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Study of Distributed Activation Energy Model Using Bivariate Distribution Function, $f\ (E_1,\ E_2)$

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ABSTRACT

This paper describes the influence of relevant parameters to biomass pyrolysis on the numerical solution of n^{th}-order distributed activation energy model (DAEM) using Frank's copula. In addition, the initial distribution function $f(E)$ is replaced by a continuous joint distribution function. Bi-variant distribution of activation energies E_1 and E_2 are assumed to represent the primary and the secondary pyrolysis reactions respectively. Temperature history is considered to vary linear with time. Thermoanalytical data is experimentally derived from TG/DTG analysis.

1. Introduction

Mathematical representation of biomass decomposition is one of the most complicating tasks, as several decomposition reactions occur simultaneously and their mechanism is unknown. Several mathematical approaches have been used to simulate the process of decomposition [1–5]. Commonly, isoconventional method is one of them, which postulates that kinetic parameters, such as the frequency factor and activation energy, vary with conversion [6–9]. There is another model named lumped kinetic, which presumes an ultimate number of parallel decomposition of n^{th} order reactions. These parallel reactions are sum up to provide overall decomposition of biomass. Conversely, the distributed activation energy or multi reaction model postulates that the series of n^{th} order parallel decomposition reactions with continuous distributed activation energies occur simultaneously and share the same frequency factor. However, principle of lumped kinetic model is congruent to DAEM, but the number of expected reactions bifurcate these two models.

Furthermore, pyrolysis is a complex process whose kinetic activities are difficult to estimate through models, as the large number of products are not easily recognised whilst experimentation. Demarcation of pyrolysis is done with help of two-step process [10,11]. A primary step involves releasing of volatile content and it takes place in lower temperature regime of pyrolysis process. The products which are obtained in this step are: light gas and tar. The reactions occur during primary pyrolysis autocatalysis the secondary reactions, which fall under high temperature regime. The emanating light gases and the aromatization of the biomass macro- molecules lead to char formation.

In this work, these two simultaneous activities are assumed to be distinguished by two different activation energies variables with the help of Frank's copula ($C_\theta(f\,(E_1);f\,(E_2))$) rather than univariant function f (E). In the literature, various types of distribution function are used to identify distribution pattern of activation energies, such as Gaussian [12], Weibull [13], Gamma [14] and Rayleigh [15]; in this study the Gamma and Rayleigh distributions are adopted. However, several other works have been done to bring some change so that intrinsic behaviour of distribution pattern of activation energies can be comprehended, which also include a second Gaussian distribution (2-DAEM) [16]. This model was also adopted by Zhang et al. [17] to model biomass pyrolysis and gasification by considering different distribution of activation energies for each class of reactions which share the same frequency factor. But it is not thumb-rule that Gaussian distribution can only provide good curve fitting with thermoanalytical data. There are fair chances of joint distribution function to provide the far better result which cannot be conceived by a univariant function. The present work encompasses application of copula to overshadow demerit of univariant and other methods which are merely based on the Gaussian function. There also exits a possibility that thermo analytical may provide asymmetrical distribution pattern of remaining mass fraction, which can either positively or negatively skewed [18].

2. Mathematical solution of distributed activation energy model

The DAEM is mainly a multi-reaction model. Postulations and

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Nomenclature

E_w	Step size width (kJ/mol)
E_s	Central Value (kJ/mol)
$Y(x)$	Lambert function
$\phi_p(E)$	Marginal distribution function for primary reactions (Gamma distribution)
$U(x)$	Heaviside step function
m	Heating rate (°C/min)
T	Temperature (°C)
R	Universal Gas constant (kJ/mol-K)
DExp	Double exponential term
$f(E)$	Distribution function
$C(f(E_1), f(E_2))$	Copula function
$\Psi_p(E)$	Marginal distribution function for secondary reactions (Rayleigh distribution)

boundary conditions of the n^{th}- order DAEM and the derived expression is given in the literature [19]. The non-isothermal n^{th}- order DAEM equation are given by Eqs. (1) and (2).

$$(1-X)=\int_0^\infty exp\left[\int_0^t Aexp\left(\frac{-E}{RT(l)}\right)dt\right]f(E)dE \quad \text{for first order} \tag{1}$$

$$(1-X)=\int_0^\infty \left[1-(1-n)[\int_0^t Aexp\left(\frac{-E}{RT(l)}\right)dt]\right]^{\frac{1}{1-n}} f(E)dE \quad \text{for } n^{th} \text{ order } (n\neq 1) \tag{2}$$

where A represents frequency factor, R is the universal gas constant, t is time and $T(l)$ is temperature experienced by the sample of biomass at any instant of time, t .

In Eq. (1), the integrand comprises of the product of double exponential term (DExp)

$$DExp \equiv exp\left[-\int_0^t Aexp\left(\frac{-E}{RT(l)}\right)dt\right],$$

and a term representing the initial distribution $f(E)$. DExp depends upon the temperature condition used in the experiment and initial distribution estimated only by physical behaviour of biomass used.

The main reason of complication associated with the solutions of Eqs. (1) and (2) is evaluation of double integral as it requires significant computing resources, especially when time taken by the iterative loops is appreciably high. However, Niksa and Lau [20] derive approximate analytical approximations to the DAEM for linearly or exponentially varying temperature. They refined the ideas of Suuberg [21] by incorporating step-function approximation to DExp. Thereafter, the resulting rapidly-varying double exponential functions is approximated by a piece-wise linear function that has been demarcated by three regions: one where DExp is zero, one where DExp is unity and one in the interval of (0, 1) where it rises linearly. In the subsequent sections, behaviour of DExp is considered first, and then an accurate approximation derived, which is also valid for physically relevant problems. However, distribution of activation energies can either adopt wide distribution or narrow distribution, with respect to width $E_{w.}$ But here in this work we confined to wide distribution case in which width of initial distribution function is relatively wider than that of DExp.

2.1. Systematic simplifications

The integrand in Eqs. (1) and (2) comprises of two terms. The first term (DExp) depends on time through the temperature range determined for the given sample. On the other hand, the second term is invariant to time but function of the distribution pattern of volatiles in the sample. Firstly, the behaviour of temperature dependent part, DExp, is evaluated for the non-isothermal condition.

Approximations to the Double exponential term (DExp) is given by Eq. (3)

$$DExp \equiv exp\left[-\int_0^t Aexp\left(\frac{-E}{RT(l)}\right)dt\right], \tag{3}$$

where $T(l)$ is the instaneous temperature which is defined at instant time 'l'.

Relation between temperature and time is given by Eq. (4)

$$T(l) = ml \tag{4}$$

In order to approximate the Eq. (3), some typical values of variables are assumed. The frequency factors are typically in the range$A \sim 10^{10}–10^{13}s^{-1}$, wheras the activation energies of interest are in the range of 100–300 kJ/mol. Variation of temperature depends on the particular experiment, here 700–1400 °C is used. It is to be noted that the DAEM model can also be applicable to combustion problem where the temperature range is significantly larger and hence it becomes easy to extrapolate the simplifications made in the temperature range of 700–1400 °C rather than the higher temperature regime.

If the temperature is taken to ramp linearly, DExp will become

$$DExp \equiv exp\left[-\int_0^t Aexp\left(\frac{-E}{Rml}\right)dl\right]$$

The integral in the exponent of Eq. (3) can be approximated by using the conventional Laplace approach where the parameter $\frac{E}{Rml}$ is suppose to be large, thus the dominant contribution from the integral is when l is near t (and the temperature is near its maximum). In this manner, the well-known asymptotic approximation to the function:

$$exp\left(-\int_0^t Aexp\left(\frac{-E}{Rml}\right)dl\right) \sim exp\left(\frac{-ARmt^2}{E}e^{-\frac{E}{Rmt}}\right) as\ \frac{E}{Rmt} \to \infty \tag{5}$$

Eq. (5) can also be written as

$$exp\left(\frac{-ARmt^2}{E}e^{-\frac{E}{Rmt}}\right) \sim exp\left(-exp\left(\frac{E_s-E}{E_w}\right)\right) \tag{6}$$

where the function varies rapidly from zero to one as E increases, over a range of size E_w around E_s and this can be further approximated as discussed below.

Defining, $g(E) = \frac{E_s-E}{E_w}$, Eq. (6) becomes

$$\sim exp(-exp(g(E)))$$

where

$$g(E) \equiv \frac{-E}{Rmt} + ln\left(\frac{ARmt^2}{E}\right)$$

As behaviour of $g(E)$ at neighbourhood of E_s is of interest, this function is expanded with the help of Taylor series,

$$g(E) \sim g(E_s) + (E-E_s)g'(E_s) + ... \tag{7}$$

Using Eq. (7) and definition of $g(E)$, E_s and E_w are chosen so that $g(E_s) = 0$ and $g'(E_s) = \frac{-1}{E_w}$
Solving these equations gives

$$E_s = RmtY(At) \text{ and } E_w = \frac{RmtE_s}{Rmt + E_s}$$

where $Y(x)$ is the LambertW function.

One can observe easily from Eq. (6) that DExp is like a smooth step-function, rising rapidly from zero to one in a range of activation energies of width E_w around the value $E = E_s$, where both E_s and E_w vary with time.