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Research paper

Higher order approximations to coal pyrolysis distribution

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ABSTRACT

Coal pyrolysis is a complex process involving a large number of chemical reactions. Pyrolysis is a key step in all coal conversion processes. The Distributed Activation Energy Model (DAEM) is a state-of-the-art approach to the problem of predicting the amount of volatile released versus activation energy or time. The distribution of mass released is usually assumed to be Gaussian. We present an inverse iterative approach together with a smoothing function to estimate the underlying distribution directly from volatilisation data.

1. Introduction

Coal pyrolysis has been the subject of numerous studies on kinetics and the amounts of total volatile yield. Some of these studies have addressed the individual volatile species and measured the kinetics of species evolution. Describing the mathematical model of coal pyrolysis is often an important part of understanding industrial processes. Modelling coal pyrolysis is important not only for improvement of combustion or gasification processes but also for processes where coal is a part of the chemical system. Establishing a model for coal pyrolysis is also relevant to the process of thermal decomposition such as devolatilization.

Important mathematical models of coal pyrolysis that have been proposed (Howard & Elliott, 1981; Solomon, Hamblen, & Carangelo, 1981) include the Single First Order Reaction model (SFOR) and the Distributed Activation Energy Model (DAEM). Subsequent researchers (Miura & Maki, 1998; Niksa & Lau, 1993; Please, McGuinness, & McElwain, 2003; Suuberg, 1983) have discussed simplifications of these models. Niksa and Lau (1993) global claimed that holding the SFOR base-rate constant is the better way to estimate nominal rates for any given thermal history. The same devolatilization rate will be predicted as in the DAEM at every instant in the thermal history. By using this approach to explore the relationship between the DAEM and the SFOR model, the activation energy is fixed. Niksa and Lau introduced an effective or nominal rate constant $\langle k \rangle$ which varies with time. They also derived analytical approximations to the DAEM for testing linear or exponential temperature ramping. The resulting rapidly varying double

exponential (DExp) function is approximated by a piece-wise linear function with three regions. That is, DExp is zero or unity, and the region in between is where it rises linearly from zero to one. This procedure can make the evaluation of the integral much easier where the initial distribution is Gaussian. Therefore it provides an accurate approximation of the full DAEM for all parameters of interest. Parameters which influence the pyrolysis process vary at different stages of the process and depending on the reactor space (Urych, 2014).

Niksa and Lau indicated that this approximate procedure (piece-wise linear function) provides a more accurate approximation to the full DAEM for all parameters (Niksa & Lau, 1993). This is a refinement of earlier ideas which used a simple step-function approximation to the double exponential term (Howard & Elliott, 1981; Pitt, 1962; Suuberg, 1983; Vand, 1943). This term jumps from zero to one at an energy which varies with time. The use of a Gaussian initial distribution with the step-function gives an error function approximation to the DAEM. This error function will be used later in this study as a foundation function for the development of the inverse problem in the wide distribution case. Niksa and Lau note that some shortcomings remain in using their approximation at lower temperatures (Niksa & Lau, 1993), particularly with the numerical solution of the equations for the position of the piecewise linear approximation.

A number of researchers have considered the inverse problem and have estimated both $f(E)$ and k_0 from three sets of experiments performed at different heating profiles without assuming any functional forms for $f(E)$ and k_0 (Maki, Takatsuno, & Miura, 1997; Miura, 1995; Miura & Maki, 1998). Here, $f(E)$ represents the distribution of

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activation energies and k_0 is the pre-exponential or frequency factor in sec^{-1} . A procedure is given (Miura & Maki, 1998) with four steps to estimate $f(E)$ and k_0 . For a linearly-ramping temperature, the double exponential term is approximated by a step function because it changes rapidly with E at a given temperature. Miura and Maki (1998) simplified found the rate of change of volatility with time is proportional to the distribution of volatiles (f). They used this relationship to obtain f from the experimental measurements. Please et al. (2003) approximations present a more accurate approximation to the double exponential, which is used in the two cases of narrow and wide distribution. A careful analysis in these two regimes is given based upon asymptotic expansions, leading to systematic methods for rapidly finding accurate approximations.

In this study we review the Simple First Order Reaction Model (SFOR) and Distributed Activation Energy Model (DAEM) in order to understand why the DAEM is a more accurate and appropriate approach to modelling coal pyrolysis. Then we consider how to solve the inverse problem of finding the distribution used by the DAEM. In this case the relative width of the initial distribution is much wider than the width of the double exponential term. Finally we focus on a method to reduce the errors due to the differencing required in the inverse problem, by first fitting an appropriate smooth function to the data. The appropriate smooth function allows the calculation of higher-order terms, and gives a better fit to data, providing a more accurate estimate of the underlying distribution in the DAEM.

2. Mathematical models of coal pyrolysis

2.1. Existing models

The development in this study follows the approaches of Howard and Elliott (1981) chemistry and Solomon and Hamblen (1983) finding. The amount and composition of the thermal decomposition products depends on the physico-chemical properties of coal and on process parameters. As the process of thermal decomposition of coal evolves, i denotes one particular reaction and coal's constituents are numbered $i = 1..n$. The thermal decomposition of coal is assumed to comprise large numbers of independent chemical reactions. Large fragments of the coal molecule are present due to depolymerization and the rupture of various bonds within the coal molecule. The strength of chemical bonds depends on the coal type and rank, related to the occurrence of different reactions at various temperature intervals. V_i denotes the released mass fraction of volatiles corresponding to the i th constituent, and V_i^* is the initial mass of constituent i in the coal. The rate of pyrolysis of the i th constituent is given by the first-order reaction equation

$$\frac{dV_i}{dt} = k_i(V_i^* - V_i) \quad (1)$$

The proportionality constant k_i is the rate coefficient that is typically taken to depend on temperature by an equation which is Arrhenius in form,

$$k_i = k_{0i} \exp\left(\frac{-E_i}{RT(t)}\right) \quad (2)$$

where k_{0i} is the pre-exponential or frequency factor in sec^{-1} , E_i is the apparent activation energy for constituent i in J/mol , R is the ideal gas constant in (J/mol/K) and $T(t)$ is the absolute temperature of the coal particle in kelvins. Values of k_{0i} , E_i , and V_i^* are estimated from matching with experimental data. Anthony and Howard (1976) summarized a collection of experimental rate constant (k_i) values, and the associated rate parameters and coal properties.

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

$$\frac{V_i^* - V_i}{V_i^*} = \exp\left(-\int_0^t k_i(u) du\right) \quad (3)$$

Then the mass of the volatiles released for reaction i is

$$V_i = V_i^* - V_i^* \exp\left(-\int_0^t k_i(u) du\right) \quad (4)$$

This development has been further refined for the SFOR and DAEM models which are briefly described in the following.

2.2. Single first order reaction model (SFOR)

The simplest method for the description of the kinetics of the pyrolysis reactions is to use a first order reaction for overall weight loss of the volatile and for individual species evolution. The development of the mathematical models above shows that if $i = 1$ then the model is referred to as the Single First Order Reaction Model (SFOR). Thus, the rate of pyrolysis is expressed as:

$$\frac{dV}{dt} = k(V^* - V) \quad (5)$$

where the rate constant k is given by:

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \quad (6)$$

Many authors have approximated the overall process of the complex decomposition and transport phenomena involved in coal pyrolysis. They assumed that decomposition occurs evenly throughout the volume of the particles as a first order reaction, and that its course is determined by the chemical structure of coal (Juntgen, 1984).

Howard and Essenhigh (1967) assumed that pyrolysis is a first order reaction with respect to the amount of undecomposed volatile matter. They use a constant rate of the Arrhenius type. Other researchers have also shown that the thermal decomposition of coal occurs via first order reactions (Badzioch & Hawksley, 1970; Pitt, 1962). The SFOR model is an approach based on holding the activation energy fixed and defining k in Equation (6) as the rate constant which varies with time, $t \rightarrow \infty$.

2.3. Distributed activation energy model (DAEM)

The DAEM is a multi-reaction model widely used to describe the thermal decomposition processes of coal pyrolysis (Pitt, 1962). The evolution of pyrolysis is assumed to involve an infinite number of independent chemical reactions with a continuous distribution of reactants. That is, many irreversible first-order parallel reactions with different rate parameters are taken to occur simultaneously. In the DAEM model, the dependence on i is replaced by a continuous dependence on activation energy E so the values of k_{0i} , E_i and V_i^* are not known apriori and the distribution of activation energies must be estimated from the experimental data.

The DAEM has been used successfully to represent the change in overall conversion and the change in the yield of a given component during the coal pyrolysis. The increase in the number of calculations required to solve the DAEM can be an issue. The model is simplified by assuming that the k_i 's differ only in activation energy so a common assumption is then to take all the pre-exponential factors, k_{0i} , to have the same value k_0 for all constituents i .

Then the number of reactions is large enough to permit the distribution of energy to be expressed as a distribution function $f(E)$, where $f(E)$ is the distribution of activation energies, representing the differences in the activation energies of many first-order irreversible reactions. Then $f(E)dE$ represents the fraction of the potential volatile loss V^* that has an activation energy between E and $E + dE$. Thus, the incremental amount of volatile material available for release from the coal can be written as:

$$dV^* = V^* f(E) dE \quad (7)$$

with the distribution function $f(E)$ normalized to satisfy

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