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New distributed activation energy model: Numerical solution and application to pyrolysis kinetics of some types of biomass

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Abstract

In the present paper, a new distributed activation energy model has been developed, considering the reaction order and the dependence of frequency factor on temperature. The proposed DAEM cannot be solved directly in a closed from, thus a method was used to obtain the numerical solution of the new DAEM equation. Two numerical examples to illustrate the proposed method were presented. The traditional DAEM and new DAEM have been used to simulate the pyrolytic process of some types of biomass. The new DAEM fitted the experimental data much better than the traditional DAEM as the dependence of the frequency factor on temperature was taken into account.
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1. Introduction

The scarcity of fossil fuel resources and the increase in biomass wastes have led to renewed interest in converting these wastes into useful energetic products (Jiang et al., 2007). In recent years, thermochemical processes have become some of the most promising ways for obtaining useful products from those biomass wastes. The study of the kinetic behavior of these products in thermal decomposition is fundamental to the optimization of their use (Conesa et al., 1995).

The models explaining the kinetic process of biomass pyrolysis may be investigated under two main headings as pseudo-mechanistic model involving one or more reactions (Capart et al., 2004) and distributed activation energy model (DAEM). The advantages, disadvantages, assumptions and restrictions of these models were given in the literatures (Conesa et al., 1995; Burnham and Braun, 1999).

The most accurate and up-to-date approach for modeling the pyrolysis kinetics of biomass is to adopt the DAEM (Sonobe and Worasuwannarak, 2007).

The DAEM was originally developed by Pitt (1962) and later adapted by Anthony and Howard (1976). It describes a complex reaction as a number of parallel first-order reactions, each occurring with its own rate coefficient. Usually, it is further assumed that all reactions share the same frequency factor. The nth-order DAEM, a phenomenological model combining a reaction order with an activation energy distribution, was originally presented by Braun and Burnham (1987) and applied for describing the sintering of hydroxyapatite later (Burnham, 2005). In the paper of Cai et al. (2006), the influences of various parameters on the numerical results of the nth-order DAEM equation were investigated.

In the present paper, the nth-order DAEM is reconsidered and improved to consider the dependence of the frequency factor on temperature. The numerical calculations of the new DAEM equation have been studied. Finally, the new DAEM has been successfully applied for describing the pyrolysis kinetics of some types of biomass.

2. New DAEM

The DAEM for biomass pyrolysis may be applied to either the total amount of volatiles released, or to the amount of an individual volatile constituent (Miura, 1995; McGuinness et al., 1999). The description here follows the development for the total amount of volatiles.

It is assumed that the original materials of biomass contain a number of constituents, which are numbered $i = 1 \ldots j$. The released (volatilized) mass fraction at time t for the ith constituent is denoted by $V_i(t)$ and the total released mass fraction for the ith constituent is V_i^*. So $V_i^* - V_i$ is the mass fraction of unreacted volatile remaining at time t. Each reaction is assumed to be a pseudo-nth-order chemical reaction, and the reaction rate can be expressed as

$$\frac{\mathrm{d}(V_i/V_i^*)}{\mathrm{d}t} = k_i(1 - V_i/V_i^*)^n \tag{1}$$

The rate coefficient k_i is usually taken to be of Arrhenius form (Pilling and Seakins, 1995),

$$k_i = A_i \mathrm{e}^{-E_i/RT} \tag{2}$$

where A_i is the frequency factor, E_i is the activation energy, R is the universal gas constant, T is the temperature.

Usually, the frequency factor is considered as a constant all over the temperature range investigated (Chen, 1996; Tang et al., 2005). However, to some solid state reactions, the frequency factor is connected with the temperature through the following relationship:

$$A_i = A_{0i}T^{m_i} \tag{3}$$

where A_{0i} is a constant, and the exponent m_i ranges from -1.5 to 2.5 (Criado et al., 2005; Cai and Liu, 2007a). In this study, the dependence of the frequency factor on temperature has been considered to the DAEM.

The solution to Eq. (1) may be written in terms of the mass of volatiles remaining to be released at time t,

$$\begin{cases} \frac{V_i}{V_i^*} = 1 - \left[1 - (1-n)\int_0^t A_{0i}T^{m_i}\mathrm{e}^{-E_i/RT}\mathrm{d}t\right]^{1/(1-n)} & n \neq 1 \\ \frac{V_i}{V_i^*} = 1 - \mathrm{e}^{-\int_0^t A_{0i}T^{m_i}\mathrm{e}^{-E_i/RT}\mathrm{d}t} & n = 1 \end{cases} \tag{4}$$

If $j = 1$, the model is referred to as the single nth-order reaction model. In contrast, the DAEM allows for a more complicated set of reactions by considering a continuous distribution of reactants.

It is assumed that all reactions share the same frequency factor and that the number of reactions is large enough to permit the distribution of energy to be expressed as a function $f(E)$, where $V_{\text{total}}^* f(E)\mathrm{d}E$ represents the fraction of the potential volatile loss V_{total}^* that has an activation energy between E and $E + \mathrm{d}E$:

$$\mathrm{d}V' = V_{\text{total}}^* f(E)\mathrm{d}E \tag{5}$$

From Eq. (5), the following equation can be obtained:

$$\int_0^\infty f(E)\mathrm{d}E = 1 \tag{6}$$

Then, V_i^* and V_i are replaced by $\mathrm{d}V'$ and $\mathrm{d}V$, respectively. By virtue of Eq. (5), Eq. (4) becomes

$$\begin{cases} \mathrm{d}V = V_{\text{total}}^*\left\{1 - \left[1 - (1-n)\int_0^t A_0 T^m \mathrm{e}^{-E/RT}\mathrm{d}t\right]^{1/(1-n)}\right\} \\ \qquad f(E)\mathrm{d}E \quad n \neq 1 \\ \mathrm{d}V = V_{\text{total}}^*\left(1 - \mathrm{e}^{-\int_0^t A_0 T^m \mathrm{e}^{-E/RT}\mathrm{d}t}\right)f(E)\mathrm{d}E \quad n = 1 \end{cases} \tag{7}$$

The integration of Eq. (7) leads to

$$\begin{cases} \frac{1}{V_{\text{total}}^*}\int_0^V \mathrm{d}V = \int_0^\infty\left\{1 - \left[1 - (1-n)\int_0^t A_0 T^m \mathrm{e}^{-E/RT}\mathrm{d}t\right]^{1/(1-n)}\right\} \\ \qquad f(E)\mathrm{d}E \quad n \neq 1 \\ \frac{1}{V_{\text{total}}^*}\int_0^V \mathrm{d}V = \int_0^\infty\left(1 - \mathrm{e}^{-\int_0^t A_0 T^m \mathrm{e}^{-E/RT}\mathrm{d}t}\right)f(E)\mathrm{d}E \quad n = 1 \end{cases} \tag{8}$$

From Eqs. (6) and (8), it follows:

$$\begin{cases} 1 - x = 1 - \frac{V}{V_{\text{total}}^*} = \int_0^\infty\left[1 - (1-n)\int_0^t A_0 T^m \mathrm{e}^{-E/RT}\mathrm{d}t\right]^{1/(1-n)} \\ \qquad f(E)\mathrm{d}E \quad n \neq 1 \\ 1 - x = 1 - \frac{V}{V_{\text{total}}^*} = \int_0^\infty \mathrm{e}^{-\int_0^t A_0 T^m \mathrm{e}^{-E/RT}\mathrm{d}t}f(E)\mathrm{d}E \quad n = 1 \end{cases} \tag{9}$$

where x is the mass fraction of releasing volatiles.

The most common heating profile used for studying the pyrolysis kinetics of biomass is the linear heating program. Under these nonisothermal conditions, Eq. (9) can be rewritten:

$$\begin{cases} 1 - x = \int_0^\infty\left[1 - (1-n)\frac{A_0}{\beta}\int_0^T T^m \mathrm{e}^{-E/RT}\mathrm{d}T\right]^{1/(1-n)} \\ \qquad f(E)\mathrm{d}E \quad n \neq 1 \\ 1 - x = \int_0^\infty \mathrm{e}^{-\frac{A_0}{\beta}\int_0^T T^m \mathrm{e}^{-E/RT}\mathrm{d}T}f(E)\mathrm{d}E \quad n = 1 \end{cases} \tag{10}$$

The $f(E)$ function is the distribution of activation energies, and several specific mathematical forms appearing in the literature are the Gaussian (Burnham and Braun, 1999), Weibull (Lakshmanan and White, 1994; Burnham et al., 2004) and Gamma distributions (Ding et al., 2005). Usually, $f(E)$ is taken to be a Gaussian distribution with a mean activation energy E_0 and a standard deviation σ, so

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}}\mathrm{e}^{-\frac{(E-E_0)^2}{2\sigma^2}} \tag{11}$$

3. Numerical solution of new DAEM

The right hand side of Eq. (10) involves a double integration, which is difficult to deal with. While a number of articles have dealt with estimating the parameters associated with DAEM (Solomon et al., 1988; Sundararaman