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A New Integral Approximation Formula for Kinetic Analysis of Nonisothermal TGA Data

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INTRODUCTION

A knowledge of kinetic behavior is essential for understanding and predicting the thermal behavior of coal conversion processes (Wen and Lee, 1979; Collett and Rand, 1980), woody material thermal decomposition (Tang and Neill, 1964), and biomass pyrolysis-gasification-combustion processes (Milne, 1979). The thermal behavior of coal, wood and related biomass is frequently studied by measuring the rate of weight loss of the material as a function of time and temperature. This information, coupled with a proposed reaction mechanism, is then used to estimate activation energies and frequency factors for Arrhenius type reaction rate expressions. This note presents a new integral approximation formula for extracting these kinetic parameters from experimental data. It will be shown that this method is superior to the commonly used integral approximation formula (Coats and Redfern, 1964).

Thermogravimetric analysis (TGA) provides a semiquantative understanding of pyrolysis under well-controlled laboratory conditions. Furthermore, by the use of fine particles and small sample sizes, phenomena related to transport problems can be minimized. Consequently, the validity of TGA data for kinetic analysis of primary pyrolysis is greatly enhanced.

Thermogravimetric analysis is normally performed in either the isothermal or nonisothermal (dynamic) mode. The advantages (Freeman and Carroll, 1958) of investigating reaction kinetics by a dynamic TGA are that considerably less experimental data are required than in the isothermal method and the kinetics can be probed over the entire temperature range in a continuous manner. In addition, when a sample undergoes significant reaction in being raised to the temperature of interest, the results obtained by the isothermal method are often questionable.

Three basic approaches to analysis of nonisothermal TGA data have been discussed in the literature. The differential method (Sharp and Wentworth, 1969) and the difference-differential method (Tang, 1967; Freeman and Carroll, 1958; Sharp and Wentworth, 1969) suffer from some inherent disadvantages. The integral method (Jahnke et al. 1960; Coats and Redfern, 1964) seems to be the best method. The Coats-Redfern equation has been used as an approximation formula for the integral method, but is not as precise as desired. A new integral approximation formula is derived below that is more precise than the Coats-Redfern equation, yet is simple and easy to apply.

DERIVATION OF APPROXIMATION FORMULA

Irreversible pyrolysis of solids is typically described by the following chemical equation:

$$sS_{(s)} \rightarrow rR_{(s)} + vV_{(g)}$$

where S, R and V are original solid, final solid residue, and volatile matter, respectively.

The decomposition rate of a solid can be represented by the general rate expression shown below.

$$\frac{d\omega}{dt} = kf(\omega) \qquad (1)$$

where ω is the decomposed fraction of solid (on the decomposable basis) at time t, $f(\omega)$ is a function of ω depending on the reaction mechanism and k is the rate constant given by the Arrhenius equation as

$$k = A\exp(-E/RT) \qquad (2)$$

where A = frequency factor, E = activation energy, R = universal gas constant, T = absolute temperature.

For a linear heating rate, say β K/min, the following relationship is valid

$$\beta = \frac{dT}{dt} \qquad (3)$$

Combining Eqs. 1, 2 and 3 and integrating between the initial temperature, T_0, and any final temperature, T, and conversion between ω_0 and ω, respectively results in Eq. 4.

$$\int_{\omega_0}^{\omega} \frac{d\omega}{f(\omega)} = \frac{A}{\beta}\int_{T_0}^{T} \exp(-E/RT)dT \qquad (4)$$

The righthand side of Eq. 4 is not analytically integrable, but can be integrated by parts to obtain the expression shown in Eq. 5.

$$\int_{T_0}^{T} \exp(-E/RT)dT = \frac{RT^2}{E}\exp(-E/RT)\bigg|_{T_0}^{T} - \int_{T_0}^{T} \frac{2RT}{E}\exp(-E/RT)dt \qquad (5)$$

Rearrangement of Eq. 5 gives Eq. 6.

$$\int_{T_0}^{T} \left(1 + \frac{2RT}{E}\right)\exp(-E/RT)dT = \frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right)\bigg|_{T_0}^{T} \qquad (6)$$

Since $2RT/E$ is much less than unity at moderate temperatures and

TABLE 1. PYROLYSIS PARAMETERS

Feedstock	Maximum Temp., K	Apparent Activation Energy, kJ/mol	Reference
Biomass	900	46–235	Antal (1981), Milne (1979), Charnet and Ray (1980)
Cellulosics	800	50–235	Tang (1967), Antal et al. (1980)
Montana Lignite	1,300	205	Anthony et al. (1975)
Pittsburgh Seam Bituminous Coal	1,300	155	Wen et al. (1979)
Pitch Materials	900	46–238	Collett and Rand (1980)
Tobacco	1,300	67–109	Baker (1978)
Ferulic Acid	600	117	Juntgen et al. (1968)
$Mg(OH)_2$	750	222–238	Fong and Chen (1977)

• Data obtained under intermediate or low heating rate pyrolysis.

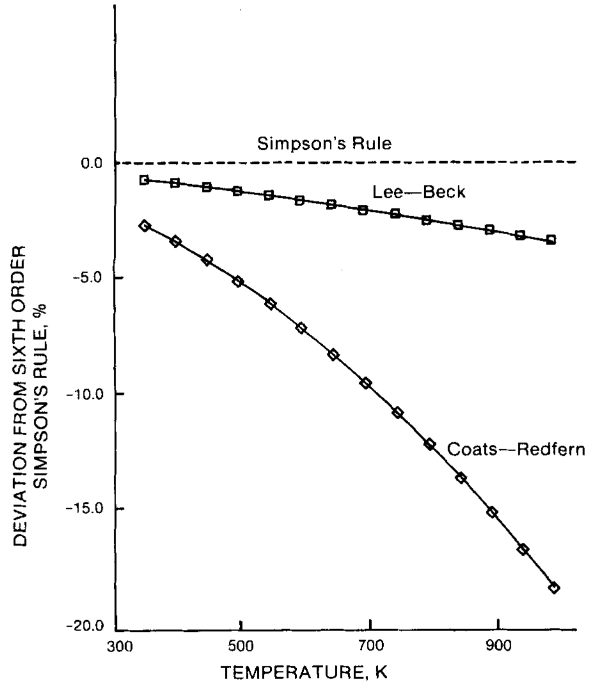

Figure 1. Comparison of approximation methods (E = 49 kJ/mol).

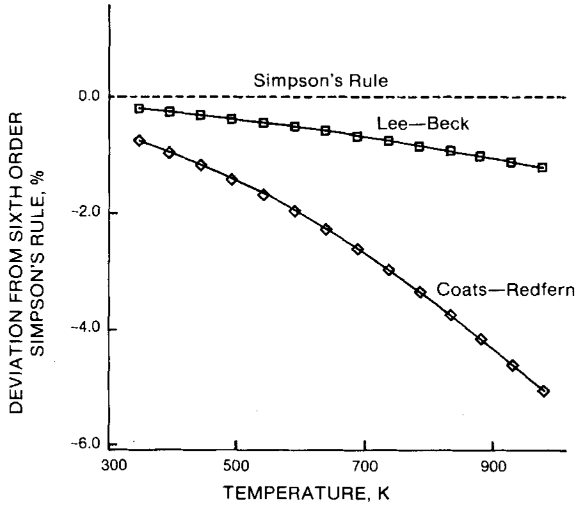

Figure 2. Comparison of approximation methods (E = 85 kJ/mol).

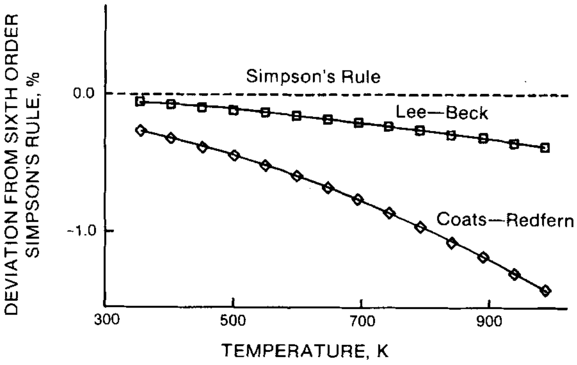

Figure 3. Comparison of approximation methods (E = 170 kJ/mol).

high activation energies, the value of $(1 + 2RT/E)$ is in the neighborhood of unity. Therefore, $(1 + 2RT/E)$ is assumed constant. Equation 6 is then rearranged to give Eq. 7.

$$\int_{T_0}^{T} \exp(-E/RT)dT \cong \left[\frac{RT^2}{E}\exp(-E/RT)\right]/(1+2RT/E)\Big|_{T_0}^{T} \tag{7}$$

Equation 7 can be substituted into Eq. 4 to obtain Eq. 8.

$$\int_{\omega_0}^{\omega}\frac{d\omega}{f(\omega)} = \frac{A}{\beta}\left[\frac{\left(\frac{RT^2}{E}\right)\exp\left(-\frac{E}{RT}\right)}{\left(1+\frac{2RT}{E}\right)} - \frac{\left(\frac{RT_0^2}{E}\right)\exp\left(\frac{-E}{RT_0}\right)}{\left(1+\frac{2RT_0}{E}\right)}\right] \tag{8}$$

The Coats-Redfern equation is shown in Eq. 9 for later comparison.

$$\int_{\omega_0}^{\omega}\frac{d\omega}{f(\omega)} \cong \frac{A}{\beta}\left[\frac{RT^2}{E}\left(1-\frac{2RT}{E}\right)\exp\left(-\frac{E}{RT}\right) - \frac{RT_0^2}{E}\left(1-\frac{2RT_0}{E}\right)\exp\left(-\frac{E}{RT_0}\right)\right] \tag{9}$$

Some commonly used mechanism cases $(f(\omega))$ are summarized in Eqs. 10–12. For first order reaction, $f(\omega) = (1 - \omega)$

$$\int_{\omega_0}^{\omega}\frac{d\omega}{f(\omega)} = ln(1-\omega_0) - ln(1-\omega) \tag{10}$$

For nth-order reaction, $f(\omega) = (1 - \omega)^n$

$$\int_{\omega_0}^{\omega}\frac{d\omega}{f(\omega)} = \left(\frac{1}{1-n}\right)[(1-\omega_0)^{1-n} - (1-\omega)^{1-n}] \tag{11}$$

For zeroth-order reaction, $f(\omega) = 1$

$$\int_{\omega_0}^{\omega}\frac{d\omega}{f(\omega)} = \omega - \omega_0 \tag{12}$$

RESULTS

Rather than analyzing specific experimental data, the objective of this analysis was to compare the approximation formulas shown in Eqs. 8 and 9. By using realistic kinetic parameters, the best ap-

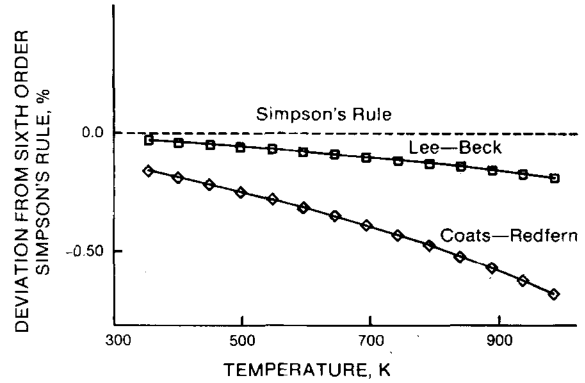

Figure 4. Comparison of approximation methods (E = 250 kJ/mol).

TABLE 2. EFFECT OF ACTIVATION ENERGY AND TEMPERATURE ON APPROXIMATION METHODS

Apparent Activation Energy, kJ/mol	Deviation from Sixth-Order Simpson's Rule, %			
	700 K		900 K	
	Lee-Beck	Coats-Redfern	Lee-Beck	Coats-Redfern
40	−2.08	−9.59	−2.92	−14.9
85	−0.67	−2.64	−1.06	−4.31
170	−0.19	−0.76	−0.32	−1.18
250	−0.10	−0.35	−0.17	−0.59

proximation method was determined. This method can then be used to analyze experimental results.

The ranges of parameters to be used was found from previous pyrolysis studies, shown in Table 1.

Four different activation energies, 41.8, 83.7, 167 and 251 kJ/mol, were chosen for comparison. The temperature ranged from 300 to 1,000 K. Figures 1–4 show the comparisons between the Coats-Redfern approximation (Eq. 9) and the present approximation (Eq. 8). The fourth-order Trapezoidal rule and the sixth-order Simpson's rule were used to calculate the reference values. Agreement between the Simpson and Trapezoidal values proved preciseness of the reference values. The results showed both approximations reflected negative deviations and, in all cases, the Lee-Beck equation is superior to the Coats-Redfern equation.

For all approximations, it is concluded that the lower the activation energy, the larger the $(2RT/E)$ value. This results in larger deviations from reference values. Higher temperature also increases the $(2RT/E)$ value and will lead to a larger deviation. Table 2 illustrates how the activation energy affects the approximations.

The maximum deviations for the Coats-Redfern formula is 18.6 and is 3.4% for the Lee-Beck formula. Accurate approximation is the most favorable characteristic for the newly developed approximation. In addition, this equation retains simplicity in calculation and formulation.

NOTATION

A = Arrhenius frequency factor, s^{-1}
E = apparent activation energy, kJ/mol
k = reaction rate constant, s^{-1}
r = stochiometric coefficient of char residue
$R_{(s)}$ = char residue
R = gas constant (8.314 J/mol·K)
s = stoichiometric coefficient of unreacted solid
$S_{(s)}$ = unreacted solid
t = time, s
T = absolute temperature, K
v = stoichiometric coefficient of volatile pyrolysis products
$V_{(g)}$ = volatile pyrolysis products

Greek Letters

β = heating rate, K/s
ω = fraction of solid pyrolyzed

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