
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 ($\beta$) which leads to a solution for the activation energy ($E_a$) and frequency factor ($A$) with the following expression:

$$\ln \left( \frac{\beta}{T_p^2} \right) = -\frac{E_a}{R} \left( \frac{1}{T_p} \right) + \ln\left( A R / E_a \right)$$

Where:

- $\beta$ = Heating rate (°K/min)
- $T_p$ = Peak Reaction Temperature (°K)
- $R$ = Gas Constant (°K-mole)
- $E_a$ = Activation energy (°K-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 ($\beta$), 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 $\beta$ by assuming constant values for activation
energy ($E_a$), frequency factor ($A$) and peak reaction temperature ($T_p$). Once $\beta$ is found then random
error is added to the peak reaction temperature ($T_{pe} = T_p + \text{Error}$) and the corresponding values for
$\ln(\frac{\beta}{T_{pe}^2})$ and $1/T_{pe}$ are found. The error is obtained with a random number drawn from a normal
distribution defined by a mean ($\mu$) equal to the assumed peak reaction temperature ($\mu=T_p$) and a fixed
variance ($\sigma^2$). Repeating this process, using different peak reaction temperatures and random error,
produces values of $\ln(\frac{\beta}{T_{pe}^2})$ 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

\[
\begin{align*}
\text{Slope} &= -\frac{E_{aa}}{R} \\
\text{Intercept} &= \frac{A_a R}{E_{aa}}
\end{align*}
\]

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 $E_a$ and $A_a$. The
experimental method used by the NDGS to determine $E_a$ and $A_a$ for various source rocks in North
Dakota typically use five heating rates (2 (2 runs), 5, 10, 20, 50 (2 runs) °C/min.). The simulations
presented here use similar heating rates (2.3 (2 runs), 5.5, 9.4, 20.8, 45.5 (2 runs) °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 ($\sigma^2 = 1 ^\circC$) 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 $A = 1 \times 10^{14}$ 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) °C and a variance of 1.0 °C. These peak temperatures and kinetic parameters are associated with heating rates of 2.3, 5.5, 9.4, 20.8, and 45.5 °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).

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

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 ($\sigma^2$) is either 1 or 3 °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 ($1 \times 10^{14}$ 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 $1 \times 10^{15}$ (blue) or $1 \times 10^{14}$ (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 $1 \times 10^{14}$ 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):

\[ A = C \cdot e^{(\Delta S/R)} \]

Where:
- $C = T \cdot k_b/h$
- $T = \text{Temperature (}{^\circ}\text{K)}$
- $k_b = \text{Boltzman constant}$
- $h = \text{Plank constant}$
- $R = \text{Gas constant}$
- $\Delta S = \text{Entropy of activation}$

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. \(1 \times 10^{14} \text{ sec}^{-1}\)). 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:

\[
E_{ac} = E_{aa} + k_{CE}(A - A_a)
\]

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 \(1 \times 10^{14} \text{ sec}^{-1}\) converted to the equivalent natural logarithm in terms of m.y. \(^{-1}\) \(\ln(A)\). \(T_{\text{max}}\) (°C) from a Rock Eval 6 analysis is included as well.

<table>
<thead>
<tr>
<th>Well Name</th>
<th>Depth</th>
<th>Formation</th>
<th>(\ln(A_a))</th>
<th>(E_{aa})</th>
<th>(E_{ac})</th>
<th>(\ln(A))</th>
<th>(T_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>N&amp;D 1-05H</td>
<td>9482</td>
<td>Bakken</td>
<td>62.86792</td>
<td>220.31043</td>
<td>222.99887</td>
<td>63.319</td>
<td>430</td>
</tr>
<tr>
<td>N&amp;D 1-05H</td>
<td>9469</td>
<td>Bakken</td>
<td>62.476843</td>
<td>218.04332</td>
<td>223.06257</td>
<td>63.319</td>
<td>426</td>
</tr>
<tr>
<td>N&amp;D 1-05H</td>
<td>9426</td>
<td>Bakken</td>
<td>61.487442</td>
<td>211.5774</td>
<td>222.49348</td>
<td>63.319</td>
<td>428</td>
</tr>
<tr>
<td>N&amp;D 1-05H</td>
<td>9410</td>
<td>Bakken</td>
<td>60.915765</td>
<td>209.29263</td>
<td>223.61591</td>
<td>63.319</td>
<td>430</td>
</tr>
<tr>
<td>Stenehjem HD 27 1</td>
<td>10992</td>
<td>Bakken</td>
<td>65.060303</td>
<td>238.66153</td>
<td>228.28337</td>
<td>63.319</td>
<td>451</td>
</tr>
<tr>
<td>Stenehjem HD 27 1</td>
<td>10923</td>
<td>Bakken</td>
<td>64.916238</td>
<td>237.46257</td>
<td>227.94303</td>
<td>63.319</td>
<td>451</td>
</tr>
<tr>
<td>Stenehjem HD 27 1</td>
<td>10971</td>
<td>Bakken</td>
<td>64.124863</td>
<td>233.11687</td>
<td>228.31393</td>
<td>63.319</td>
<td>451</td>
</tr>
<tr>
<td>Stenehjem HD 27 1</td>
<td>10906</td>
<td>Bakken</td>
<td>61.701548</td>
<td>221.30029</td>
<td>230.9403</td>
<td>63.319</td>
<td>452</td>
</tr>
</tbody>
</table>
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 $1 \times 10^{14}$ sec$^{-1}$.

References:


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.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>WELL NAME</th>
<th>Core Depth (ft.)</th>
<th>$S_1$ mg Oil gc sample</th>
<th>$S_2$ mg HC gc sample</th>
<th>$S_3$ mg CO2 gc sample</th>
<th>$T_{MAX}$ (°C)</th>
<th>LECO TOC (wt %)</th>
<th>HI $100X_{S_2}$ TOC</th>
<th>OI $100X_{S_2}$ TOC</th>
<th>PI $S_1$ ($S_1+S_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16532-1</td>
<td>N&amp;D 1-05 H</td>
<td>9410.5</td>
<td>9.33</td>
<td>101.83</td>
<td>1.50</td>
<td>430</td>
<td>17.03</td>
<td>598</td>
<td>9</td>
<td>0.084</td>
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<tr>
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<td>N&amp;D 1-05 H</td>
<td>9426</td>
<td>8.41</td>
<td>67.64</td>
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<td>428</td>
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<td>9469</td>
<td>11.79</td>
<td>101.70</td>
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<td>12</td>
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<tr>
<td>16532-4</td>
<td>N&amp;D 1-05 H</td>
<td>9482.5</td>
<td>11.41</td>
<td>54.82</td>
<td>0.65</td>
<td>430</td>
<td>10.70</td>
<td>512</td>
<td>6</td>
<td>0.172</td>
</tr>
<tr>
<td>10906</td>
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<td>10906</td>
<td>5.64</td>
<td>11.62</td>
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<td>6.83</td>
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<td>451</td>
<td>12.24</td>
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<td>4</td>
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<td>Stenehjem HD 27-1</td>
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<td>6.11</td>
<td>19.68</td>
<td>0.42</td>
<td>451</td>
<td>13.48</td>
<td>146</td>
<td>3</td>
<td>0.24</td>
</tr>
</tbody>
</table>

8
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 ($T_p$ °C) and heating rate ($b$ °C/min). The linear regression equation and $R^2$ value are posted for each data set.

**Stenehjem HD 27 1 10906**

\[ y = -26618x + 24.524 \]
\[ R^2 = 0.9914 \]

**Stenehjem HD 27 1 10923**

\[ y = -29013x + 27.652 \]
\[ R^2 = 0.9904 \]
$$y = -28424x + 26.881$$
$$R^2 = 0.9945$$

$$y = -29141x + 27.792$$
$$R^2 = 0.9964$$
y = -25174x + 23.794
R² = 0.9983

y = -25448x + 24.355
R² = 0.9986
\[ y = -26226x + 25.314 \]
\[ R^2 = 0.9967 \]

\[ y = -26499x + 25.695 \]
\[ R^2 = 0.9935 \]