MGPB

Study of the Distributed Activation Energy Model using different Probability Distribution Functions for the Isothermal Pyrolysis Problem

The Mining-Geology-Petroleum Engineering Bulletin
UDC: 550.8:552.1
DOI: 10.17794/rgn.2017.4.1

Original scientific paper

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Abstract

The main aim of this paper is to do the comparative analysis of predicted results obtained by using the various probability distribution functions. The predicted n^{th}order distributed activation energy model (DAEM) results are obtained after applying the asymptotic expansion technique on the DAEM. Pyrolysis of loose biomass under the isothermal condition is considered to know the validity of the distributed activation energy model (DAEM) for the different type of distribution functions of activation energies $f(E)$.

Keywords:

Distributed Activation Energy Model (DAEM), isothermal pyrolysis, distribution function, asymptotic technique

1. Introduction

Mathematically, the detailed study of decomposition kinetics of biomass pyrolysis is one of the most complicated tasks. As several decomposition reactions occur and unfamiliarity with them, demands an accurate and reliable mathematical approach to be adopted. For the same good cause, there are various approaches which can be used to describe the process of degradation of biomass (**Khawam and Flanagan, 2006; Varhegyi, 2007**). Usually, the approaches used are isoconversional models, which presume that kinetic parameters, such as the frequency factor and activation energy depend on the extent of conversion (**Aboyade et al., 2011**). Another model often used is the so-called lumped kinetic model (**Nowicki et al., 2008**) which presumes an ultimate number of parallel decomposition n^{th} order reactions. These partial reactions contribute to the overall decomposition mechanism. Besides these models, there is a model known as the distributed activation energy model (DAEM) which has frequently been used. This model belongs to multi-reaction models. DAEM postulates that many decomposition n^{th} order reactions with distributed activation energies occur simultaneously (**Günes and Günes, 2002; Miura and Maki, 1998; Sonobe and Worasuwannarak, 2008; Dhaundiyal and Singh, 2016**). Moreover, the principle concept of the lumped kinetic model has some similarity and the main demarcation is of the number of expected decomposition reactions. If the number of reactions increases to one-hundred decomposition reactions, it would be approaching the distributed activation kinetic model. DAEM cannot only be applicable for determining the kinetics biomass pyrolysis but it is also used for ascertaining the behaviour of other thermally degradable materials (**Quan et al. 2009**). The calculation of this model may require many evaluations of the double integral term, containing rapidly varying functions which in turn creates significant numerical difficulties. Another main problem is the appearance of a double exponential term which arises in solving the DAEM for isothermal pyrolysis. In order to tackle such a situation, and to find the accurate approximation, asymptotic methodology is implemented.

The aim of this work is to analyse the degree of reliability of various distributions for determining the distribution function of activation energies in the distributed activation energy model equations and to predict the best reliable and accurate distribution type for the isothermal pyrolysis of loose biomass.

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2. Methods

2.1. The Isothermal n^{th} order DAEM

The DAEM is a multi-reaction model which postulates that the decomposition mechanism is comprised of a large number of independent, parallel and the first order chemical reactions with different activation energies. Assumptions and restrictions of the n^{th} order DAEM and the derivation of its equations are reported in literature (**Cai et al., 2006**). The isothermal n^{th} order DAEM is given below:

$$1 - X = \begin{cases} \int_0^\infty exp\left[\int_0^t Aexp\left(\frac{-E}{RT}\right)dt\right] f\left(E\right)dE, \quad \text{first order reaction} \\ \int_0^\infty \left[1-\left(1-n\right)\int_0^t Aexp\left(\frac{-E}{RT}\right)dt\right]^{\frac{1}{(1-n)}} f\left(E\right)dE, \; n \neq 1 \end{cases} \tag{1}$$

In the equation (1), E is the activation energy, A is the frequency factor, R is the ideal gas constant, n is the reaction order, T is the absolute temperature, X is the mass fraction of releasing volatiles and $f(E)$ is the distribution of activation energies. Mainly, $f(E)$ is considered to be a Gaussian distribution, but it is possible to have the other distribution types which are more appropriate for the distribution of molecular activation energies. It may be advantageous to select an asymmetric distribution for modelling the kinetics of biomass pyroylsis, over a symmetric distribution (**Dhaundiyal and Singh 2017**)

In the beginning, Niksa and Lau were the first who deduced an analytical approximation to the DAEM for a linearly and exponentially varying temperature profile (**Howard, 1981**). The approach implemented here is similar to that of Niksa and Lau, but it is a more systematic and accurate approximation. Let's assume a double exponential term in Equation (1) as:

$$DExp = exp\left(-\int_0^t Ae^{-\frac{E}{RT(l)}}dt\right) \tag{2}$$

where E can take any positive value and $T(l)$ is the temperature at an instant of time (l)

In order to carry out the proposed approach, it is very necessary to assume some typical values of parameters and functions on which **Equation (2)** depends. The frequency factors are usually in the range of $10^{10} \leq A \leq 10^{13}$ s^{-1}, whereas the activation energies usually vary between 100-300 kJ mol^{-1}. The range of temperature depends on a particular condition of the experiment. Here, the isothermal problem of pyrolysis is being discussed so the temperature remains constant throughout the pyrolysis process. The same approach can also be applicable to a combustion problem where the interval of temperature is higher than any other process. For the systematic simplification, the isothermal conditions are imposed on **Equation (2)**. Take a typical value $\frac{E}{RT} \sim 10$ whereas $tA \sim 10^{10}$. The large size of both of these parameters makes the function vary rapidly with E. To motivate and demonstrate the simplification technique, take $T(l) = T_0$, then DExp becomes

$$DExp \equiv exp\left(-tAe^{-\frac{E}{RT_0}}\right) \tag{3}$$

Equation (3) can also be written as,

$$\sim exp\left[-exp\left(\frac{E_s - E}{E_w}\right)\right] \tag{4}$$

As E increases with a step size of E_w around central value, E_s, the function varies rapidly from zero to one and this can be approximated as follows.

$$\text{Let } g\left(E\right) = \left(\frac{E_s - E}{E_w}\right). \tag{5}$$

Then Equation (4) can be expressed as,

$$\sim exp\left[-exp\left(g\left(E\right)\right)\right]$$

where, $g\left(E\right)\equiv-\ln\left(tA\right)-\frac{E}{RT_0}$ (6)

As behaviour of a function is to be investigated in the neighbourhood of E_s, therefore expand with the help of the Taylor series expansion about the central value $E = E_s$.

$$g\left(E\right)\sim g\left(E_s\right)+\left(E-E_s\right)g'\left(E_s\right)+\ldots \quad (7)$$

Using **Equation** (**6**) and the definition of g (E), E_s and E_w are chosen in such a manner that

$$g\left(E_s\right)=0 \text{ and } g'\left(E_s\right)=\frac{-1}{E_w}$$

After simplifying Equations (6) and (7), we get:

$$E_s \equiv RT_0 ln\left(tA\right) \quad (8)$$

$$E_w \equiv RT_0 \quad (9)$$

Introduce the rescaling factor 'y' to rescale energy as:

$$y=\frac{E}{E_0}$$

For isothermal pyrolysis, $T(l) = T_0$

$$y_s \equiv \frac{RT_0\ln\left(\tau\right)}{E_0} \text{ and } y_w \equiv\frac{RT_0}{E_0}$$

where τ = tA is the time scale.

2.2. Asymptotic expansion

The double exponential term (DExp) in **Equation (2)** behaves similarly to a smoothly varying step-function, which rises rapidly from zero to one in a domain of activation energy of step-size E_w around the value $E= E_s$, where both E_s and E_w vary with time. In **Equation (1)**, DExp is multiplied by the initial distribution of activation energies $f(E)$. In this paper, the width of DExp is relatively narrow as compared to the width of the initial distribution function. However, the shape of the total integrand may vary with type of distribution function and the limit imposed on the **Equation (1)**. The wide distribution case, the various types of distribution functions, and the outcome obtained after implementing them is discussed in subsequent sections. Probability functions are approximated by using the step-function U, in such a manner as stated in the literature (**Howard, 1981; Vand, 1943; Pitt, 1962; Suuberg, 1983; Dhaundiyal and Singh 2017**) that is,

$$U\left(y-y_s\right)=\begin{cases}0, & y<y_s\\ 1, & y\geq y_s\end{cases}$$

Case (a) Gaussian distribution

In this case, the function $f(E)$ is supposed to vary as a normal distribution function. Let's assume:

$$f\left(E\right)=\frac{1}{\sqrt{2\pi\sigma}}exp\left(-\beta\left(y-1\right)^2\right),$$

where $\beta=\frac{{E_0}^2}{2\sigma^2}, 1\ll\beta$

The **Equation (1)** can be written as:

$$1-X=\sqrt{\frac{\beta}{\pi}}\int_0^\infty\left[exp\left(-exp\left(\frac{y_s-y}{y_w}\right)\right)-U\left(y-y_s\right)\right]e^{\left(-\beta(y-1)^2\right)}dy+\sqrt{\frac{\beta}{\pi}}\int_{y_s}^\infty e^{\left(-\beta(y-1)^2\right)}dy \tag{10}$$

The second term in **Equation (10)** is a complementary error function, and therefore it can be easily evaluated. The integrand in the first integral contains a function that is negligibly small everywhere except at neighbourhood of $y = y_s$. Therefore, this can be approximated easily by expanding the initial distribution term with the help of the Taylor series expansion about $y = y_s$, giving:

$$R.H.S=\sqrt{\frac{\beta}{\pi}}\int_0^\infty\left[exp\left(-exp\left(\frac{y_s-y}{y_w}\right)\right)-U\left(y-y_s\right)\right]\Big(1+2\beta\left(y_s-1\right)\left(y-y_s\right)$$

$$+\frac{2\beta\left(1+2\beta\left(y_s-1\right)\right)\left(y-y_s\right)^2}{2!}+\ldots\Big)e^{\left(-\beta(y_s-1)^2\right)}dy+\frac{1}{2}erfc\left(\sqrt{\beta}\left(y_s-1\right)\right) \tag{11}$$

Each of the integral terms is obtained with the help of the Taylor series expansion and these can be separately integrated to yield:

$$1-X=\sqrt{\frac{\beta}{\pi}}y_w e^{\left(-\beta(y_s-1)^2\right)}\left[\alpha_0-2\beta y_w\left(y_s-1\right)\alpha_1+\beta y_w{}^2\left\{2\beta\left(y_s-1\right)^2-1\right\}\alpha_2+\frac{2}{3}y_w{}^3\beta^2\left\{2\left(y_s-1\right)+2\beta\left(y_s-1\right)^3+1\right\}\alpha_3\right]+$$

$$+\frac{1}{2}erfc\left(\sqrt{\beta}\left(y_s-1\right)\right) \tag{12}$$

The values of α_i need to be computed, since they are invariably independent of any other parameters.

α0 ≈ –0.5772, α1 ≈ –0.98906, α2 ≈ –1.81496, α3 ≈ –5.89037, α4 ≈ –7.3969

The remaining integrals to be evaluated are given by:

$$\alpha_i=\int_{-\infty}^\infty x^i\left(e^{-e^{-x}}-U\left(x\right)\right)dx,\ i=0,1,2,3\ldots$$

Equation (12) is the required expression for the first order reaction. In the same manner, the expression for the n^{th} order reaction by using Equation (1) can be obtained as:

$$1-X=\sqrt{\frac{\beta}{\pi}}\int_0^\infty \exp\left(-\beta\left(y-1\right)^2\right)-\sqrt{\frac{\beta}{\pi}}\left[\int_0^\infty exp\left(\left(\frac{y_s-y}{y_w}\right)-\beta\left(y-1\right)^2\right)+\frac{n}{2}\left(\int_0^\infty exp\left(2\left(\frac{y_s-y}{y_w}\right)-\beta\left(y-1\right)^2\right)\right)\right]$$

$$=\sqrt{\frac{\beta}{\pi}}\int_0^\infty \exp\left(-\beta\left(y-1\right)^2\right)-\frac{1}{2}erfc\left(\sqrt{\beta}(y_s-1\right)+y_w e^{\left(-\beta(y_s-1)^2\right)}\sqrt{\frac{\beta}{\pi}}\Big[(B_0-2y_w\beta\left(y_s-1\right)B_1$$

$$+\beta y_w{}^2\left\{2\beta\left(y_s-1\right)^2-1\right\}B_2-\frac{2}{3}y_w{}^3\beta^2\left(y_s-1\right)B_3\left\{\left(2\beta\left(y_s-1\right)^2-3\right)\right\}\Big]+\frac{n}{2}\Big[\frac{1}{2}erfc\left(\sqrt{\beta}(y_s-1\right)-\frac{1}{2}y_w e^{\left(-\beta(y_s-1)^2\right)}$$

$$\sqrt{\frac{\beta}{\pi}}\left[(C_0-2y_w\beta\left(y_s-1\right)C_1+\beta y_w{}^2\left\{2\beta\left(y_s-1\right)^2-1\right\}C_2-\frac{2}{3}y_w{}^3\beta^2\left(y_s-1\right)C_3\left\{\left(2\beta\left(y_s-1\right)^2-3\right)\right\}\right]\Big]$$

The values of B_i and C_i are required to be evaluated once, as they are independent of any other parameters

*B*0 ≈ –0.36788, *B*1 ≈ –0.23567, *B*2 ≈ –0.17273, *B*3 ≈ –0.13607

*C*0 ≈ –0.56767, *C*1 ≈ –0.35150, *C*2 ≈ –0.25250, *C*3 ≈ –0.19642

The remaining integral terms can be represented as:

$$B_i = \int_{-\infty}^{\infty} x^i \left(e^{-x} - U(x)\right) dx$$

$$C_i = \int_{-\infty}^{\infty} x^i \left(e^{-2x} - U(x)\right) dx$$

Case (b) Weibull distribution

Assuming the probability distribution *f (*E) as:

$$f(E) = \frac{\beta}{\eta}\left(\frac{E-\Upsilon}{\eta}\right)^{(\beta-1)} exp\left[\left(\frac{E-\Upsilon}{\eta}\right)^{\beta}\right] \tag{13}$$

In **Equation (13)**, η is the width parameter, β is the shape parameter and ϒ is the activation energy threshold or location parameter of the Weibull distribution, where, $E \geq 0$, $\eta \geq 0$, $\beta \geq 0$; Υ, η and E are expressed in $kJmol^{-1}$. The mean and variance of distribution is denoted by E_0 and σ^2 respectively and given by:

$$E_0 = \Upsilon + \eta\Gamma\left(\frac{1}{\beta}+1\right)$$

$$\sigma^2 = \eta^2\Gamma\left(\frac{2}{\beta}+1\right) - \eta^2\Gamma^2\left(\frac{1}{\beta}+1\right)$$

The importance of the threshold value of activation energy provides the smallest value of energy required to initiate all the reactions. Due to this reason, the lowest limit of "*dE*" in the Equation (1) is replaced by Υ. The isothermal n^{th} order DAEM for the Weibull distribution is expressed as:

$$1 - X = \beta\alpha^{\beta}\int_0^{\infty}\left[\exp\left(-exp\left(\frac{k_s-k}{k_w+1}\right)\right) - \mathrm{U}(k-k_s)\right]k^{(\beta-1)}\exp\left(-(\alpha k)^{\beta}\right)dk \tag{14}$$

where $k = y - 1$

Suppose $f(k) = k^{\beta-1}\exp\left(-(\alpha k)^{\beta}\right)$

For $k = k_s$ expand $f(k)$ with the help of the Taylor expansion:

$$f(k) = \Big[k_s^{(\beta-1)}\exp\left(-(\alpha k_s)^{\beta}\right) - (k-k_s)k_s^{\beta-2}\exp\left(-(\alpha k_s)^{\beta}\right)\left(\beta - \beta(\alpha k_s)^{\beta} - 1\right)$$

$$+\frac{(k-k_s)^2}{2!}k_s^{\beta-3}\exp\left(-(\alpha k_s)^{\beta}\right)\left\{\beta^2\left(-3(\alpha k_s)^{\beta} + (\alpha k_s)^{2\beta}+1\right) + 3\beta\left((\alpha k_s)^{\beta}-1\right)+2\right\} - \frac{(k-k_s)^3}{3!}k_s^{\beta-4}\exp\left(-(\alpha k_s)^{\beta}\right)$$

$$\left\{\alpha^2\beta^4\left(-k_s^2\right)\left((\alpha k_s)^{\beta}-1\right) + \beta^3\left(-(\alpha k_s)^2 - 7(\alpha k_s)^{\beta} + 3(\alpha k_s)^{2\beta}+1\right) - 3\beta^2\left(-6(\alpha k_s)^{\beta} + (\alpha k_s)^{2\beta}+2\right)\right.$$

$$\left.-11\beta\left((\alpha k_s)^{\beta}-1\right)-6\right\}+\ldots\Big] \tag{15}$$

From **Equations (14)** and **(15)**, we have:

$$1 - X = \beta\alpha^{\beta}\int_0^{\infty}\left[\exp\left(-exp\left(\frac{k_s-k}{k_w+1}\right)\right) - \mathrm{U}(k-k_s)\right]f(k)\,dk + \beta\alpha^{\beta} erfc\left((\alpha k)^{\frac{\beta}{2}}\right) \tag{16}$$

Putting $x = \dfrac{k-k_s}{k_w+1}$, we have:

$$1-X = \beta\alpha^{\beta}\left(k_s^{(\beta-4)}\exp\left(-\left(\alpha k_s\right)^{\beta}\right)\right)\left(k_w+1\right)\int_0^{\infty}\left[\exp\left(-exp\left(-x\right)\right)-\mathrm{U}\left(k-k_s\right)\right]$$

$$\left[k_s^{3}-\left(k_w+1\right)k_s^{2}\left(\beta-\beta\left(\alpha k_s\right)^{\beta}-1\right)+\frac{\left(k_w+1\right)^{2}}{2!}k_s\left\{\beta^{2}\left(-3\left(\alpha k_s\right)^{\beta}+\left(\alpha k_s\right)^{2\beta}+1\right)+3\beta\left(\left(\alpha k_s\right)^{\beta}-1\right)+2\right\}-\frac{\left(k_w+1\right)^{3}}{3!}\right.$$

$$\left.\left\{\alpha^{2}\beta^{4}\left(-k_s^{2}\right)\left(\left(\alpha k_s\right)^{\beta}-1\right)+\beta^{3}\left(-\left(\alpha k_s\right)^{2}-7\left(\alpha k_s\right)^{\beta}+3\left(\alpha k_s\right)^{2\beta}+1\right)-3\beta^{2}\left(-6\left(\alpha k_s\right)^{\beta}+\left(\alpha k_s\right)^{2\beta}+2\right)-11\beta\left(\left(\alpha k_s\right)^{\beta}-1\right)-6\right\}+\ldots\; dx\right]$$

After simplification, we have:

$$1-X = \beta\alpha^{\beta}\left(k_s^{(\beta-4)}\exp\left(-\left(\alpha k_s\right)^{\beta}\right)\right)\left(k_w+1\right)\left[k_s^{3}A_0-\left(k_w+1\right)k_s^{2}A_1\left(\beta-\beta\left(\alpha k_s\right)^{\beta}-1\right)+\frac{\left(k_w+1\right)^{2}}{2!}A_2k_s\right.$$

$$\left\{\beta^{2}\left(-3\left(\alpha k_s\right)^{\beta}+\left(\alpha k_s\right)^{2\beta}+1\right)+3\beta\left(\left(\alpha k_s\right)^{\beta}-1\right)+2\right\}-\frac{\left(k_w+1\right)^{3}}{3!}A_3\left\{\alpha^{2}\beta^{4}\left(-k_s^{2}\right)\left(\left(\alpha k_s\right)^{\beta}-1\right)+\beta^{3}\left(-\left(\alpha k_s\right)^{2}-7\left(\alpha k_s\right)^{\beta}\right.\right.$$

$$\left.\left.+3\left(\alpha k_s\right)^{2\beta}+1\right)-3\beta^{2}\left(-6\left(\alpha k_s\right)^{\beta}+\left(\alpha k_s\right)^{2\beta}+2\right)-11\beta\left(\left(\alpha k_s\right)^{\beta}-1\right)-6\right\}+\ldots\right]+\beta\alpha^{\beta}erfc\left(\left(\alpha k\right)^{\frac{\beta}{2}}\right) \quad (17)$$

The remaining integrals can be expressed as:

$$A_i = \int_{-\infty}^{\infty} x^{i}\left(exp\left(-x\right)-U\left(x\right)\right)dx,\; i = 0,1,2,3\ldots$$

The values of A_1 are evaluated once, as they are independent of other parameters and the first few values are:

$A_0 \approx -0.5722$ $A_1 \approx -0.98906$ $A_2 \approx -1.81496$ $A_3 \approx -5.89037$.

Equation (17) is the required expression for the first order reactions (n=1)
Similarly for the n^{th}order reactions (n≠1), we have:

$$\left(1-X\right)_{n^{th}} = \int_1^{\infty}\beta\alpha^{\beta}\left(y-1\right)^{(\beta-1)}exp\left[-\left(\alpha\left(y-1\right)\right)^{\beta}\right]dy-\int_1^{\infty}\beta\alpha^{\beta}\left(y-1\right)^{(\beta-1)}exp\left[\left(\frac{y_s-y}{y_w}\right)\right]exp\left[-\left\{\left(\alpha\left(y-1\right)\right)^{\beta}\right\}\right]dy$$

$$+\frac{n}{2}\int_1^{\infty}\beta\alpha^{\beta}\left(y-1\right)^{(\beta-1)}exp\left[\left(\frac{y_s-y}{y_w}\right)\right]\left(exp\left(\frac{y_s-y}{y_w}\right)\right)^{2}+\ldots dy \quad (18)$$

Equation (18) can be rewritten as:

$$\left(1-X\right)_{n^{th}} = (\int_0^{\infty}\beta\alpha^{\beta}\left(k\right)^{(\beta-1)}exp\left[-\left(\alpha\left(k\right)\right)^{\beta}\right]dk-\int_0^{\infty}\beta\alpha^{\beta}\left(exp\left(\frac{k_s-k}{k_w+1}\right)-U\left(k-k_s\right)\right)k^{(\beta-1)}\exp\left(-\left(\alpha k\right)^{\beta}\right)dk$$

$$+\frac{n}{2}\beta\alpha^{\beta}\int_0^{\infty}\left[\left(k\right)^{(\beta-1)}\left(exp\left(2\left(\frac{k_s-k}{k_w+1}\right)\right)-U\left(k-k_s\right)\right)\right]\exp\left(-\left(\alpha k\right)^{\beta}\right)dk$$

$$-\left(\frac{2n-1}{6}\right)\beta\alpha^{\beta}\int_0^{\infty}\left[\left(k\right)^{(\beta-1)}\left(exp\left(3\left(\frac{k_s-k}{k_w+1}\right)\right)-U\left(k-k_s\right)\right)\right]\exp\left(-\left(\alpha k\right)^{\beta}\right)dk$$

$$+\frac{n}{2}\beta\alpha^{\beta}\int_{k_s}^{\infty}k^{\beta-1}\exp\left(-\left(\alpha k\right)^{\beta}\right)dk-\beta\alpha^{\beta}\int_{k_s}^{\infty}k^{\beta-1}\exp\left(-\left(\alpha k\right)^{\beta}\right)dk-\frac{(2n-1)}{6}\beta\alpha^{\beta}\int_{k_s}^{\infty}k^{\beta-1}\exp\left(-\left(\alpha k\right)^{\beta}\right)dk+\ldots$$

For $\beta = 2$,

$$(1-X)_{n^{th}} = \frac{(n-1)}{6}a(1-CDF)+\left[1-2\alpha^2(k_w+1)(k_s)\left(\int_0^\infty\left(exp(-x)-U(x)\right)dx-\frac{n}{2}\int_0^\infty\left(exp(-x)^2-U(x)\right)dx^\beta\right.\right.$$

$$+\left(\frac{2n-1}{6}\right)\beta\alpha\int_0^\infty\left[(k)^{(\beta-1)}\left(exp\left(3\left(\frac{k_s-k}{k_w+1}\right)\right)-U(k-k_s)\right)\right]dk+\ldots\Bigg)\left(1-\frac{x(\mathrm{k_w}+1)}{k_s}\left(1-\beta(\alpha k_s)^\beta\right)+\left(\frac{x(\mathrm{k_w}+1)}{k_s}\right)^2\right.$$

$$\left(4\left(-3(\alpha k_s)^2+(\alpha k_s)^4+1\right)+6\left((\alpha k_s)^2-1\right)+2\right)-\left(\frac{x(\mathrm{k_w}+1)}{k_s}\right)^3$$

$$\left.\left.\left(\alpha^2 16\left(-k_s^2\right)\left((\alpha k_s)^2-1\right)+8\left(-(\alpha k_s)^2-7(\alpha k_s)^2+3(\alpha k_s)^4+1\right)-12\left(-6(\alpha k_s)^2+(\alpha k_s)^4+2\right)-22\left((\alpha k_s)^2-1\right)-6\right)\right)\right] \quad (19)$$

After further simplification of **Equation (19)**, we obtain:

$$X_{n^{th}} = \frac{a(n-1)}{6}(1-CDF)+\left[1-2\alpha^2(k_w+1)(k_s)\exp\left(-(\alpha k_s)^2\right)\left(\left(\mathrm{L}_0-\frac{\mathrm{n}}{2}\mathrm{B}_0+\frac{(2\mathrm{n}-1)\mathrm{C}_0}{6}\right)\right.\right.$$

$$-\left(\frac{\mathrm{k_w}+1}{\mathrm{k_s}}\right)\left(1-2(\alpha k_s)^2\right)\left(\mathrm{L}_1-\frac{\mathrm{n}}{2}\mathrm{B}_1+\frac{(2\mathrm{n}-1)\mathrm{C}_1}{6}\right)+\left(\frac{k_w+1}{k_s}\right)^2\left(4\left(-3(\alpha k_s)^2+(\alpha k_s)^4+1\right)+6\left((\alpha k_s)^2-1\right)+2\right)$$

$$\left(\mathrm{L}_2-\frac{\mathrm{n}}{2}\mathrm{B}_2+\frac{(2\mathrm{n}-1)\mathrm{C}_2}{6}\right)-\left(\frac{k_w+1}{k_s}\right)^3\left(-16\alpha^2 k_s^2\left((\alpha k_s)^2-1\right)+8\left(-(\alpha k_s)^2-7(\alpha k_s)^2+3(\alpha k_s)^4+1\right)\right.$$

$$\left.\left.\left.+12\left(-6(\alpha k_s)^2+(\alpha k_s)^4+2\right)-22\left((\alpha k_s)^2-1\right)-6\right)\left(\mathrm{L}_3-\frac{\mathrm{n}}{2}\mathrm{B}_3+\frac{(2\mathrm{n}-1)\mathrm{C}_3}{6}\right)\right)\right] \quad (20)$$

where $CDF = 1-e^{-(\alpha k_s)^\beta}$,

$L_0 \approx -0.36788,\ L_1 \approx -0.23576,\ L_2 \approx -0.17273,\ L_3 \approx -0.13607$

$B_0 \approx -0.56767,\ B_1 \approx -0.35150,\ B_2 \approx -0.25250,\ B_3 \approx -0.19642$

$C_0 \approx -0.68326\ C_1 \approx -0.41102\ C_2 \approx -0.29061\ C_3 \approx -0.22387$

Case (c) Gamma distribution

In this case, the probability distribution function $f(E)$ varies as:

$$f(E) = \frac{E^{(\lambda-1)}e^{-\frac{E}{\eta}}}{\eta^\lambda\Gamma(\lambda)}\ for\, E>0 \quad (21)$$

where λ is a scale parameter expressed in kJ/mol and η is a dimensionless positive shape parameter. The mean and the variance of distribution are given as:

$$E_0 = \frac{\lambda}{\eta}$$

$$\sigma^2 = \frac{\lambda}{\eta^2}$$

$$1-X = \int_0^\infty exp\left(-exp\left(\frac{E_s-E}{E_w}\right)\right)\frac{E^{(\lambda-1)}e^{-\frac{E}{\eta}}}{\eta^\lambda\Gamma(\lambda)}dE$$

Let's assume:

$$h(E) = -\exp\left(\frac{E_s - E}{E_w}\right) - \frac{E}{\eta}, \text{ then}$$

$$1 - X = \int_0^\infty exp\left(h(E)\right)\frac{E^{(\lambda-1)}}{\eta^\lambda \Gamma(\lambda)} dE$$

or

$$1 - X = \frac{\alpha}{\Gamma(\lambda)}\int_0^\infty y^{(\lambda-1)} exp\left(h(y)\right) dy \tag{22}$$

Let, $\alpha = \frac{\sigma^{2\lambda}}{E_0}$. For practical purposes $\alpha \ll 1$ then we have:

$$1 - X = \frac{\alpha}{\Gamma(\lambda)}\int_0^\infty \left(\exp\left(-exp\left(\frac{y_s - y}{y_w}\right)\right) - H(y - y_s)\right) y^{(\lambda-1)} \exp\left(-\left(\sigma\sqrt{y}\right)^2\right) dy + \frac{\alpha}{\sigma^{2\lambda}\Gamma(\lambda)}\Gamma\left(\lambda, \sigma^2 y_s\right) \tag{23}$$

where $\Gamma\left(\lambda, \sigma^2 y_s\right)$ is the upper incomplete Gamma function. Suppose:

$$S(y) = y^{(\lambda-1)}\exp\left(-\left(\sigma\sqrt{y}\right)^2\right)$$

$$S(y) \sim S(y_s) + (y - y_s)S'(y_s) + \frac{(y - y_s)^2}{2!}S''(y_s) + \frac{(y - y_s)^3}{3!}S'''(y_s) + \ldots$$

$$S(y) \sim exp\left(-\left(\sigma\sqrt{y_s}\right)^2\right)\left[y_s^{(\lambda-1)} - (y - y_s)\mathrm{y}_\mathrm{s}^{(\lambda-2)}\left(-\lambda + \sigma^2 y_s + 1\right) + \frac{(y - y_s)^2}{2} y_s^{(\lambda-3)}\right.$$
$$\left(\sigma^4 y_s^2 + 2(1-\lambda)\sigma^2 y_s + \left(\lambda^2 - 3\lambda + 2\right)\right) - \frac{(y - y_s)^3}{6} y_s^{(\lambda-4)}$$
$$\left.\left(\sigma^6 y_s^3 + 3(1-\lambda)\sigma^4 y_s^2 + \left(3\lambda^2 - 9\lambda + 6\right)\sigma^2 y_s - \lambda^3 + 6\lambda^2 - 11\lambda + 6\right)\right] \tag{24}$$

Putting $\frac{y - y_s}{y_w} = x, dy = y_w dx$ in Equation (24), we have:

$$S(y) \sim exp\left(-\left(\sigma\sqrt{y_s}\right)^2\right)\left[y_s^{(\lambda-1)} - y_w x \mathrm{y}_\mathrm{s}^{(\lambda-2)}\left(-\lambda + \sigma^2 y_s + 1\right) + \frac{(y_w x)^2}{2} y_s^{(\lambda-3)}\left(\sigma^4 y_s^2 + 2(1-\lambda)\sigma^2 y_s + \left(\lambda^2 - 3\lambda + 2\right)\right)\right.$$
$$\left.-\frac{(y_w x)^3}{6} y_s^{(\lambda-4)}\left(\sigma^6 y_s^3 + 3(1-\lambda)\sigma^4 y_s^2 + \left(3\lambda^2 - 9\lambda + 6\right)\sigma^2 y_s - \lambda^3 + 6\lambda^2 - 11\lambda + 6\right)\right]$$

From **Equations (23)** and **(24)**, we have:

$$1 - X = \frac{\alpha}{\Gamma(\lambda)}\int_0^\infty \left(\exp\left(-exp(-x)\right) - H(x)\right) exp\left(-\left(\sigma\sqrt{y_s}\right)^2\right)\left[y_s^{(\lambda-1)} - y_w x \mathrm{y}_\mathrm{s}^{(\lambda-2)}\left(-\lambda + \sigma^2 y_s + 1\right)\right.$$
$$+\frac{(y_w x)^2}{2} y_s^{(\lambda-3)}\left(\sigma^4 y_s^2 + 2(1-\lambda)\sigma^2 y_s + \left(\lambda^2 - 3\lambda + 2\right)\right) - \frac{(y_w x)^3}{6} y_s^{(\lambda-4)}\left(\sigma^6 y_s^3 + 3(1-\lambda)\sigma^4 y_s^2\right.$$
$$\left.\left.+\left(3\lambda^2 - 9\lambda + 6\right)\sigma^2 y_s - \lambda^3 + 6\lambda^2 - 11\lambda + 6\right)\right] y_w dx + \frac{\alpha}{\sigma^{2\lambda}\Gamma(\lambda)}\Gamma\left(\lambda, \sigma^2 y_s\right)$$

or

$$1-X\sim\frac{\alpha}{\Gamma(\lambda)}exp\left(-\left(\sigma\sqrt{y_s}\right)^2\right)y_s^{(\lambda-1)}y_w\left[L_0-\frac{y_w}{y_s}L_1\left(-\lambda+\sigma^2y_s+1\right)+\frac{1}{2}\left(\frac{y_w}{y_s}\right)^2L_2\left(\sigma^4y_s^2+2(1-\lambda)\sigma^2y_s+\left(\lambda^2-3\lambda+2\right)\right)\right.$$

$$\left.-\frac{1}{6}\left(\frac{y_w}{y_s}\right)^3L_3\left(\sigma^6y_s^3+3(1-\lambda)\sigma^4y_s^2+\left(3\lambda^2-9\lambda+6\right)\sigma^2y_s-\lambda^3+6\lambda^2-11\lambda+6\right)\right] \quad (25)$$

We know that:

$$\frac{\Gamma\left(\lambda,\sigma^2y_s\right)}{\Gamma(\lambda)}=1-P\left(\lambda,\sigma^2y_s\right)$$

where $P\left(\lambda,\sigma^2y_s\right)=\frac{\gamma\left(\lambda,\sigma^2y_s\right)}{\Gamma(\lambda)}$ is the lower cumulative distribution.

Coefficient L_i is independent of any parameters and some values are evaluated as:

$L_0\approx-0.5772, L_1\approx-0.98906, L_2\approx-1.81496, L_3\approx-5.89037$

The remaining integral terms are estimated as:

$$L_n\equiv\int_{-\infty}^{\infty}x^n\left(e^{-e^{-x}}-H(x)\right)dx$$

Equation (25) is the required expression for the first order reaction.
In the same manner, the approximations can be obtained for the n^{th} order reactions by invoking Equation (1).
Equation (1) for the n^{th} order reaction is written as:

$$(1-X)_{n^{th}}\sim\int_0^{\infty}\left[1-exp\left(\frac{y_s-y}{y_w}\right)+\frac{n}{2}exp\left(2\left(\frac{y_s-y}{y_w}\right)\right)-\frac{(2n-1)}{6}exp\left(3\left(\frac{y_s-y}{y_w}\right)\right)+\ldots\right]\frac{\alpha y^{(\lambda-1)}\exp\left(-\left(\sigma\sqrt{y}\right)^2\right)}{\Gamma(\lambda)}dy \quad (26)$$

Using the wide distribution limit, **Equation (25)** is expressed as:

$$(1-X)_{n^{th}}\sim\int_0^{\infty}\left[1-\left(exp\left(\frac{y_s-y}{y_w}\right)-H\left(y_s-y\right)\right)+\frac{n}{2}\left(exp\left(2\left(\frac{y_s-y}{y_w}\right)\right)-H\left(y_s-y\right)\right)\right.$$

$$\left.-\frac{(2n-1)}{6}\left(exp\left(3\left(\frac{y_s-y}{y_w}\right)\right)--H\left(y_s-y\right)\right)+\ldots\right]\frac{\alpha y^{(\lambda-1)}\exp\left(-\left(\sigma\sqrt{y}\right)^2\right)}{\Gamma(\lambda)}dy$$

or

$$(1-X)_{n^{th}}\sim\frac{\alpha}{\sigma^{2\lambda}}\left(1+\frac{(n-5)}{6\Gamma}\frac{\Gamma\left(\lambda,\sigma^2y_s\right)}{(\lambda)\Gamma}\right)+\frac{\alpha}{(\lambda)}exp\left(-\left(\sigma\sqrt{y_s}\right)^2\right)y_s^{(\lambda-1)}y_w\left[\left(\left(P_0+\frac{n}{2}M_0-\frac{(2n-1)}{6}N_0\right)\right.\right.$$

$$-\frac{y_w}{y_s}\left(P_1+\frac{n}{2}M_0-\frac{(2n-1)}{6}N_1\right)\left(-\lambda+\sigma^2y_s+1\right)+\frac{1}{2}\left(\frac{y_w}{y_s}\right)^2\left(P_2+\frac{n}{2}M_2-\frac{(2n-1)}{6}N_2\right)\left(\sigma^4y_s^2+2(1-\lambda)\sigma^2y_s+\left(\lambda^2-3\lambda+2\right)\right)$$

$$\left.\left.-\frac{1}{6}\left(\frac{y_w}{y_s}\right)^3\left(P_3+\frac{n}{2}M_3-\frac{(2n-1)}{6}N_3\right)\left(\sigma^6y_s^3+3(1-\lambda)\sigma^4y_s^2+\left(3\lambda^2-9\lambda+6\right)\sigma^2y_s-\lambda^3+6\lambda^2-11\lambda+6\right)\right)\right] \quad (27)$$

The coefficient P_n,M_n and N_n values are evaluated as:

$P_0\approx-0.36788$ $P_1\approx-0.23576$ $P_2\approx-0.17273$ $P_3\approx-0.13607$
$M_0\approx-0.56767$ $M_1\approx-0.35150$ $M_2\approx-0.25250$ $M_3\approx-0.19642$
$N_0\approx-0.68326$ $N_1\approx-0.41102$ $N_2\approx-0.29061$ $N_3\approx-0.22387$

The other integral terms can be evaluated as:

$$P_n \equiv \int_{-\infty}^{\infty} x^i \left(exp(-x) - U(x)\right) dx,\ i = 0,1,2,3\ldots.$$

$$M_n \equiv \int_{-\infty}^{\infty} x^i \left(exp(-2x) - U(x)\right) dx,\ i = 0,1,2,3\ldots$$

$$N_n \equiv \int_{-\infty}^{\infty} x^i \left(exp(-3x) - U(x)\right) dx,\ i = 0,1,2,3\ldots$$

Case (d) Rayleigh distribution

Here in this case $f(E)$ is assumed to vary as the Rayleigh distribution.
Let

$$f(E) = \frac{E}{\beta^2} exp\left(\frac{-E^2}{2\beta^2}\right) \tag{28}$$

The relationship between the scale parameter and the mean and variance is stated as:

$$E_0 = \beta\sqrt{\frac{\pi}{2}}$$

$$\sigma^2 = \left(\frac{4-\pi}{2}\right)\beta^2$$

Equation (28) is modified by using wide distribution limit:

$$1 - X = \frac{\pi}{2}\int_0^{\infty} y\left[\exp\left(\left(-exp\left(\frac{y_s - y}{y_w}\right)\right)\right) - H(y - y_s)\right] exp\left(-\frac{\pi}{2}y^2\right) dy + \frac{\pi}{2}\int_0^{\infty} yexp\left(-\frac{\pi}{2}y^2\right) dy$$

or

$$1 - X = \frac{\pi}{2}\int_0^{\infty} y\left[\exp\left(\left(-exp\left(\frac{y_s - y}{y_w}\right)\right)\right) - H(y - y_s)\right] exp\left(-\frac{\pi}{2}y^2\right) dy + \left(1 - C(y_s)\right) \tag{29}$$

where:

$$C(y_s) = 1 - \exp\left(-\frac{\pi}{2}{y_s}^2\right)$$

As from **Equation (29)**, it can be seen that the first integral is multiplied by a function that is very small everywhere but near the point $y = y_s$. So, the integrand is approximated with the help of the Taylor series expansion.

Let, $D(y) = y\left(exp\left(-\frac{\pi}{2}y^2\right)\right)$, then:

$$D(y) \sim D(y_s) + (y - y_s)D'(y_s) + \frac{(y - y_s)^2}{2!}D''(y_s) + \frac{(y - y_s)^3}{3!}D'''(y_s)$$

or

$$D(y) \sim y_s\left(exp\left(-\frac{\pi}{2}{y_s}^2\right)\right)\left(1 - \frac{(y - y_s)}{y_s}\left(\pi {y_s}^2 - 1\right) + \pi\frac{(y - y_s)^2}{2!}\left(\pi {y_s}^2 - 3\right) - \frac{(y - y_s)^3}{y_s 3!}\pi\left(\left(\pi {y_s}^2\right)^2 - 6\pi {y_s}^2 + 3\right)\right)$$

Replacing $x = \frac{y - y_s}{y_w}$, we obtain the required expression:

$$1 - X = \frac{\pi}{2}\int_0^{\infty} y_w\left[\exp\left(\left(-exp(-x)\right)\right) - H(x)\right] y_s\left(exp\left(-\frac{\pi}{2}{y_s}^2\right)\right)\left(1 - \frac{y_w}{y_s}x\left(\pi {y_s}^2 - 1\right) + \pi\frac{{y_w}^2}{2!}x^2\left(\pi {y_s}^2 - 3\right)\right.$$

$$\left. - \frac{{y_w}^3 x^3}{3! y_s}\pi\left(\left(\pi {y_s}^2\right)^2 - 6\pi {y_s}^2 + 3\right) + \ldots\right) dx + \left(1 - C(y_s)\right)$$

After the Taylor series expansion, the terms that arise can be separately integrated to get the results for the first order reaction (*n=1*), as:

$$1-X\sim\frac{\pi}{2}\left(exp\left(-\frac{\pi}{2}y_s^2\right)\right)\left(y_w y_s M_0-y_w^2 M_1\left(\pi y_s^2-1\right)+\pi\frac{y_w^3 y_s}{2}M_2\left(\pi y_s^2-3\right)-\frac{y_w^4}{6}\pi M_3\left(\left(\pi y_s^2\right)^2-6\pi y_s^2+3\right)+\ldots\right)+\left(1-C\left(y_s\right)\right) \quad (30)$$

Coefficient M_n needs to be evaluated once, as it is invariable to any parameters. Approximated values of the coefficients are:

$$M_0\approx-0.5772, M_1\approx-0.98906, M_2\approx-1.81496, M_3\approx-5.89037.$$

The remaining values of coefficient are equivalent to the following integral:

$$M_n\equiv\int_{-\infty}^{\infty}x^i\left(e^{-e^{-x}}-H\left(x\right)\right)$$

Furthermore, to carry out the simplification for the n^{th} order reaction , we have:

$$\left(1-X\right)_{n^{th}}=\int_0^{\infty}\left[1-\left(exp\left(\frac{y_s-y}{y_w}\right)-H\left(y_s-y\right)\right)+\frac{n}{2}\left(exp\left(2\left(\frac{y_s-y}{y_w}\right)\right)-H\left(y_s-y\right)\right)-\frac{(2n-1)}{6}\left(exp\left(3\left(\frac{y_s-y}{y_w}\right)\right)-H\left(y_s-y\right)\right)+\ldots\right]$$

$$\frac{\pi}{2}y_s\left(exp\left(-\frac{\pi}{2}y_s^2\right)\right)\left(1-\frac{\left(y-y_s\right)}{y_s}\left(\pi y_s^2-1\right)+\pi\frac{\left(y-y_s\right)^2}{2!}\left(\pi y_s^2-3\right)-\frac{\left(y-y_s\right)^3}{y_s 3!}\pi\left(\left(\pi y_s^2\right)^2-6\pi y_s^2+3\right)\right)dy+\left(\frac{n-5}{6}\right)\left(1-C\left(y_s\right)\right) \quad (31)$$

The terms that arise while solving Equation (31) can be integrated exactly in the same manner as in Equation (30) to obtain the desired results as given below:

$$\left(1-X\right)_{n^{th}}\sim\frac{\pi}{2}exp\left(-\frac{\pi}{2}y_s^2\right)\left[y_w y_s\left(P_0+\frac{n}{2}Q_0-\frac{\left(2n-1\right)}{6}R_0\right)-y_w^2\left(P_1+\frac{n}{2}Q_1-\frac{\left(2n-1\right)}{6}R_1\right)\left(\pi y_s^2-1\right)+\pi\frac{y_w^3 y_s}{2}\right.$$

$$\left.\left(P_2+\frac{n}{2}Q_2-\frac{\left(2n-1\right)}{6}R_2\right)\left(\pi y_s^2-3\right)-\frac{y_w^4}{6}\pi\left(P_3+\frac{n}{2}Q_3-\frac{\left(2n-1\right)}{6}R_3\right)\left(\left(\pi y_s^2\right)^2-6\pi y_s^2+3\right)\right]+\left(\frac{n-5}{612}\right)\left(1-C\left(y_s\right)\right)$$

The initial values of P_n, Q_n and R_n coefficients are:

$P_0\approx-0.36788$ $P_1\approx-0.23576$ $P_2\approx-0.17273$ $P_3\approx-0.13607$

$Q_0\approx-0.56767$ $Q_1\approx-0.35150$ $Q_2\approx-0.25250$ $Q_3\approx-0.19642$

$R_0\approx-0.68326$ $R_1\approx-0.41102$ $R_2\approx-0.29061$ $R_3\approx-0.22387$

2.3. Application of Isothermal pyrolysis of loose biomass

For the application point of view, the asymptotic technique is very successfully applied for each and every distribution case. A sample of Cedrus Deodara leave is considered in order to carry out mathematical analysis of its chemical kinetics with the help of DAEM equations. Thermoanalytical data is obtained by using thermogravimetric analysis and differential thermal analysis (TGA/DTA) (Exstar 6300). The temperature is kept constant throughout the pyrolysis process, whereas nitrogen is used as a purging atmosphere. The various probability distribution functions are tested one by one and simulated results are obtained. Moreover, the chemical composition of a tested sample is obtained with the help of a CHNS-O analyser (Flash EA 1112). For determining the calorific value, Dulong's formula is used (Speight, 1994). **Table 1** shows elemental composition of loose biomass sample.

Table 1. Elemental composition of Cedrus Deodara leaves

C %	N%	O%	S%	H%	HHV (kJ/kg)
47.175	1.888	32.511	0.00	8.879	21.318

2.4. Overview of computation algorithm

Computation of each probability distribution function is performed with the help of Matlab software. Iterative cycles are used to find out the smallest possible value of root mean squared error (RMSE). **Figure 1** shows the algorithm used for the computation of numerical solution of the n^{th} order DAEM for different distribution functions.

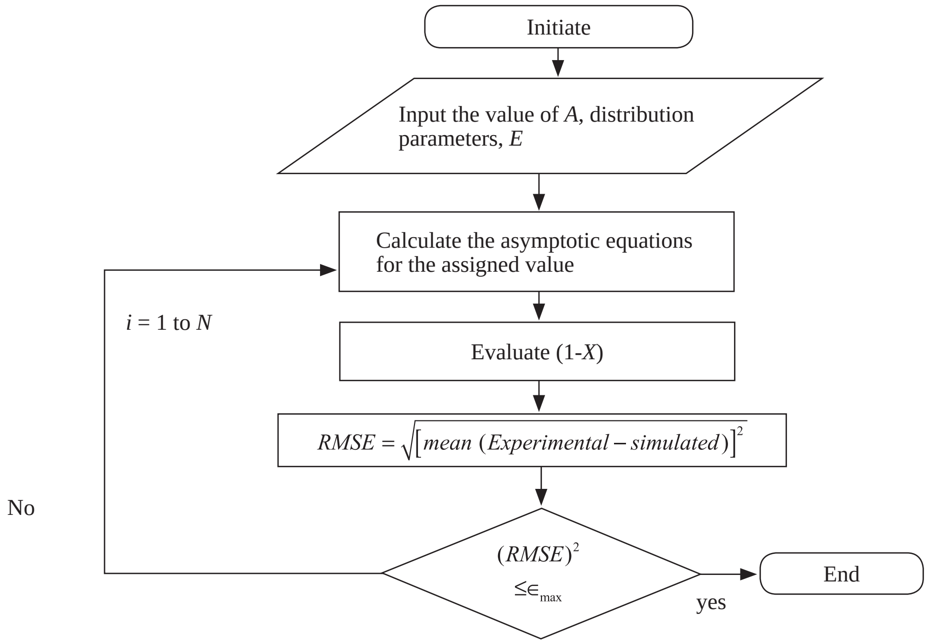

Figure 1: Iterative flow chart of a designed algorithm

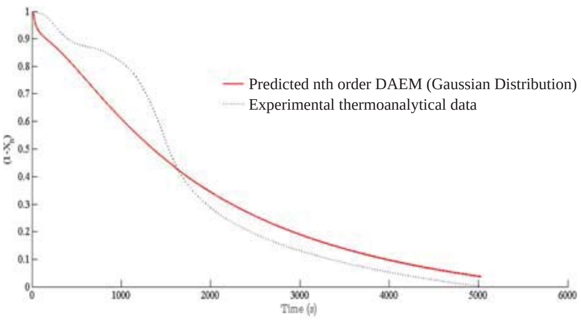

Figure 2: A comparison between experimental data and the n^{th} order Gaussian DAEM prediction

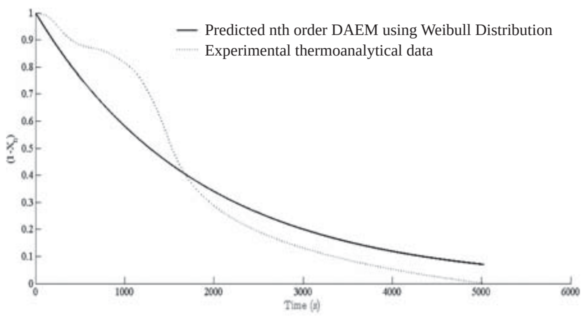

Figure 3: A comparison between experimental data and the n^{th} order Weibull DAEM prediction

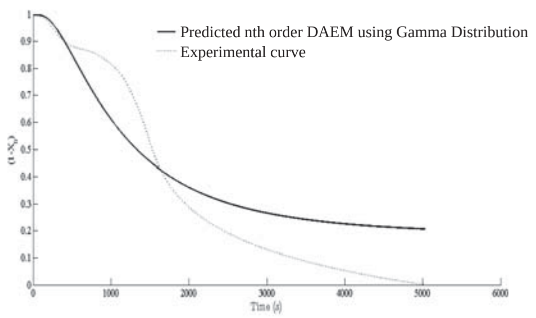

Figure 4: A comparison between experimental data and the n^{th} order Gamma DAEM distribution

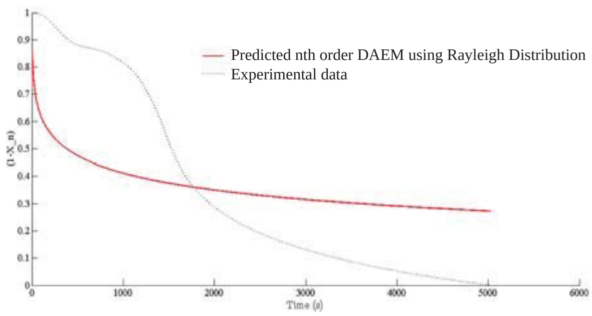

Figure 5: A comparison between experimental data and the n^{th} order Rayleigh distribution

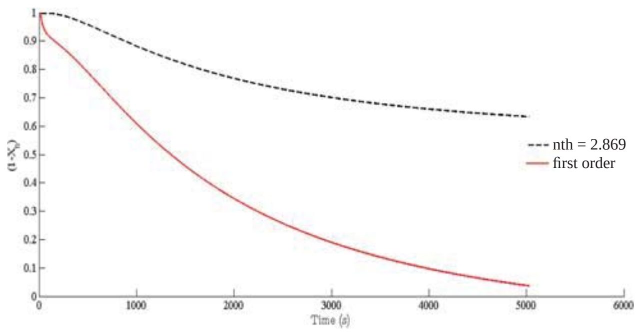

Figure 6: The effect of reaction order on the numerical solution of the n^{th} order DAEM Gaussian distribution

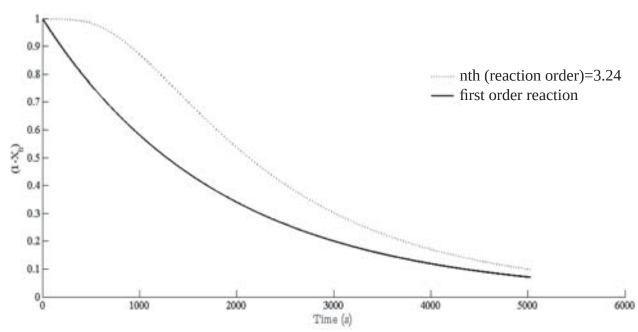

Figure 7: The effect of reaction order on the numerical solution of the n^{th} order DAEM Weibull distribution

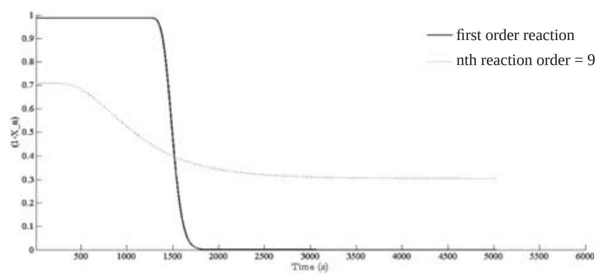

Figure 8: The effect of reaction order on the numerical solution of the n^{th} order DAEM Gamma distribution

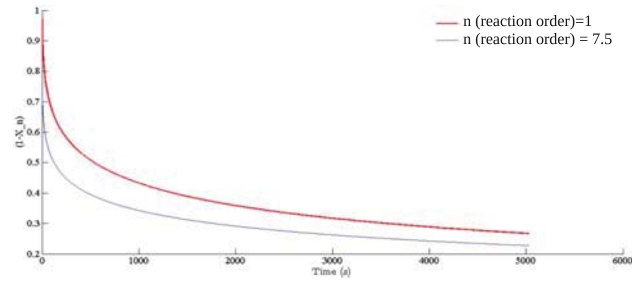

Figure 9: The effect of reaction order on the numerical solution of the n^{th} order DAEM Rayleigh distribution

3. Result and Discussions

To determine the prediction of the n^{th} order DAEM for different probability functions of activation energies, the asymptotic technique has been adopted. In the beginning of pyrolytic reactions, the (1-X) curve must be close to one; whereas it has been observed in **Figure 2** the remaining mass fraction is also equal to one but the relative variation of conversion rate as compared to experimental data is negligibly small until the inflexion point. The Gaussian distribution prediction for the n^{th}-order DAEM holds good after the inflexion point of experimental curve. Comparatively, the Gaussian curve for biomass pyrolysis is shifted towards the right as time proceeds. Such behaviour is encountered as the central value $\left(\forall 1 \ll y_s\right)$ is increasing with time and the first integral of **Equation (10)** decides the attribute of the Gaussian curve with respect to time. It has also been observed that the remaining mass fraction, obtained with the help of the Gaussian distribution, approaches zero as time increases.

Unlike the Gaussian distribution, the Weibull prediction for the n^{th} order DAEM in **Figure 3** behaves exactly the same but the remaining mass fraction curve becomes asymptotic to the experimental curve and the time scale (τ) has shifted up for the same conversion rate (i.e. Conversion rate for the simulated curve found to be maximum at different time scale than that of experimental, or conversion will be less than one at same time scale for the predicted curve obtained with the help of the Weibull distribution). A comparison between experimental and the n^{th} order Gamma DAEM prediction is illustrated in **Figure 4**. The Gamma distribution accurately predicts the biomass pyrolysis with the help of the asymptotic technique in the beginning of pyrolysis reactions but drastically deviates from the desired results as the time increases. The attribute of the Gamma distribution for the isothermal pyrolysis is similar to the experimental curve to some extent but at a different time scale. Contrary to the Gaussian and the Weibull distribution, the Gamma distribution is not monotonously decreasing or increasing. The remaining mass fraction curve is shifted up with time scale. A comparison of experimental data with the n^{th} order Rayleigh DAEM is depicted in **Figure 5**. The behaviour of the Rayleigh distribution is purely logarithmic in nature and the remaining mass fraction curve doesn't provide a well-fitting curve with the experimental result for isothermal pyrolysis of biomass. One common thing which has been observed in each and every distribution is that the time scale is shifted up for every remaining mass fraction curve. The effect of reaction order (n) on the mass fraction curves (1-X) for the Gaussian distribution is shown in **Figure 6**. The Gaussian distribution provides a good fit for the first order reaction, whereas in **Figure 7**, the experimental curve closely resembles the Weibull distribution for a reaction order of. The effect of reaction order on the Gamma distribution is depicted in **Figure 8**. According to the (1-X) curve, the simulated results hold good for a reaction order (n) of $1 < n < 9$. For the Rayleigh distribution, in **Figure 9**, the simulated curves are matching with each other for all the values that lie in the range $1 < n < 7.5$.

4. Conclusion

The results obtained with the help of asymptotic prediction are very beneficial to provide a better insight to determine the mathematical behaviour of a distributed activation energy model for different activation energy functions $f(E)$. The mathematical description of the n^{th} order DAEM for various probability functions should not exactly be juxtaposed with the experimental behaviour of biomass. For the same input parameters, this can qualitatively be stated that the Gamma distribution and the Gaussian distribution provide a better fitting curve than that of other probability distribution functions. The realistic value of reaction order for the isothermal problem may vary between $1 \leq n < 4$. While activation energies vary from 8.33 to 40.75 kJ/mol for the isothermal pyrolysis of Cedrus Deodara leave.

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