Multistep and Distributed Reactivity Models for Kinetic Analysis

Alan K. Burnham

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Typical thermal analysis approach to kinetics

\[ \frac{d\alpha}{dt} = k(T)f(\alpha)h(\alpha) \]

where \( \alpha \) is conversion or fraction reacted, \( t \) is time, \( k \) is the rate constant,

\[ k(T) = A \exp(-E/RT) \]

\( f(\alpha) \) is the dependence of the reaction rate on conversion,

and \( h(\alpha) \) is the pressure dependence on conversion

\( h(\alpha) \) is usually unity but is also commonly a power law \((P^n)\) or a deviation from equilibrium \((1-P/P_{eq})\)

Many materials have multiple components that might behave additively:

\[ \frac{d\alpha_i}{dt} = k_i(T)f_i(\alpha_i) \]

*IMPORTANT ASSUMPTION

The separation of temperature and conversion dependence is not universally true, but it is usually a good approximation

It is an isoconversional assumption
“The Table” is repeated *ad nauseam* in the thermal analysis literature

<table>
<thead>
<tr>
<th>Reaction model</th>
<th>Code</th>
<th>Differential form, ( f(\alpha) )</th>
<th>Integral form, ( g(\alpha) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{st}) order</td>
<td>F1</td>
<td>1-(\alpha)</td>
<td>-ln(1-(\alpha))</td>
</tr>
<tr>
<td>Pseudo 2(^{nd}) order</td>
<td>F2</td>
<td>((1-\alpha)^2)</td>
<td>1/(1-(\alpha)) -1</td>
</tr>
<tr>
<td>nth order</td>
<td>Fn</td>
<td>((1-\alpha)^n)</td>
<td>(1/(n-1) [(1-\alpha)^{(1-n)}-1] )</td>
</tr>
<tr>
<td>Contracting cylinder</td>
<td>R2</td>
<td>2(1-(\alpha))(^{1/2})</td>
<td>1-(1-(\alpha))(^{1/2})</td>
</tr>
<tr>
<td>Contracting sphere</td>
<td>R3</td>
<td>3(1-(\alpha))(^{2/3})</td>
<td>1-(1-(\alpha))(^{1/3})</td>
</tr>
<tr>
<td>Power law</td>
<td>(P_v)</td>
<td>(v\alpha^{(v-1)/v})</td>
<td>(\alpha^{1/v})</td>
</tr>
<tr>
<td>Avrami-Erofe’ev</td>
<td>Ap</td>
<td>(p(1-\alpha)[-\ln(1-\alpha)]^{(p-1)/p})</td>
<td>([-\ln(1-\alpha)]^{1/p})</td>
</tr>
<tr>
<td>Extended Prout-Tompkins</td>
<td>ePT</td>
<td>((1-\alpha)^n(1-q(1-\alpha))^m)</td>
<td>no analytical solution</td>
</tr>
<tr>
<td>1D diffusion</td>
<td>D1</td>
<td>(\frac{1}{2} \alpha^{-1})</td>
<td>(\alpha^2)</td>
</tr>
<tr>
<td>2D diffusion</td>
<td>D2</td>
<td>([-\ln(1-\alpha)]^{-1})</td>
<td>((1-\alpha)\ln(1-\alpha)+\alpha)</td>
</tr>
<tr>
<td>3D diffusion (Jander)</td>
<td>D3</td>
<td>(\frac{3}{2}(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1})</td>
<td>([1-(1-\alpha)^{1/3}]^2)</td>
</tr>
<tr>
<td>3D diffusion (G-B)</td>
<td>D4</td>
<td>(\frac{3}{2} [(1-\alpha)^{-1/3}-1])</td>
<td>1-2(\alpha/3)-(1-(\alpha))(^{2/3})</td>
</tr>
</tbody>
</table>

Equations in white boxes are relevant to this talk
I and others often use fraction remaining, \(x=1-\alpha\)

\[
g(\alpha)=\int_0^\alpha \frac{d\alpha}{f(\alpha)}=\int_0^t k(T)dt
\]
Reactions of real materials deviate from first-order mainly in two ways.

![Fraction Reacted](image1)

![Reaction Rate](image2)
Fossil fuels and other complex materials require a reactivity distribution

Inferred average molecular structures

**oil-prone kerogen**


**bituminous coal**

Parallel reactions can be used to model distributed chemical reactivity

- Let A, B, and C be lumped chemical species

- The reactions of $A_i$ and $B_i$ are independent parallel reactions

- Ordinarily, reaction channels from A are lumped together then partitioned into $B_i$ independent of $A_i$

- It is possibly in principle to have a more complicated mapping of $A_i$ to $B_i$, but normally there is insufficient information

- For char-forming materials, often there is only one channel from A to B then a reaction manifold from B to C
There are multiple approaches to modeling reactivity distributions

Isoconversional

\[
\ln \left( \frac{d\alpha}{dt} \right)_{\alpha, i} = \ln[f(\alpha)A_\alpha] - E_\alpha/RT_{\alpha, i}
\]

Power law in time

\[ \alpha = kt^n \quad (n<1) \]

\( \approx \) Gamma distribution in \( k \)

Pseudo nth-order reaction

\[ \frac{d\alpha}{dt} = k (1 - \alpha)^n \]

\( \approx \) Gamma distribution in \( k \)

\( \approx \) power law in \( t \)

Continuous E distributions

Gaussian, Weibull, etc.

Discrete distributions

\( E \) only and \( E \) with \( \ln(A)=a+bE \)
Power law and distributed E models give similar results for vitrinite maturation

- Woody plant debris (vitrinite) becomes more reflective as it becomes more graphitic during heating by burial
- Modeling vitrinite reflectance is ubiquitous for calibrating paleothermal histories used in petroleum system modeling
- Easy%Ro (Sweeney and Burnham, *AAPG Bull.*, 1991) is the most commonly used parallel kinetic model (E distribution) for vitrinite reflectance
Various approaches can be used for sigmoidal reactions

- **Sequential**
  - $A \xrightarrow{k_1} B \xrightarrow{k_2} C$
  - $\frac{dB}{dt} = -\frac{dA}{dt} - \frac{dC}{dt}$

- **Autocatalytic**
  - $A \xrightarrow{k_1} B$; $A + B \xrightarrow{k_2} 2B$

- **JMAEK**
  - Overlapping nucleation-growth or homogeneous reaction

$$
A = e^{-k_1 t}
$$
$$
B = \frac{k_1}{k_2 - k_1} e^{-k_1 t} - e^{-k_2 t}
$$
$$
C = \frac{1}{k_2 - k_1} [k_2 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_2 t})]
$$

$$
\frac{dA}{dt} = -k_1 A - k_2 AB;
$$
$$
\frac{d\alpha}{dt} = k_1 (1 - \alpha)^{n_1} + k_2 \alpha^m (1 - \alpha)^{n_2}
$$
$$
n_1 = n_2
$$
$$
z = k_1 / k_2 \approx 1 - q
$$
$$
\approx k_2 (1 - \alpha)^n (1 - q(1 - \alpha))^m
$$

$$
\alpha = 1 - \exp(-kt^p)
$$
$$
\frac{d\alpha}{dt} = pk (1-\alpha) [-\ln(1-\alpha)]^{(p-1)/p}
$$
$$
= k' (1 - \alpha)^b \alpha^a
$$

---
ePT = autocatalytic = mn logistic = nucleation-growth
How to develop a kinetic model

1. Acquire reproducible data free of heat and mass transport resistances for high conversions under a variety of thermal histories
   - A mixture of isothermal and nonisothermal data is good
2. Examine the data for characteristic features (look at it!)
3. Fit the data with a sequence of increasingly sophisticated methods
A rough guide for ramped heating of ordinary samples is to be below 100 mg°C/min for large samples.

For large samples, you can measure thermal gradients and convolve with chemical kinetics.

Sample size, g

Heating rate, °C/min

8-kg OS cylinders
ΔT = 8, 25, 70, 180 °C @ 0.03, 0.1, 0.3, 1 °C/min

40-g OS cylinders
ΔT = 7, 20, 110 °C @ 2, 5, 60 °C/min

OS powder @ 14.3°C/min
ΔT = 8 °C for 90 g compared to 5 mg

Cellulose @ 150 °C/min
ΔT = 16+δ

7+δ, 3+δ, δ

HMX
ΔT = 1, 7 °C for cellulose

Boundary of Hajiilo et al.

Boundary of Lyon et al.

typical heated grid experiment

good
Successful model fitting requires a sequence of analysis steps

Preliminary analysis
- inspect reaction profiles for multiple reactions
- check constancy of E by isoconversional analysis
- examine profile shape for acceleratory, deceleratory, or auto-catalytic character

Choose one or more probable models

Single Reaction
- Linear model fitting
- Nonlinear model fitting

Complex reaction
- Nonlinear model fitting
Some materials may need multiple reactions

Polycarbonate—skewed to low T

Polysulfone—skewed to high T (2 rxns?)

Polyvinylacetate—clearly 2 rxns

Secondary stages may require a reactivity distribution in addition

Burnham & Braun, E&F (1999)
Burnham, JTAC (2000)
Friedman and Kissinger methods are good first steps

» Friedman (1964)
- The isoconversional assumption is that the reaction at each conversion $\alpha$ has a specific $A$ and $E$ value regardless of the thermal history leading to that conversion

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[f(\alpha)A_{\alpha}] - \frac{E_{\alpha}}{RT_{\alpha,i}}$$

- For a first-order reaction, one can model the entire reaction as an infinitely sequential first-order reactions: $f(\alpha_i) = (1-\alpha_i)$

» Kissinger (1957)

$$\frac{dx}{dt} = -kx \quad x = \text{fraction remaining}$$

$$d(dx/dt)/dT = 0 = -xdk/dT - kdx/dT$$

$$0 = -xdk/dT - k(dx/dt)(dt/dT)$$

$$ln(\beta/RT_{max}^2) = ln(A/E) - E/RT_{max}$$

- Rigorously correct for first-order reactions and an excellent approximation for nth-order, nucleation-growth, and E-distribution models
A simple example with three parallel reactions having $E=49$, 51, and 53 kcal/mol

Friedman plot for $\alpha = 0.1, 0.3, 0.5, 0.7, 0.9$
For multiple heating rates, the width and shape of the reaction curves are revealing.

First estimate $A$ and $E$ using Kissinger's method.

FWHH = full width at half height
Generalized reaction rate master plots are also useful to deduce appropriate models.

**Generalized Reduced Reaction Rate**

\[
\frac{(d\alpha/dt)_i}{(d\alpha/dt)_{0.5}} \exp \left[ \frac{E}{R} \left( \frac{1}{T_i} - \frac{1}{T_{0.5}} \right) \right]
\]

Gotor et al., *JPCA* (2000)
**Bakken (Type II) petroleum source rock**

<table>
<thead>
<tr>
<th>Model</th>
<th>E Parameter</th>
<th>kcal/mol</th>
<th>$A$, s$^{-1}$</th>
<th>$n$</th>
<th>$\sigma$</th>
<th>r.s.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friedman</td>
<td>E at 50% conv.</td>
<td>55.26</td>
<td>6.34e14</td>
<td>1</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>Kissinger</td>
<td>E for $T_{\text{max}}$</td>
<td>50.72</td>
<td>3.74e13</td>
<td>1</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>nth-order</td>
<td>E</td>
<td>51.89</td>
<td>8.85e13</td>
<td>1.60</td>
<td>0</td>
<td>0.127</td>
</tr>
<tr>
<td>Gaussian E</td>
<td>$E_0$</td>
<td>53.13</td>
<td>1.70e14</td>
<td>1</td>
<td>2.32</td>
<td>0.147</td>
</tr>
<tr>
<td>Discrete E</td>
<td>Primary E</td>
<td>53.00</td>
<td>1.23e14</td>
<td>1</td>
<td>0</td>
<td>0.006</td>
</tr>
</tbody>
</table>

**Fit to Discrete E-Distribution Model**

![Graph showing fields of application for various models and normalized reaction rate over temperature.]

- **Asymmetry** vs. **Relative FWHH**
- **Normalized reaction rate** vs. **Temperature, C**
Examples of E distributions from Type II petroleum source rocks

- **Bakken**
  - LLNL: \( A = 9.8 \times 10^{13} \text{ s}^{-1} \)
  - Arco: \( A = 1.8 \times 10^{14} \text{ s}^{-1} \)

- **Kimmeridge**
  - LLNL: \( A = 2.9 \times 10^{14} \text{ s}^{-1} \)
  - Arco: \( A = 1.8 \times 10^{14} \text{ s}^{-1} \)

- **La Luna**
  - LLNL: \( A = 6.0 \times 10^{13} \text{ s}^{-1} \)
  - Arco: \( A = 7.7 \times 10^{13} \text{ s}^{-1} \)

- **Posidonia**
  - LLNL: \( A = 5.9 \times 10^{13} \text{ s}^{-1} \)
  - KFA: \( A = 1.8 \times 10^{14} \text{ s}^{-1} \)

- **New Albany**
  - LLNL: \( A = 2.0 \times 10^{14} \text{ s}^{-1} \)
  - HISI: \( A = 3.7 \times 10^{13} \text{ s}^{-1} \)

- **Woodford**
  - LLNL: \( A = 2.6 \times 10^{14} \text{ s}^{-1} \)
  - HISI: \( A = 1.8 \times 10^{10} \text{ s}^{-1} \)
Caution for extrapolation: $A$ is not really constant for reactivity distributions.

Type II source rock
Friedman isoconversional analysis

Extended Discrete

$\ln(A) = a + bE$

Discrete

- Extended Discrete #1
- Extended Discrete #2
- Isoconversional

Fraction converted

Temperature, °C

3 °C/m.y.
Bituminous coal fits to either a discrete $E$ distribution or two Gaussian $E$ distributions

- TGA data converted to fraction volatilized
- Can be analyzed as fractions reacted or absolute reaction rate

**Graph:**
- Title: Two Gaussian reactions
- X-axis: Temperature, C
- Y-axis: Fraction reacted
- Graph shows multiple curves representing different models

**Table:**

<table>
<thead>
<tr>
<th>Bit. Coal Model</th>
<th>E parameter</th>
<th>kcal/mol</th>
<th>$A$, s$^{-1}$</th>
<th>n</th>
<th>sigma</th>
<th>r.s.s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friedman</td>
<td>E at 50% conv.</td>
<td>59.00</td>
<td>6.23e14</td>
<td>1</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>Kissinger</td>
<td>E for $T_{max}$</td>
<td>57.05</td>
<td>4.13e14</td>
<td>1</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>nth-order</td>
<td>E</td>
<td>48.96</td>
<td>8.11e12</td>
<td>5.02</td>
<td>0</td>
<td>0.196</td>
</tr>
<tr>
<td>Gaussian E</td>
<td>Mean E</td>
<td>61.52</td>
<td>3.92e15</td>
<td>1</td>
<td>11.3</td>
<td>0.799</td>
</tr>
<tr>
<td><strong>Two Gaussian</strong></td>
<td>Mean E’s</td>
<td>55.7, 61.5</td>
<td>2.56e14</td>
<td>1</td>
<td>3.1, 2.0</td>
<td>0.024</td>
</tr>
<tr>
<td>Discrete E</td>
<td>Primary E</td>
<td>59.00</td>
<td>3.21e15</td>
<td>1</td>
<td>0</td>
<td>0.009</td>
</tr>
</tbody>
</table>

**Note:**
- BP approach for petroleum source rocks

*Diagram*:
- Composition relation among various models
- X-axis: $A$, s$^{-1}$
- Y-axis: $E$, kcal/mol
Fitting the Discrete $E$ distribution simultaneously to rates and fractions reacted is best.

**Fit to Rates**
- r.s.s.
- Rates: 0.023
- Cum: 0.035

**Fit to Integrals**
- r.s.s.
- Rates: 0.051
- Cum: 0.009

**Fit to Both**
- r.s.s.
- Rates: 0.024
- Cum: 0.014
Some kerogens are narrower than a first-order reaction

Proposed structure of cell wall of B. Braunii

1, 7, and 50 °C/min
Burnham et al., E&F (1996)
An autocatalytic model works best for Boghead coal

<table>
<thead>
<tr>
<th>Model</th>
<th>E Parameter</th>
<th>kcal/mol</th>
<th>A, s⁻¹</th>
<th>n</th>
<th>m</th>
<th>r.s.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friedman</td>
<td>E at 50% conv.</td>
<td>58.51</td>
<td>1.24e15</td>
<td>1</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>Kissinger</td>
<td>E for T_max</td>
<td>50.72</td>
<td>4.09e14</td>
<td>1</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>Serial A→B</td>
<td>E</td>
<td>55.78</td>
<td>6.93e14</td>
<td>1</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>Serial B→C</td>
<td>E</td>
<td>57.53</td>
<td>6.93e14</td>
<td>1</td>
<td>0</td>
<td>0.250</td>
</tr>
<tr>
<td>ePT</td>
<td>E</td>
<td>57.45</td>
<td>7.73e14</td>
<td>1.02</td>
<td>0.32</td>
<td>0.138</td>
</tr>
</tbody>
</table>

![Graph showing normalized reaction rate and temperature for ePT and serial models](image)

![Graph showing fields of application for various models](image)
Isothermal pyrolysis gives unambiguous evidence for a serial or nucleation-growth model

Isothermal fluidized-bed pyrolysis, Burnham et al., *E&F* (1996)

<table>
<thead>
<tr>
<th>serial</th>
<th>Fits to Frejus fluidized-bed data: 473-512 °C</th>
<th>nuc-growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, s⁻¹</td>
<td>1.42×10¹⁴</td>
<td>A, s⁻¹</td>
</tr>
<tr>
<td>E1, kcal/mol</td>
<td>54.4</td>
<td>1.24×10¹⁴</td>
</tr>
<tr>
<td>E2, kcal/mol</td>
<td>54.6</td>
<td>54.5</td>
</tr>
<tr>
<td>r.s.s.</td>
<td>0.32</td>
<td>r.s.s.</td>
</tr>
</tbody>
</table>
Char-forming polymers typically combine autocatalytic and distributed reactivity reactions

- Thermal decomposition of poly(vinyl chloride)
  - Kissinger analysis
    \[ A = 2.08 \times 10^{10} \text{ s}^{-1}; \quad E = 31.93 \text{ kcal/mol} \]

Four model variations gave equivalent quality fits—also fitting $n_1$ gave slight improvements ($n_1 \sim 1.2$)

<table>
<thead>
<tr>
<th>Char model</th>
<th>$f_1$</th>
<th>$A_1$</th>
<th>$E_1$</th>
<th>$m_1$</th>
<th>$n_1$</th>
<th>$f_2$</th>
<th>$A_2$</th>
<th>$E_2$</th>
<th>$\sigma_2$</th>
<th>$n_2$</th>
<th>r.s.s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>nth-order</td>
<td>0.62</td>
<td>2.3e10</td>
<td>31.0</td>
<td>0.65</td>
<td>1</td>
<td>0.38</td>
<td>7.6e10</td>
<td>35.1</td>
<td>0</td>
<td>1.7</td>
<td>0.021</td>
</tr>
<tr>
<td>Gaussian</td>
<td>0.60</td>
<td>2.3e10</td>
<td>31.0</td>
<td>0.67</td>
<td>1</td>
<td>0.40</td>
<td>2.0e11</td>
<td>36.5</td>
<td>3.5</td>
<td>1</td>
<td>0.020</td>
</tr>
<tr>
<td>nth-gauss</td>
<td>0.61</td>
<td>1.9e10</td>
<td>30.8</td>
<td>0.67</td>
<td>1</td>
<td>0.39</td>
<td>1.9e11</td>
<td>36.2</td>
<td>2.3</td>
<td>1.5</td>
<td>0.020</td>
</tr>
<tr>
<td>mn-logistic</td>
<td>0.63</td>
<td>1.7e10</td>
<td>30.7</td>
<td>0.66</td>
<td>1</td>
<td>0.37</td>
<td>5.1e10</td>
<td>34.9</td>
<td>-0.10</td>
<td>1.6</td>
<td>0.020</td>
</tr>
</tbody>
</table>
An E-distribution model works better for interrupted heating of source-sink species

- Char yield and subsequent decomposition depends on pyrolysis conditions
- A good kinetic model will work for partial reaction, cooling, the reheating
- Only a parallel reaction model (explicit distribution of reactivity) works for species generated and consumed (essential for many reaction networks)
- Distributions of activation energy are the most common

Pyrolysis of spruce wood powder

L.N. Samuelsson et al. / Fuel Processing Technology 149 (2016) 275–284

Wood pyrolysis data provided for model fitting
Preliminary analysis suggests char pyrolysis has a higher $E$ than do xylan and cellulose.

Friedman analysis

Nucleation

Weibull

Nth-Order

Gaussian

Kissinger analysis

$A = 2.97 \times 10^{12} \text{ s}^{-1}$

$E = 42.5 \text{ kcal/mol}$
Similar fits are obtained using nth-order and autocatalytic models for the cellulose component.

Simultaneous fits to reaction rates and fractions reacted:
- A in s\(^{-1}\); E in kcal/mol; \(f_i = 0.38, 0.42, 0.20\)
- Plots show reaction rate normalized by calculated rate

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>E</th>
<th>n</th>
<th>σ</th>
<th>r.s.s. rates</th>
<th>r.s.s frac reac</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.15x10(^{13})</td>
<td>42.2</td>
<td>0.64</td>
<td>4.7%</td>
<td>0.33</td>
<td>0.04</td>
</tr>
<tr>
<td>2</td>
<td>1.09x10(^{13})</td>
<td>41.1</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.47x10(^{16})</td>
<td>55.0</td>
<td>9.0</td>
<td>5%</td>
<td>0.91</td>
<td>0.09</td>
</tr>
<tr>
<td>4</td>
<td>4.00x10(^{13})</td>
<td>42.4</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5.65x10(^{16})</td>
<td>55.0</td>
<td>11.1</td>
<td>5%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The three spruce powder kinetic models give equivalent predictions for isothermal conditions.

The decision on which to use for a specific application depends on what kind of compositional modeling is desired.
Summary and Conclusions

- Isoconversional and model fitting methods are both useful and complementary.
- Some applications require distributed reactivity and complex competitive reaction networks:
  - Beyond typical thermal analysis software and methodologies.
  - Commonly available in other application communities.

Acknowledgments

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Robert Braun for providing continuing software programming support.