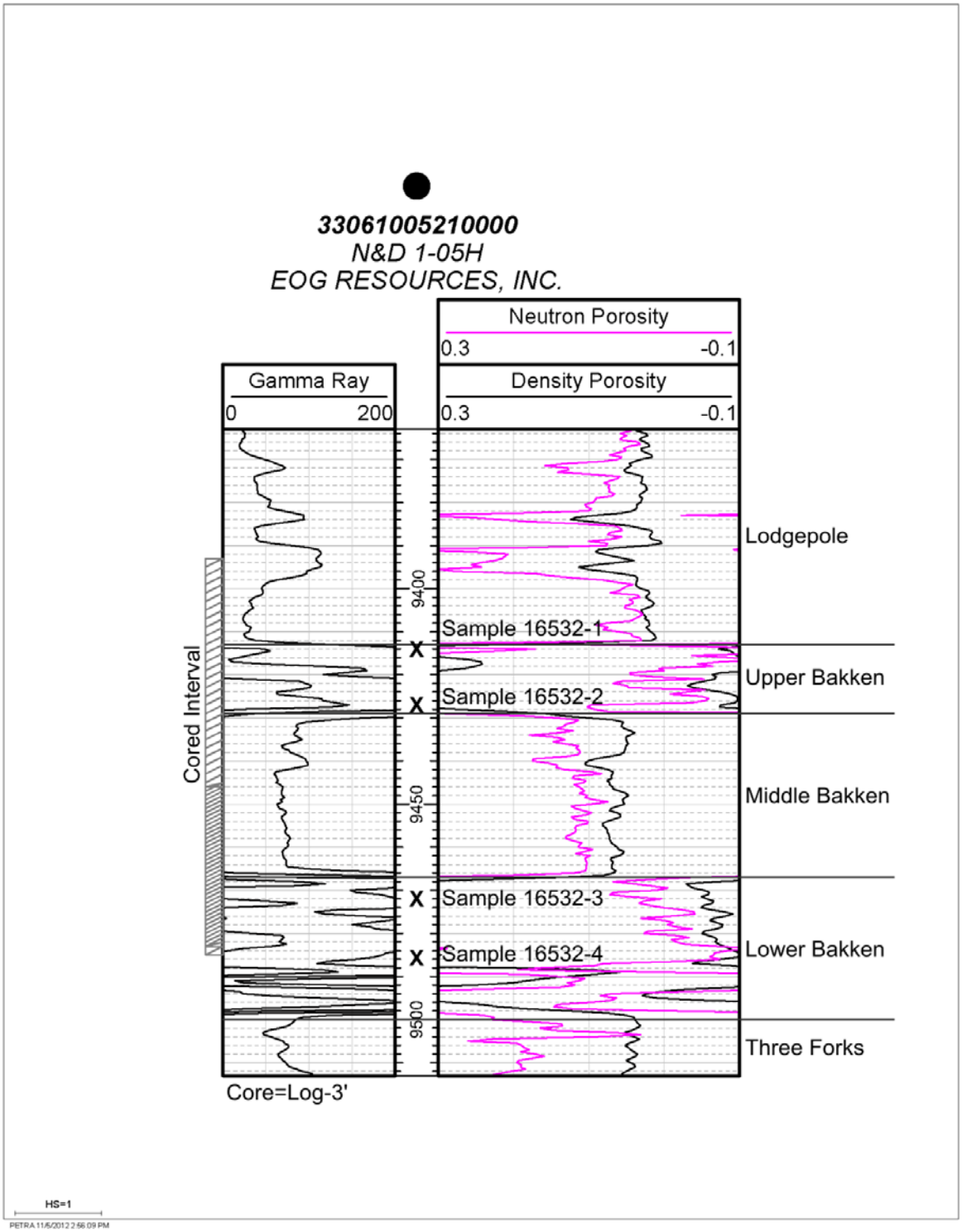
Waples, D.W., S. Safwat, R. Nagdy, R. Coskey, and J.E. Leonard, 2010, A new method for obtaining personalized kinetics from archived Rock-Eval data, applied to the Bakken Formation, Williston Basin, AAPG International Conference and Exhibition Abstracts Volume, 7 pp.

Waples, D. W., 2000. The kinetics of in-reservoir oil destruction and gas formation: constraints from experimental and empirical data, and from thermodynamics, Organic Geochemistry, v. 31, p. 553-575.

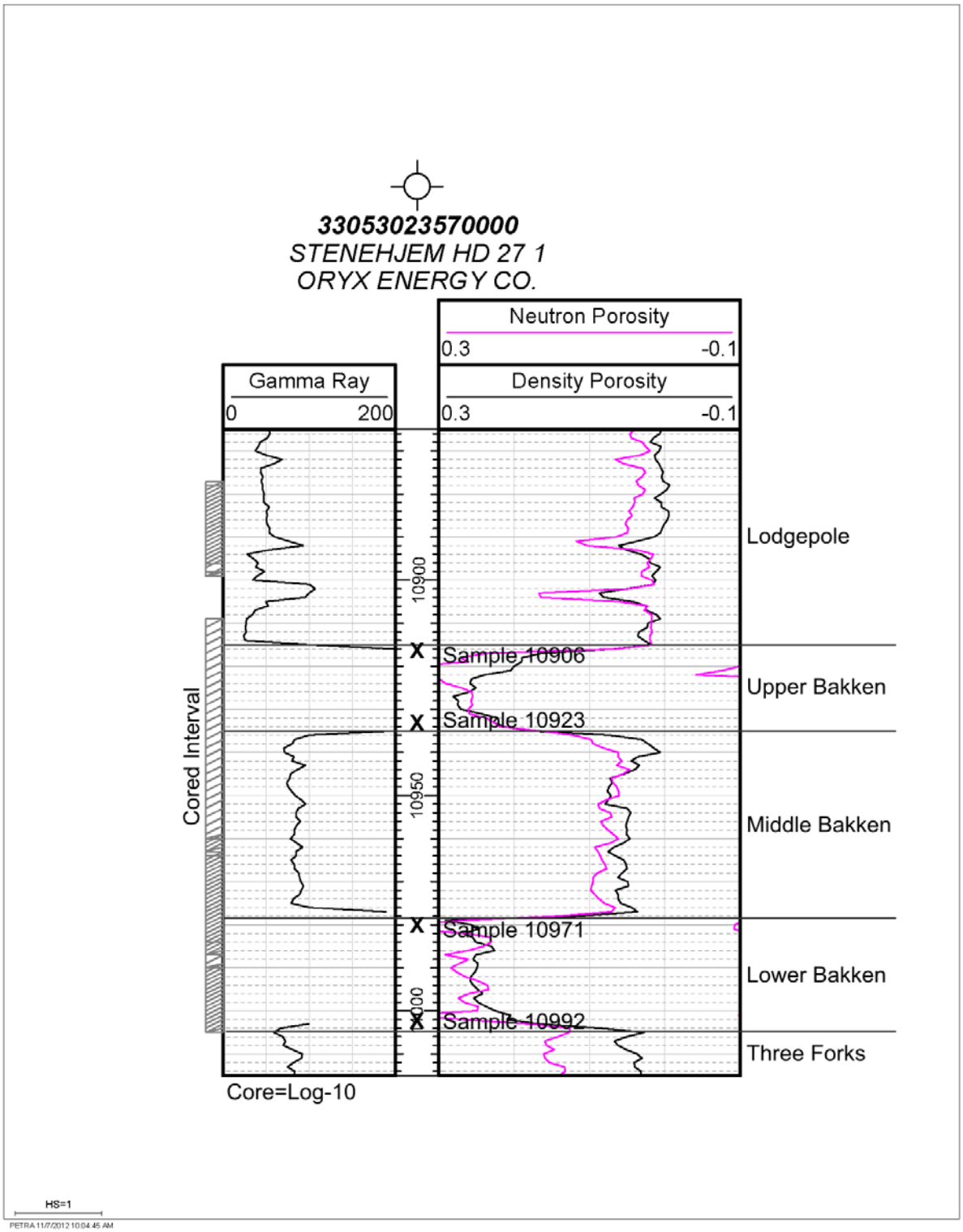
Appendix I

Results from Rock Eval 6 and LECO TOC analysis of samples from the N&D 1 05 H and Stenehjem HD 27-1.

Sample ID	WELL NAME	Core Depth (ft.)	S_1 mg Oil / g sample	S_2 mg HC / g sample	S_3 mg CO_2 / g sample	T_{MAX} (°C)	LECO TOC (wt %)	HI $100XS_2$ / TOC	OI $100XS_3$ / TOC	PI $S_1/(S_1+S_2)$
16532-1	N&D 1-05 H	9410.5	9.33	101.83	1.50	430	17.03	598	9	0.084
16532-2	N&D 1-05 H	9426	8.41	67.64	0.71	428	11.57	584	6	0.111
16532-3	N&D 1-05 H	9469	11.79	101.70	2.24	426	18.30	556	12	0.104
16532-4	N&D 1-05 H	9482.5	11.41	54.82	0.65	430	10.70	512	6	0.172
10906	Stenehjem HD 27-1	10906	5.64	11.62	0.49	452	6.83	170	7	0.33
10923	Stenehjem HD 27-1	10923	5.35	15.02	0.42	451	9.30	161	5	0.26
10971	Stenehjem HD 27-1	10971	5.97	18.96	0.47	451	12.24	155	4	0.24
10992	Stenehjem HD 27-1	10992	6.11	19.68	0.42	451	13.48	146	3	0.24

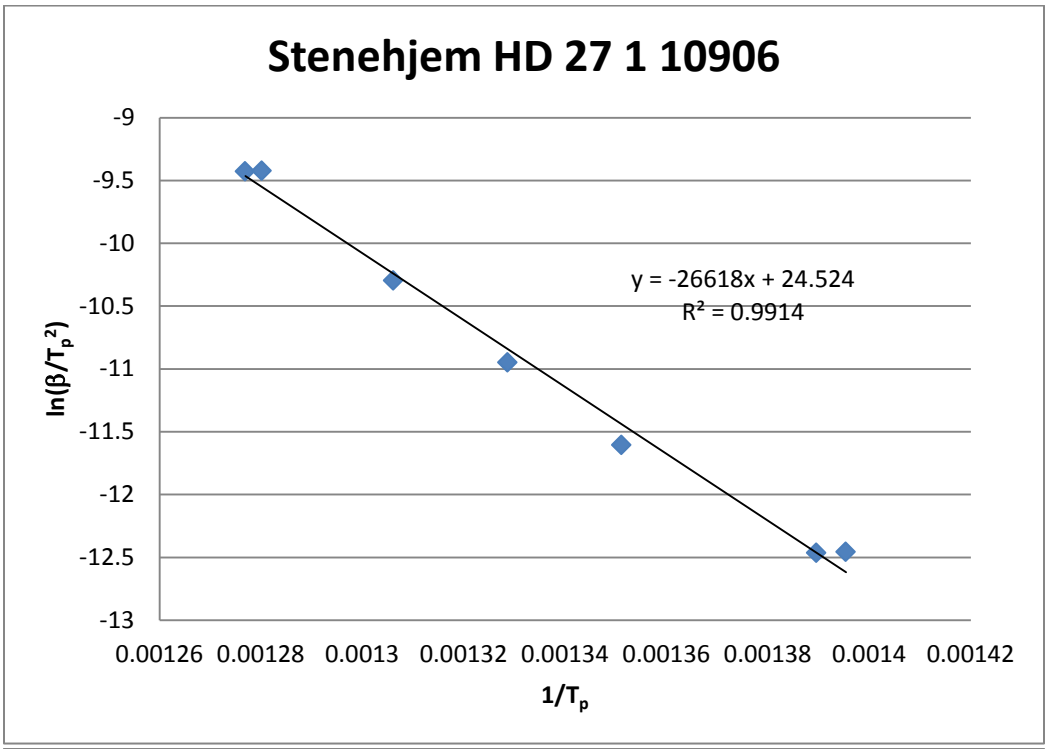


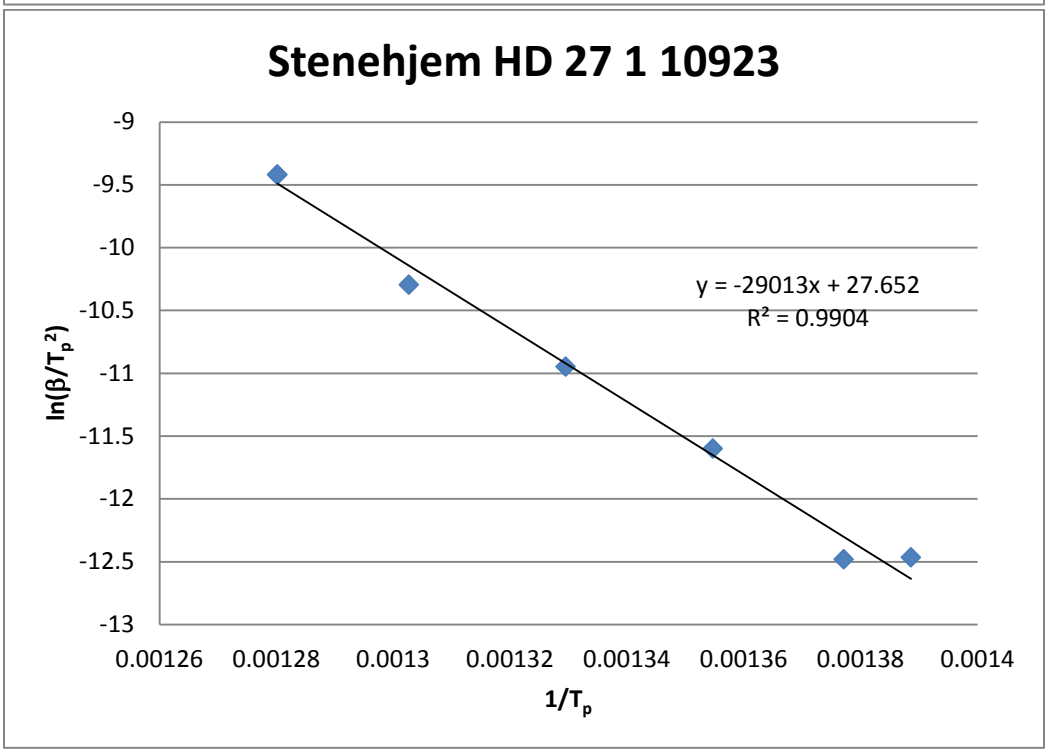
Gamma Ray, Neutron and Density of the N&D 1 05 H showing sample locations and formation boundaries and cored interval.

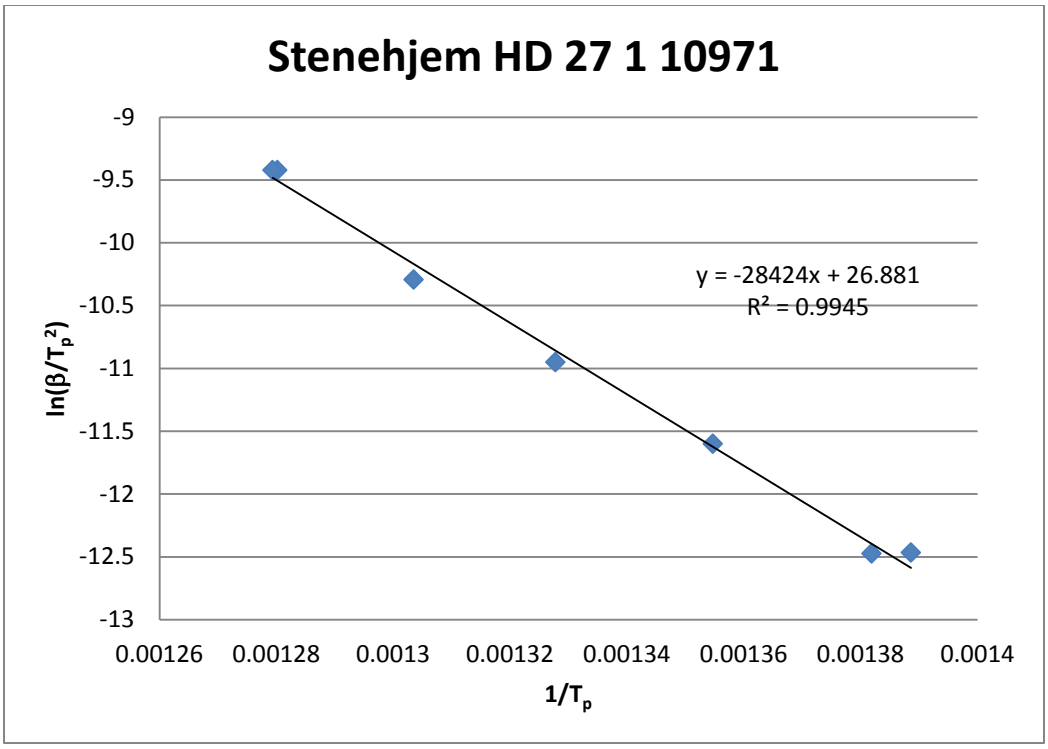


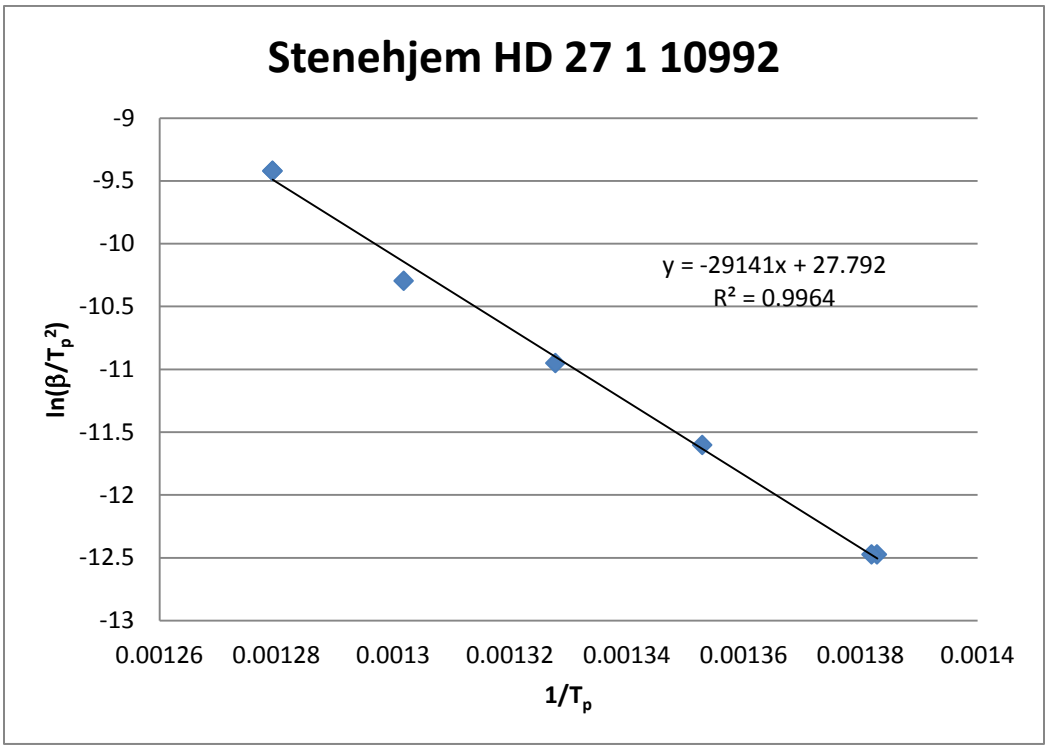
Gamma Ray, Neutron and Density of the Stenehjem HD 27 1 showing sample locations, formation boundaries and cored interval.

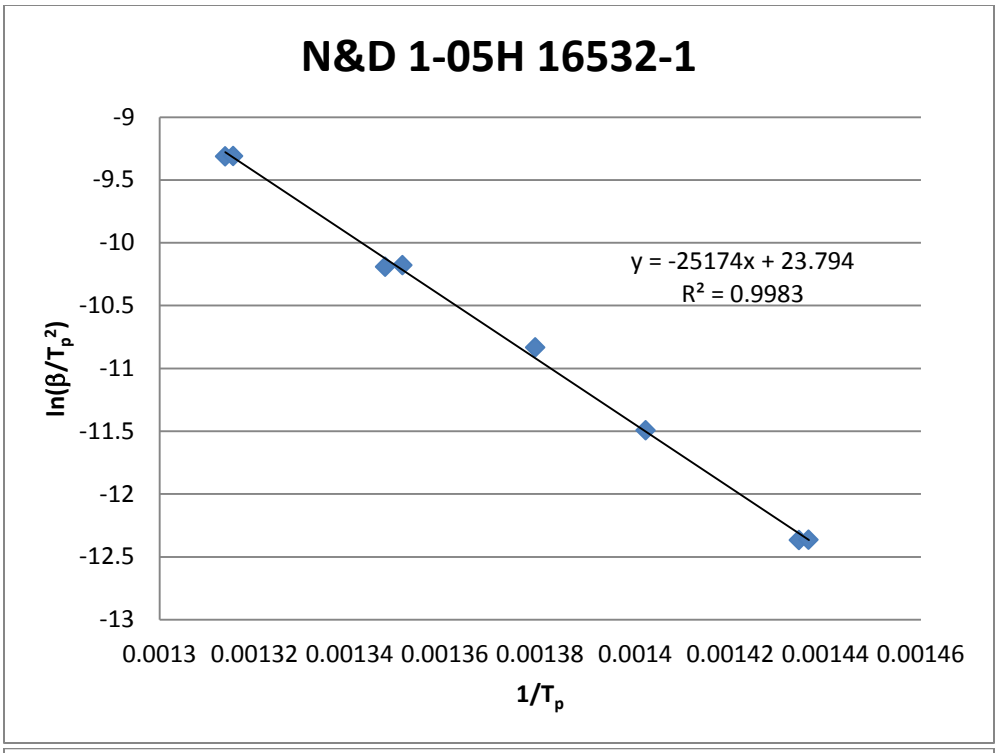
Kissinger plots used to find the apparent activation energy and frequency factor using the peak reaction temperature (T_p ^oC) and heating rate (b ^oC/min). The linear regression equation and R^2 value are posted for each data set.

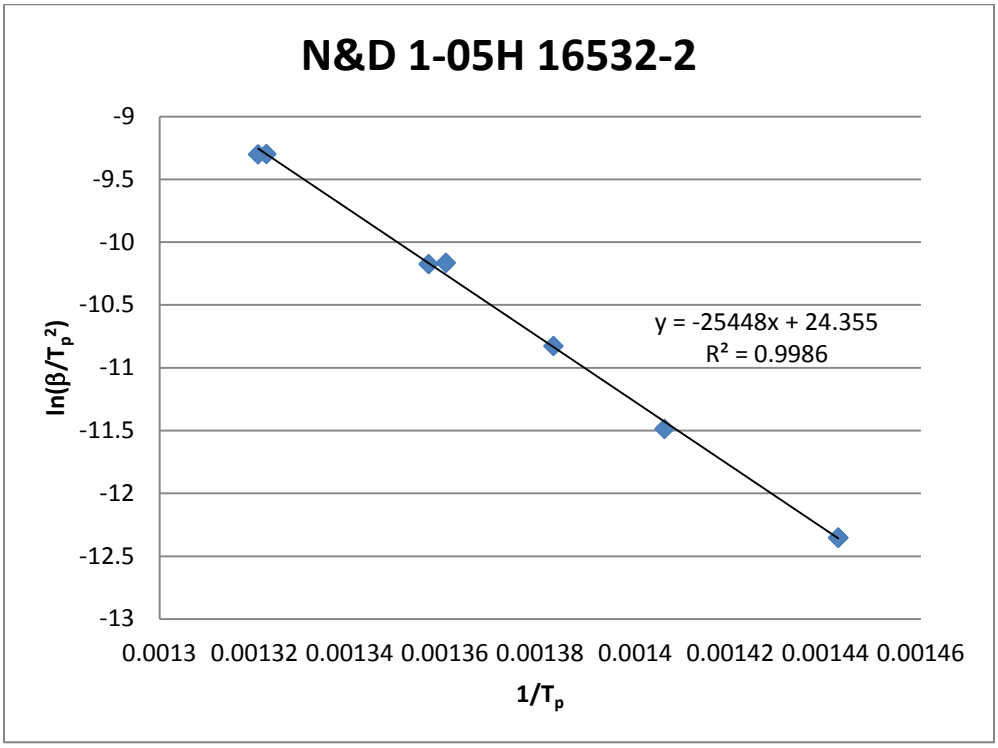


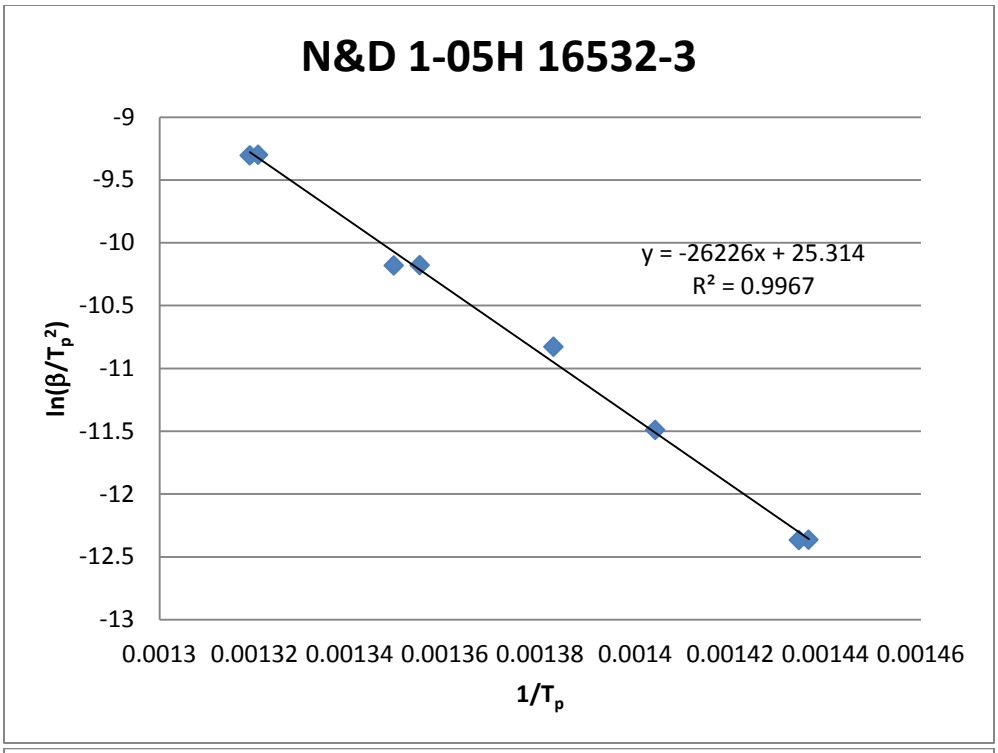



Stenehjem HD 27 1 10971
-9
-9.5
-10
-10.5
-11
-11.5
-12
-12.5
-13
ln(β/T_p^2)
y = -28424x + 26.881
R² = 0.9945
0.00126
0.00128
0.0013
0.00132
0.00134
0.00136
0.00138
0.0014
1/T_p


Stenehjem HD 27 1 10992
-9
-9.5
-10
-10.5
-11
-11.5
-12
-12.5
-13
ln(β/T_p^2)
y = -29141x + 27.792
R² = 0.9964
0.00126
0.00128
0.0013
0.00132
0.00134
0.00136
0.00138
0.0014
1/T_p


N&D 1-05H 16532-1
-9
-9.5
-10
-10.5
-11
-11.5
-12
-12.5
-13
ln(β/T_p^2)
y = -25174x + 23.794
R² = 0.9983
0.0013 0.00132 0.00134 0.00136 0.00138 0.0014 0.00142 0.00144 0.00146
1/T_p


N&D 1-05H 16532-2
-9
-9.5
-10
-10.5
-11
-11.5
-12
-12.5
-13
ln(β/T_p^2)
y = -25448x + 24.355
R² = 0.9986
0.0013 0.00132 0.00134 0.00136 0.00138 0.0014 0.00142 0.00144 0.00146
1/T_p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-13
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y = -26226x + 25.314
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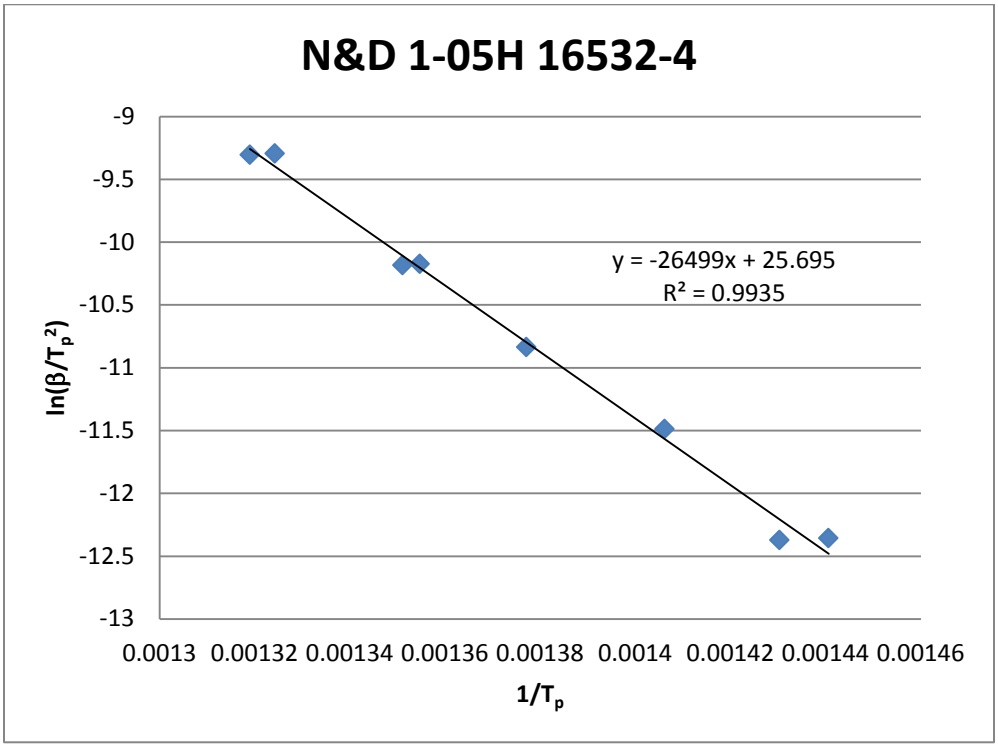
1/T_p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-10
-10.5
-11
-11.5
-12
-12.5
-13
ln(β/T_p^2)
y = -26499x + 25.695
R² = 0.9935
0.0013 0.00132 0.00134 0.00136 0.00138 0.0014 0.00142 0.00144 0.00146
1/T_p