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TECHNICAL NOTES

A method for determination of chemical rate mostly encountered in coal combustion processes

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INTRODUCTION

Chemical kinetics provides essential information about the material characteristics needed to solve the problem of chemically reactive flow systems and combustion processes. Generally speaking, it is difficult to find an acceptable form of chemical reactions occurring in coal and liquid fuel combustion which are widely used in industry. In this study, coal combustion is only of interest due to the fact that the details of the chemical reactions in liquid fuel combustion are rather poorly understood with one exception of which a structural analogy can be considered between pyrolyzing softening coals (behaves like liquid above 650 K) and heavy oil droplets [1]. The concept of a Gaussian distribution of activation energies of chemically reactive species has been usually used and found to be reasonable in describing the combustion of coal, oil shale and cellulose [2, 3].

The objective of this note is to determine the chemical rate, k_p, and the extent of thermal decomposition, ξ, during the combustion of coal by employing a concept of Gaussian distributed activation energies. The present method for these calculations is an extension of the method described by Suuberg [4].

New development for determination of properties, mainly chemical rate, k_p, and extent, ξ, has been achieved with a few modifications to a previously developed model. Hence, approximate solutions have been obtained for the chemical rate, k_p, and the extent, ξ, in terms of temperature, T, and critical activation energies, E_c.

FORMULATION

Conversion of the chemical structure into so-called metaplast (intermediates) is simply described by the following:

$$\text{Chemical structure} \xrightarrow[k_p]{} \text{Metaplast.}$$

The assumption is made here that there is a unique value of the Arrhenius pre-exponential, k_0, regardless of the activation energy. Constant k_0 models may indicate for example that the entropies of formation of activated complexes leading to the release of a particular species are similar to those described above.

The rate, k_p, is now given as follows:

$$k_p = \frac{\mathrm{d}\xi}{\mathrm{d}t} \tag{1}$$

where ξ is the fractional decomposition of the above structures, or since

$$\xi = 1 - \frac{Q}{Q_0} \tag{2}$$

and

$$k_p = -\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{Q}{Q_0}\right) \tag{3}$$

where Q is the amount of unreacted structure left at any time.

If q_k is some measure of the amount of material which will decompose with an activation energy, E, to yield volatile products, then

$$\frac{\mathrm{d}q_k}{\mathrm{d}t} = -k_0 q_k \exp\left(-\frac{E}{RT}\right). \tag{4}$$

Integration of equation (4) over time gives

$$\frac{q_k}{q_{k0}} = \exp\left[-\int_0^t k_0 \exp\left(-\frac{E}{RT}\right)\mathrm{d}T\right]. \tag{5}$$

The amount of species 'k' present at time zero is assumed to be given by a distribution function, $f(E)$, such that

$$q_{k0} = Q_0\, f(E)\,\mathrm{d}E \tag{6}$$

where

$$f(E) = \frac{1}{\sigma\sqrt{(2\pi)}}\exp\left[-\frac{(E-E_0)^2}{2\sigma^2}\right] \tag{7}$$

where E_0 is the mean activation energy of the distribution and σ the standard deviation.

The total amount of decomposable material, Q, at any time may be obtained by integrating overall activation energies as follows:

$$Q = \int_0^\infty q_k\,\mathrm{d}E. \tag{8}$$

The conversion, ξ, then is given as

$$\xi = 1 - \int_0^\infty \exp\left[\int_0^t -k_0 \exp\left(-\frac{E}{RT}\right)\mathrm{d}t\right] f(E)\,\mathrm{d}E. \tag{9}$$

The assumption has been made in the above equation that the pre-exponential factors, k_0, for all species 'k' are equal. Apparently one can write the rate of loss of the material, q_k, by taking the derivative in equation (8) as follows:

$$\frac{\mathrm{d}q_k}{\mathrm{d}t} = -k_0 Q_0 f(E)\,\mathrm{d}E \exp\left(-\frac{E}{RT}\right) \times \exp\left[\int_0^t -k_0 \exp\left(-\frac{E}{RT}\right)\mathrm{d}t\right]. \tag{10}$$

This is the usual starting point for distributed activation energy analysis. Since this integral rarely leads to closed form solutions, numerical integration is generally employed. However, one can certainly investigate the behaviour of the integrand in equation (10) which allows the integrals of this type to be reduced to very simple functions. A closed form solution is given below and is useful in understanding the physics of the pyrolysis better. It also reduces the computational time. Considering the time integral, a general time–temperature history may be a heating period, an iso-

NOMENCLATURE

b_c cooling rate [K s^{-1}]
b_h heating rate [K s^{-1}]
E activation energy [J mol^{-1}]
E_0 mean activation energy of the distribution [J mol^{-1}]
k_p chemical rate [s^{-1}]
k_0 pre-exponential factor [10^{13} s^{-1}]
q_k mass of species 'k' present in pyrolyzing material [kg]
Q_k total mass of reactive species at time t [kg]
Q_0 total mass of reactive species at time zero [kg]
R universal gas constant, 8.314 J mol^{-1} K^{-1}
t time [s]
T temperature [K].

Greek symbols
ξ extent of decomposition of the pyrolyzed material
σ standard deviation [J mol^{-1}].

thermal period, and a cooling period. Often reasonable linear approximations are made to these periods. In our case an isothermal period is excluded for simplicity.

During the heating period

$$T = b_h t + T_0 \quad \text{and} \quad \frac{dT}{dt} = b_h \tag{11}$$

and during the cooling period

$$T = -b_c t + T_p \quad \text{and} \quad \frac{dT}{dt} = -b_c \tag{12}$$

where T_p represents the maximum temperature attained during the course of combustion or pyrolysis. Inserting the definition of $f(E)$ and making a change of variables in the integral over time (changing to temperature) one obtains

$$k_p = k_0 \int_0^\infty \frac{1}{\sigma\sqrt{(2\pi)}} \exp\left[-\frac{(E-E_0)^2}{2\sigma^2} - \frac{E}{RT}\right] \times \exp\left[-k_0 \int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right)\frac{dT}{b_h}\right] dE \tag{13}$$

and considering the last integral over time (or temperature), one can use the following approximation:

$$\int \exp\left(-\frac{E}{RT}\right) dT \cong \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right) \tag{14}$$

which is valid for the case $E/RT \gg 1$. Then the rate k_p becomes

$$k_p = k_0 \int_0^\infty \frac{1}{\sigma\sqrt{(2\pi)}} \exp\left[-\frac{(E-E_0)^2}{2\sigma^2} - \frac{E}{RT}\right] \exp\left[-\frac{k_0}{b_h}\frac{R}{E} \times \left\{T^2 \exp\left(-\frac{E}{RT}\right) - T_0^2 \exp\left(-\frac{E}{RT_0}\right)\right\}\right] dE. \tag{15}$$

At the beginning of the combustion process the temperatures are so low that the last term inside the double exponential can be neglected. Now if one lets $F = F(E)$, then

$$F = F(E) = \exp\left[-\frac{k_0}{b_h}\frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right)\right]. \tag{16}$$

This function shows a steep behaviour so that the integrand may be approximated by a step function at the critical value of activation energy $E = E_c$. At the values of $E < E_c$, the integrand has a value of zero, while at $E > E_c$, the double exponential term has a value of unity. This can be seen in Fig. 1. The problem often arises how exactly to determine the critical value of E_c. A new technique is now proposed resulting in a formula for the values of E_c.

Let

$$X = \frac{E}{RT} \quad \text{and} \quad A = \frac{k_0 T}{b_h}. \tag{17}$$

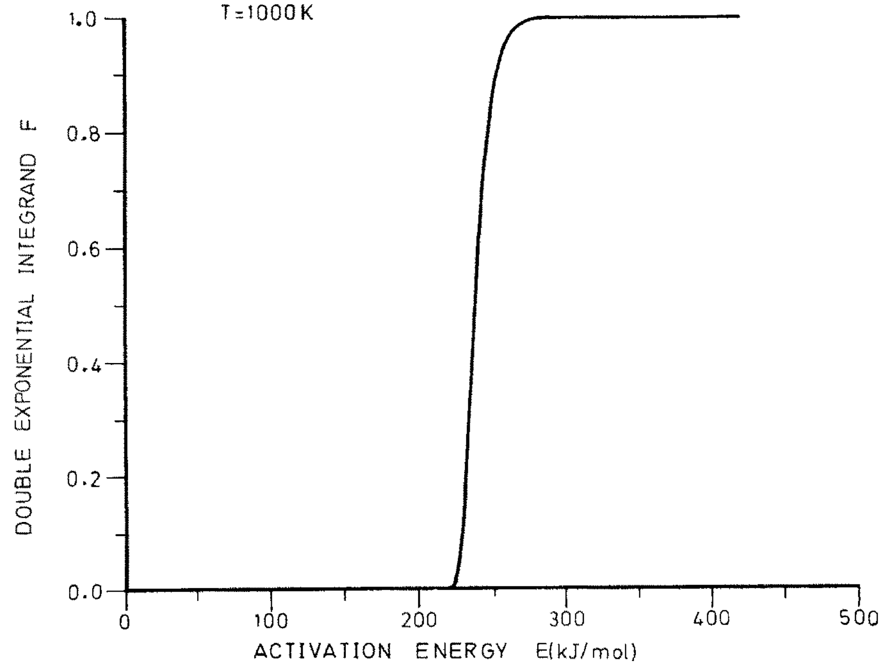

FIG. 1. $F = F(E)$ curve.

Thus

$$F = \exp\left[-\frac{A}{X}\exp(-X)\right]. \tag{18}$$

As can be seen in Fig. 1, there will be a turning point during the steep rise. By taking the logarithm in equation (18) one can write

$$X\exp(X)\ln F = -A. \tag{19}$$

Taking the derivative with respect to X one has the following for F':

$$F' = -F\ln F\left(1+\frac{1}{X}\right). \tag{20}$$

Considering $X \gg 1$

$$F' = -F\ln F. \tag{21}$$

In order to find the turning point one can take the derivative once again

$$F'' = -F'(1+\ln F). \tag{22}$$

At the turning point $F'' = 0$ and obviously $F' \neq 0$, thus

$$\ln F = -1. \tag{23}$$

Solving for F, one obtains

$$F = \exp(-1) = 0.3678. \tag{24}$$

This turning point will also be in the vicinity of the critical value of E_c. Since the steep rise occurs in a narrow range the critical value of E_c will be calculated at the turning point. Thus one has

$$\ln X + X = \ln A. \tag{25}$$

The solution to this equation for X will give the critical value of X_c.

Let

$$X_0 = \ln A \quad \text{and} \quad X = X_0(1-\theta). \tag{26}$$

Here $\theta \ll 1$. This means the solution is approximately equal to X_0. Then

$$\ln X_0(1-\theta) + X_0(1-\theta) = \ln A \tag{27}$$

or

$$\ln X_0 + \ln(1-\theta) + X_0 - X_0\theta = \ln A. \tag{28}$$

Since $X_0 = \ln A$ and $\ln(1-\theta) = -\theta$ for $\theta \ll 1$, one obtains the solution

$$\theta = \frac{\ln\ln A}{1+\ln A}. \tag{29}$$

Now one has the solution to the main equation as follows:

$$X_c = \left(1 - \frac{\ln\ln A}{1+\ln A}\right)\ln A. \tag{30}$$

This formula is very useful for obtaining the critical value of E_c with great accuracy. Thus one only needs a hand calculator to determine the critical value of E_c just knowing the parameter A or the pre-exponential k_0, temperature T, heating rate b_h. Some of the critical values of E_c and corresponding temperatures are given in Table 1. Since one now has the value of E_c, one can approximate the integral as follows:

$$k_p \cong k_0 \int_{E_c}^{\infty} \frac{1}{\sigma\sqrt{(2\pi)}}\exp\left[-\frac{(E-E_0)^2}{2\sigma^2} - \frac{E}{RT}\right]\mathrm{d}E. \tag{31}$$

By mathematical manipulation one obtains the chemical rate, k_p, as follows:

$$k_p = k_0\exp\left[\frac{\sigma^2}{2R^2T^2} - \frac{E_0}{RT}\right]\cdot\frac{1}{2}\operatorname{erfc}(u_c) \quad \text{if } u_c > 0 \tag{32}$$

Table 1. Calculated values of critical activation energies, E_c

$T(K)$	$\ln A$	X_c	E_c (kJ mol^{-1})
400	29.02	25.76	85.73
500	29.24	25.98	108.05
600	29.42	26.15	130.54
700	29.57	26.30	153.17
800	29.71	26.43	175.90
900	29.82	26.54	198.74
1000	29.93	26.64	221.67
1100	30.02	26.74	244.68
1200	30.11	26.82	267.76
1300	30.19	26.90	290.90

or

$$k_p = k_0\exp\left[\frac{\sigma^2}{2R^2T^2} - \frac{E_0}{RT}\right]\left(1 - \frac{1}{2}\operatorname{erfc}|u_c|\right) \quad \text{if } u_c < 0 \tag{33}$$

where

$$u_c = \frac{E_c - E_0}{\sqrt{2}\sigma} + \frac{\sigma}{\sqrt{2}RT}. \tag{34}$$

The extent, ξ, can be calculated as follows:

$$\xi = 1 - \frac{Q}{Q_0} \tag{35}$$

where the ratio Q/Q_0 is approximated as

$$\frac{Q}{Q_0} = \int_{E_c}^{\infty} \frac{1}{\sigma\sqrt{(2\pi)}}\exp\left[-\frac{(E-E_0)^2}{2\sigma^2}\right]\mathrm{d}E. \tag{36}$$

Then for the ratio Q/Q_0

$$\frac{Q}{Q_0} = \frac{1}{2}\operatorname{erfc}(y_c) \quad \text{if } y_c > 0 \tag{37}$$

or

$$\frac{Q}{Q_0} = 1 - \frac{1}{2}\operatorname{erfc}(|y_c|) \quad \text{if } y_c < 0 \tag{38}$$

where

$$y_c = \frac{E_c - E_0}{\sqrt{2}\sigma}. \tag{39}$$

Now for the extent, ξ, one has

$$\xi = 1 - \frac{1}{2}\operatorname{erfc}(y_c) \quad \text{if } y_c > 0 \tag{40}$$

or

$$\xi = \frac{1}{2}\operatorname{erfc}(|y_c|) \quad \text{if } y_c < 0 \tag{41}$$

where

$$y_c = \frac{E_c - E_0}{\sqrt{2}\sigma}. \tag{42}$$

CONCLUDING REMARKS

Since the chemical rate, k_p, the extent, ξ, and the ratio, Q/Q_0, depend on the critical activation energy, E_c, one only needs to calculate the value of E_c to determine these properties. Of course, all these properties also depend on the selection of the mean activation energy, E_0, and the standard deviation, σ. In this study, the values of $E_0 = 209.4$ kJ mol^{-1}, $\sigma = 41.9$ kJ mol^{-1} and $b_h = 1000$ K s^{-1} have been chosen [1].

The key result is the estimate of the value of critical acti-

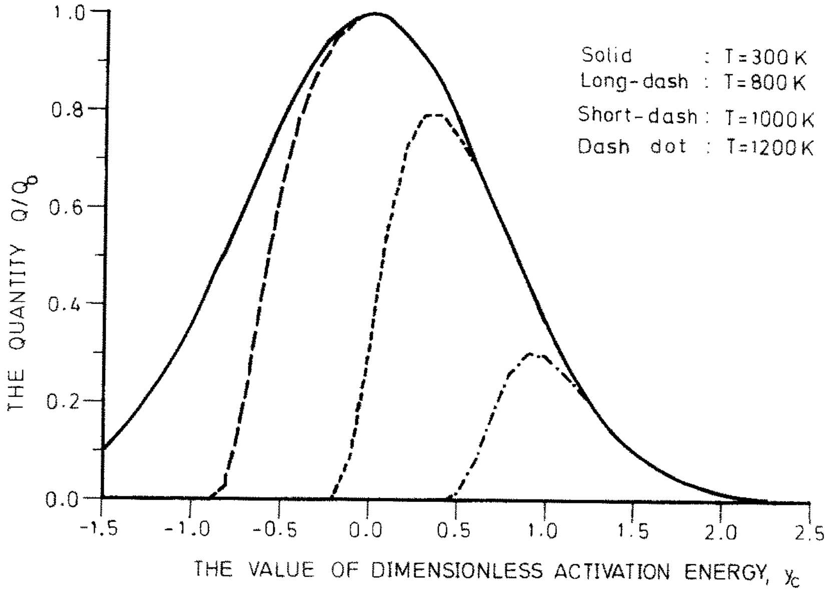

FIG. 2. Q/Q_0 curve.

vation energy, E_c, which is given by

$$E_c = X_c RT \quad \text{where} \quad X_c = \left(1 - \frac{\ln \ln A}{1 + \ln A}\right) \ln A. \tag{43}$$

Thus for the critical value of E_c one obtains

$$E_c = RT\left(1 - \frac{\ln \ln A}{1 + \ln A}\right) \ln A. \tag{44}$$

With this value of E_c in hand, one obtains the pyrolyzed material ratio, Q/Q_0, from equations (37) and (38). The graphical representation of Q/Q_0 for different temperatures can be seen in Fig. 2.

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Boundary effects on natural convection heat transfer for cylinders and cubes

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INTRODUCTION

MANY STUDIES have been done in the past concerning natural convection heat transfer into a fluid medium of infinite extent. More recently several studies have examined natural convection heat transfer to an enclosed fluid, where the convective motion is limited. Useful correlation equations have been developed for each case.

One difficulty often encountered in using these empirical equations is determining the range of gap width over which the equations for convection within an enclosure are applicable and when the equations for heat transfer into an infinite atmosphere apply. The object of this study was to examine heat transfer within an enclosure, increasing the gap width ratio over that studied previously to determine the bounds within which enclosure equations are applicable. The existing correlation equations were first analyzed to determine the range of gap width ratios which would most likely form the bounds for the two sets of equations. Bodies of varying sizes were then built to cover the range of gap width ratios required by the analysis.

The analysis showed that for Ra_b ranging from 10^5 to 10^{10},