APPROXIMATION TO DISTRIBUTED ACTIVATION ENERGY MODEL FOR RESIDUAL LOGGING OF CEDRUS DEODORA USING WEIBULL DISTRIBUTION

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ABSTRACT. The paper focuses to explain the influence of some relevant parameters of biomass pyrolysis on the numerical solution of isothermal n^{th} order distributed activation energy model (DAEM). The upper limit of "dE", the frequency factors, the reaction order, the shape and location parameters of the Weibull distribution are studied. These parameters have been used for estimating the kinetic parameters of the isothermal Weibull DAEM from thermo analytical data of loose biomass. Moreover, asymptotic approach has been adopted to find the solution of DAEM.

Keywords: Pyrolysis, distributed activation energy model (DAEM), isothermal kinetics, asymptotic solution, Weibull distribution.

1. INTRODUCTION

India produces 450–500 tonnes of biomass per year which contributes 23% of India's primary energy, whereas 77% is obtained through various conventional sources of energy. More than 40% of energy is being produced via coal sources. Hitherto, the overdependence on the fossil fuels captured the energy sector, while the huge share of biomass is dumped on the forest floor. The collateral damage due to fossil fuel can be known by the fact that the average temperature of the earths surface rises with increasing concentration of CO_2 and other green house gases (GHGs) in the atmosphere. The consequence of global warming due to conventional fuels affect the level of glacier. It has been reported that Gangotri glacier retreated by 3 km from its original position in two centuries. Therefore, it is dire need of alternative new renewable energy source which can neutralize the effect of pollutants. For the same good cause, utilization of residual biomass would help to slow down the depletion of fossil fuel reservoirs and prevent the unexpected forest inferno.

Merits of using biomass is to observe it as a CO_2- neutral source of energy as the evolved amount of CO_2 during combustion is balanced by the amount of CO_2 needed for the photosynthesis process. Instead of getting heat, biomass can also be used for synthesis of bio-fuel through the process of pyrolysis. During the pyrolysis process, the biomass changes into gases, liquid oils and char. The literature dealing with pyrolysis and thermal analysis is broadly discussed in the papers of Colomba Di Blasi [1] and John E.White [2].

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Mathematically simulating the biomass decomposition kinetics is one of main problems of pyrolysis as several decomposition reactions occur simultaneously and their mechanisms are unknown, various mathematical tools have been adopted for successful elaboration of the process of decomposition [3, 4, 5, 6, 7]. The most common approach used for estimating kinetic parameters is isoconversional models, which presume that kinetic parameters, namely frequency factor and activation energy are inconstant during the process of decomposition but are function of conversion (X) [8]. Another model named as the lumped kinetic model [9, 10, 11], propounds a large number of parallel decomposition n^{th} order reactions. These partial reactions contribute to overall decomposition process of biomass. Recently, the distributed activation energy model has been adopted frequently. This model belongs to multi-reaction models as it presumes that several decomposition n^{th} order reactions with distributed activation energies take place simultaneously [12, 13, 14]. The objective of the lumped kinetic model is very similar to the DAEM and the main difference is in the number of expected decomposition reactions. The distributed activation energy model is only used for describing decomposition process of biomaterial, but it can also be applicable for thermal decomposition of coal [15] and other thermally degradable material [16, 17].

Distributed activation energy model (DAEM) contains rapidly varying functions, which may require the large computational effort and therefore creates significant numerical difficulties. Asymptotic expansion is used to allow rapid calculation of DAEM solution and give an accurate approximation to double integrals which are demarcated by two distinct and physically relevant regimes. Thus, the method provides a rapid and highly effective way of estimating kinetic parameters and the distribution of activation energies among other components of biomass. Application of asymptotic technique encompasses the problem of computational fluid dynamics (C.F.D) and modeling of coal-fired boilers, where it is important to estimate the double integral quickly. The reason of using asymptotic expansion is clear from its analytical insight into solution behaviour, as the asymptotic forms are explicit in nature.

In this study, the accurate approximation of DAEM for isothermal pyrolysis and the influence of various parameters related to biomass pyrolysis on the numerical solution of the isothermal n^{th} order DAEM using Weibull distribution are discussed.

2. Material and Methods

2.1. **Modeling of biomass pyrolysis.** The DAEM is a type of multi reaction models, which postulated that the decomposition mechanism takes a large number of independent, parallel and the first order chemical reactions with different activation energies. The isothermal n^{th} order DAEM equation is shown below.

$$(1 - X) = \begin{cases} \int_0^\infty \exp\left[-\int_{T_0}^T \frac{A}{\theta} \exp\left(\frac{-E}{RT} \right) dT \right] f(E)dE, & n = 1 \\ \int_0^\infty \left[1 - (1-n)\int_{T_0}^T \frac{A}{\theta} \exp\left(\frac{-E}{RT} \right) dT \right]^{\left(\frac{1}{1-n} \right)} f(E)dE, & n(n^{th}\ order) \neq 1 \end{cases} \quad (1)$$

where, E is activation energy, A is the frequency factor, R is the universal gas constant, θ is the heating rate, n is the reaction order, T is the absolute temperature, T_0 is the initial reaction temperature and $f(E)$ is the distribution of activation energies.

Choosing an appropriate alternative distribution function for the molecular activation energies, the better converging mathematical solution of DAEM can be obtained. It would be very promising to use an asymmetric distribution to know the kinetic activities of biomass pyrolysis, such as the Weibull distribution over a symmetric one [18]. Moreover,

the Weibull distribution is mathematically flexible and hence it can be optimized without much constraint. The Weibull distribution can be expressed as:

$$f(E) = \frac{\beta}{\eta} \left(\frac{E - \gamma}{\eta} \right)^{(\beta - 1)} \exp \left[\left(\frac{E - \gamma}{\eta} \right)^{\beta} \right] \tag{2}$$

In the equation (2), η is the width parameter, β is the shape parameter and γ is the activation energy threshold or location parameter of the Weibull distribution, where $E \geq 0$, $\eta \geq 0$, $\beta \geq 0$; γ, η and E are expressed in kJmol^{-1}.

The mean and variance of distribution is denoted by E_0 and σ^2 respectively.

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

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

Significance of threshold value of activation energy γ tells the least value of activation energies need to commence all the reactions. Therefore, the lowest limit of 'dE' in the equation (1) is substitute with $E = \gamma$. The non-isothermal n^{th} – order DAEM involved Weibull distribution is expressed as:

$$1 - X = \begin{cases} \int_{\gamma}^{i} nfty \frac{\beta}{\eta} \left(\frac{E-\gamma}{\eta} \right)^{(\beta-1)} \exp \left[-\int_{T_0}^{T} \frac{A}{\theta} \exp \left(-\frac{E}{RT} \right) dT - \left(\frac{E-\gamma}{\eta} \right)^{\beta} \right] dE \\ \qquad\qquad\qquad\qquad \text{(first order)} \\ \int_{\gamma}^{\beta} \frac{\beta}{\eta} \left(\frac{\beta-\gamma}{\eta} \right)^{(\beta-1)} \exp \left[-\left(\frac{E-\gamma}{\eta} \right)^{\beta} \right] \left[1 - (1-n) \int_{T_0}^{T} \frac{A}{\theta} \exp \left(\frac{-E}{RT} \right) dT \right]^{\left(\frac{1}{1-n} \right)} dE \\ \qquad\qquad\qquad\qquad n^{th} \ order \ (n \neq 1) \end{cases}$$

$$\tag{3}$$

2.2. **Asymptotic technique.** As it can be seen from equation (3), there are two integrals. The first part is double exponential term (DExp) that depends on time through temperature range applied in the experiment. The inner 'dT' integration is defined as the temperature integral or Arrhenius integral. The second part is invariable of time and varies with distribution function $f(E)$. The isothermal temperature profile is adopted wherin the temperature remains constant with time.

Approximations to the double exponential term are tackled first, where $T(l)$ is specified and E can take any positive value.

$$DExp = \exp \left[-\int_0^t \frac{A}{\theta} \exp \left(-\frac{E}{\text{Rel}} \right) dl \right] \tag{4}$$

To demonstrate the systematic simplification of this integrand, it is important to assume the typical values of some parameters and the functions upon which it depends. The value of frequency factor, A is the range of $10^{10} - 10^{13}$ s^{-1}, while activation energies are in range of $100 - 300$ kJmol^{-1}. Taking $\frac{E}{RT_0} \sim 10$ kJ/mol and $tA \sim 10^{10}$.

In order to simplify further, the isothermal regime is adopted. In addition to that the constant value of frequency factor for every decomposition reaction.

Let,

$$T(l) = T_0$$

Taking $\frac{E}{RT_0} \sim 10$ kJ/mol and $tA \sim 10^{10}$. The large size of both these parameters makes the function vary rapidly with E, therefore equation (4) can be rewritten as:

$$\sim \exp \left(-tAe^{-\frac{E}{RT_0}} \right)$$

After further simplification, we get

$$\sim \exp\left(-\exp\left(\frac{E_s - E}{E_w}\right)\right)$$

where

$$E_s \equiv RT_0 \ln(tA) \text{ and } E_w \equiv RT_0$$

Double exponential term (DExp) in equation (4) term observe as a smooth step-function which arise rapidly from zero to one in a range of activation energies of step size E_w about the value $E = E_s$, where both E_s and E_w vary with time. Another important thing to be noted that the shape of the total integrand significantly depends on the type of distribution we have chosen for the biomass pyrolysis problem. When $f(E)$ initial distribution goes wide as compared to step size of E_w, the total integrand approaches similar to distribution function. The initial distribution is progressively chopped off from the left as time proceeds. Whereas, in narrow distribution the whole integrand remains the same as the initial distribution, with amplitude progressively dominate by DExp. More symmetrical distribution than that of wide distribution is obtained with the help of Narrow distribution. Although the location of its maximum does not remain fixed, as it changes with time. Only wide distribution is covered under purview of this paper.

To carry out the approach, the Weibull distribution is taken as the initial distribution $f(E)$, centred at E_0 with variance σ^2.

$$1 - X = \int_\gamma^\infty \frac{\beta}{\eta}\left(\frac{E - \gamma}{\eta}\right)^{(\beta-1)} \exp(h(E)) dE \tag{5}$$

where

$$h(E) = \left\{-\exp\left(\frac{E_s = E}{E_w}\right) - \left(\frac{E - \gamma}{\eta}\right)^\beta\right\}$$

Energy is rescaled into non-dimensional factor by y.

$$y_s = \frac{E_s}{\gamma}, \quad y = \frac{E}{\gamma} \text{ and } y_w = \frac{E_w}{\gamma}$$

where, $\alpha = \frac{\gamma}{\eta}$.

After introducing the non-dimensional factor in the given problem, we obtained

$$1 - X = \int_1^\infty \beta\alpha^\beta(y-1)^{\beta-1} \exp(h(y)) dy \tag{6}$$

where

$$h(y) = \left\{-\exp\left(\frac{y_s - y}{y_w}\right) - (\alpha(y-1))^\beta\right\}$$

Put $k = y - 1$ in equation (6), we have

$$X = \beta\alpha^\beta \int_0^\infty k^{(\beta-1)} \exp(h(k+1)) dk$$

2.3. **Wide distribution.** In case of wide distribution the initial distribution is much wider than DExp. To solve the given problem, the limit $k_w \sqrt[\beta]{\alpha} \ll 1$ is adopted. The function DExp leaps from zero to one at vicinity of $k = k_s$ in such a way that has previously been approximated with the help of step-function [19, 20, 21, 22].

$$U(k - k_s) = \begin{cases} 0, & k < k_s \\ 1, & k \geq k_s \end{cases}$$

$$1 - X = \beta \alpha^\beta \int_0^\infty \left[\exp\left(-\exp\left(\frac{k_s - k}{k_w + 1} \right) \right) - U(k - k_s) \right] k^{(\beta - 1)} \exp(-(\alpha k)^\beta) dk \quad (7)$$

Assume $f(k) = k^{\beta - 1} \exp(-(\alpha k)^\beta)$.

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

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

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

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

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

$$\left. -3\beta^2(-6(\alpha k_s)^\beta + (\alpha k_s)^{2\beta} + 2) - 11\beta((\alpha k_s)^\beta - 1) - 6 \} + \cdots \right]$$

$$(8)$$

From equations (7) and (8)

$$1 - X = \beta \alpha^\beta \int_0^\infty \left[\exp\left(-\exp\left(\frac{k_s - k}{k_w + 1} \right) \right) - U(k - k_s) \right] f(k) dk + \beta \alpha^\beta erfc((\alpha k)^{\frac{\beta}{2}}) \quad (9)$$

Put $x = \frac{k - k_s}{k_w + 1}$

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

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

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

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

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

After simplification, we have

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

$$+ \frac{(k_w + 1)^2}{2!} A_2 k_s \{ \beta^2(-3(\alpha k_s)^\beta + (\alpha k_s)^{2\beta} + 1) + 3\beta((\alpha k_s)^\beta - 1) + 2 \}$$

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

$$+ 3(\alpha k_s)^{2\beta} + 1) - 3\beta^2(-6(\alpha k_s)^\beta + (\alpha k_s)^{2\beta} + 2) - 11\beta((\alpha k_s)^\beta - 1)$$

$$\left. -6 \} + \cdots \right] + \beta \alpha^\beta erfc((\alpha k_s)^{\frac{\beta}{2}})$$

$$(10)$$

The remaining integrals can be shown as:

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

The values of A_i 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 (10) is the required expression for the first order reactions ($n = 1$). In the similar manner for n^{th} order reactions ($n \neq 1$)

$$(1 - X)n^{th} = \int_1^{\infty} \beta \alpha^{\beta} (y - 1)^{(\beta-1)} \exp\left[-(\alpha(y-1))^{\beta}\right] dy - \inf_1^{\infty} \beta \alpha^{\beta}$$

$$(y-1)^{(\beta-1)} \exp\left[\left(\frac{y_s - y}{y_w}\right)\right] \exp\left[-\{(\alpha(y-1))^{\beta}\}\right] dy$$

$$+ \frac{n}{2} \int_1^{\infty} \beta \alpha^{\beta} (y-1)^{(\beta-1)} \exp\left[\left(\frac{y_s - y}{y_w}\right)\right] \left(\exp\left(\frac{y_s - y}{y_w}\right)\right)^2 + \cdots dy \tag{11}$$

Equation (11) can be rewritten as

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

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

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

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

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

For $\beta = 2$,

$$(1 - X)n^{th} = \frac{(n-1)}{6} \alpha(1 - CDF) + \left[1 - 2\alpha^2(k_w + 1)(k_s)\right.$$

$$\left(\int_0^{\infty} (\exp(-x) - U(x)) dx - \frac{n}{2} \int_0^{\infty} (\exp(-x^2) - U(x)) dx\right.$$

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

$$\left(1 - \frac{x(k_w + 1)}{k_s}(1 - \beta(\alpha k_s)^{\beta}) + \left(\frac{k(k_w + 1)}{k_s}\right)^2\right.$$

$$\left.(4(-3(\alpha k_s)^2) + (\alpha k_s)^4 + 1) + 6((\alpha k_s)^2 - 1) + 2) - 22\left((\alpha k_s)^2 - 1\right) - 6\right)\right] \tag{12}$$

After further simplification of equation (12), we obtained

$$
\begin{aligned}
Xn^{th} = {} & \frac{\alpha(n-1)}{6}(1-CDF) + \Big[1 - 2\alpha^2(k_w+1)(k_s)\exp(-(\alpha k_s)^2) \\
& \left((L_0 - \frac{n}{2}B_0 + \frac{(2n-1)C_0}{6}) - \left(\frac{k_w+1}{k_s}\right)(1 - 2(\alpha k_s)^2)\right) \\
& \left(L_1 - \frac{n}{2} - \frac{n}{2}B_1 + \frac{(2n-1)C_1}{6}\right) + \left(\frac{k_w+1}{k_s}\right)^2 \\
& (4(-3(\alpha k_s)^2) + (\alpha k_s)^4 + 1) + 6((\alpha k_s)^2 - 1) + 2\Big)\left(L_2 - \frac{n}{2}B_2 + \frac{(2n-1)C_2}{6}\right) \\
& - \left(\frac{k_w+1}{k_s}\right)^3(-16\alpha^2 k_s^2((\alpha k_s)^2 - 1) + 8(-(\alpha k_s)^2 - 7(\alpha k_s)^2 \\
& + 3(\alpha k_s)^4 + 1) + 12(-6(\alpha k_s)^2) + (\alpha k_s)^4 + 2) \\
& - 22((\alpha k_s)^2 - 1) - 6)\left(L_3 - \frac{n}{2}B_3 + \frac{(2n-1)C_3}{6}\right)\Big)\Big]
\end{aligned}
\tag{13}
$$

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

The generalized form of $X_{n^{th}}$ for arbitrary value of shape parameter β is given by the expression

$$
\begin{aligned}
X_{n^{th}} = {} & \frac{(n-1)}{12}\alpha\beta(1-CDF) + \Big[1 - \beta\alpha^\beta y_w(k_s)^{(\beta-1)}\exp(-(\alpha k_s)^\beta) \\
& \left((A_0 - \frac{n}{2}B_0 + \frac{(2n-1)C_0}{6}) - \frac{y_w}{k_s}(\beta - \beta(\alpha k_s)^\beta) - 1\right) \\
& \left(A_1 - \frac{n}{2}B_1 + \frac{(2n-1)C_1}{6}\right) + \left(\frac{y_w}{k_s}\right)^2(\beta^2(-3(\alpha k_s)^\beta) + (\alpha k_s)^{2\beta} + 1) + 3\beta((\alpha k_s)^\beta - 1) + 2) \\
& \left(A_2 - \frac{n}{2}B_2 + \frac{(2n-1)C_2}{6}\right) - \left(\frac{y_w}{k_s}\right)^3\left(\alpha^2\beta^4\left(-k_s^2\right)\left((\alpha k_s)^\beta - 1\right)\right. \\
& + \beta^3(-(\alpha k_s)^2) - 7(\alpha k_s)^\beta + 3(\alpha k_s)^{2\alpha} + 1) \\
& - 3\beta^2(-6(\alpha k_s)^\beta + (\alpha k_s)^{2\beta} + 2) - 11\beta((\alpha k_s)^\beta - 1)) - 6)\left(A_3 - \frac{n}{2}B_3 + \frac{(2n-1)C_3}{6}\right)\Big]
\end{aligned}
$$

$$
\begin{array}{llll}
L_0 \approx -0.36788, & L_1 \approx -0.23576, & L_2 \approx -0.17273, & L_3 \approx -0.13607 \\
B_0 \approx -0.56767, & C_1 \approx -0.41102, & C_2 \approx -0.29061, & C_3 \approx -0.22387
\end{array}
$$

The remaining integrals are evaluated by

$$
L_i = \int_{-\infty}^{\infty} x^i(\exp(-x) - U(x))dx, \quad i = 0,1,2,3\ldots
$$

$$
B_i = \int_{-\infty}^{\infty} x^i(\exp(-2x) - U(x))dx, \quad i = 0,1,2,3\ldots
$$

$$
C_i = \int_{-\infty}^{\infty} x^i(\exp(-3x) - U(x))dx, \quad i = 0,1,2,3,\ldots
$$

Equation (13) is derived expression for n^{th} order reaction.

2.4. **Application of loose biomass.** Dried leaves of Cedrus deodara underwent thermo gravimetric analysis. Chemical composition of the sample was measured with the help of CHNS (O) (Flash EA 1112 series). Calorific value of the sample was estimated with the help of Dulong's formula. Pyrolysis of sample has been performed by using thermo-gavimetric equipment, Exstar TG/DTA 6300. Nitrogen has been as an inert atmosphere. Thermocouple type 'R' was used to measure the sample and the furnace temperature. It is to be noted that the results of this paper is used in the simulation process to obtain the nth order Weibull DAEM prediction. Figure 7 demonstrates that the n

TABLE 1. Chemical composition of dried leaves sample of Cedrus deodara

C%	H%	O%	N%	S%	*H.H.V(MJ/kg)
47.68	7.6765	32.511	2.0285	0.000	21.318

*Higher heating value

(a)   (b)

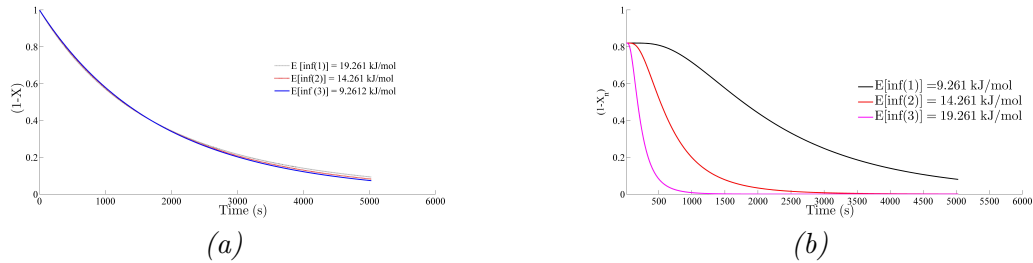FIGURE 1. The effect of upper limit (E_∞) of 'dE' integral on the numerical solution ($T_0 = 564\,\text{K}$, $A = 1.4\,\text{s}^{-1}$, $\eta = 785.85\,\text{kJ/mol}$, $Y = 4.4\,\text{kJ/mol}$, $\beta = 2$ and $n = 2.2$ (a- first order reaction, b- n^{th} order reaction)

(a)   (b)
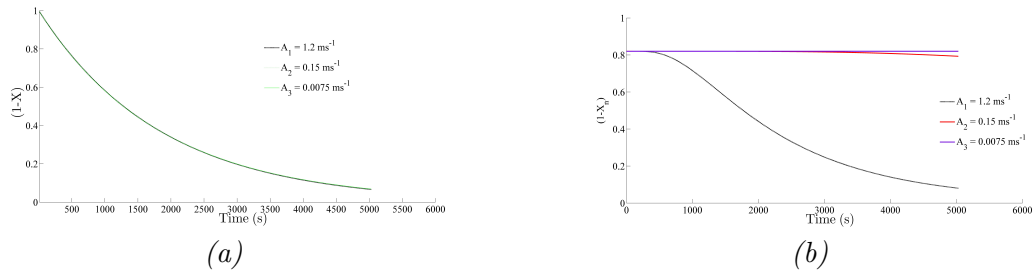
FIGURE 2. The effect of frequency factors (A) on the numerical solution ($T_0 = 564\,\text{K}$, $E_\infty = 8.42\,\text{kJ/mol}$, $\eta = 785.85\,\text{kJ/mol}$, $Y = 4.4\,\text{kJ/mol}$, $\beta = 2$ and $n = 2.2$ (a- first order reaction, b- n^{th} order reaction)

3. RESULT AND DISCUSSIONS

For numerical solution, the upper limit of ¿dE' integral must be known. The influence of parameters, which are relevant to loose biomass pyrolysis is analysed with the help of asymptotic expansion of nth order DAEM equation. The effect of upper limit (E_∞) on the numerical solution is depicted in the figure 1. At the intitial stage of pyrolytical reaction,
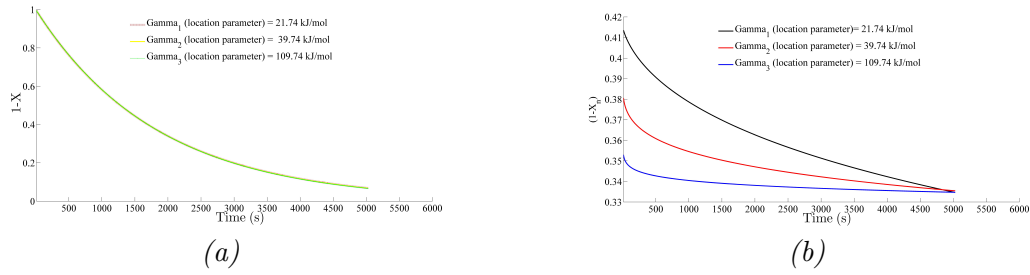
FIGURE 3. The effect of location parameter (Y) of the Weibull distribution on the numerical solution ($T_0 = 564\,\mathrm{K}$, $E_\infty = 8.42\,\mathrm{kJ/mol}$, $\eta = 785.85\,\mathrm{kJ/mol}$, $A = 1.4\,\mathrm{s}^{-1}$ $\beta = 2$ and $n = 2.2$ (a- first order reaction, b- n^{th} order reaction)
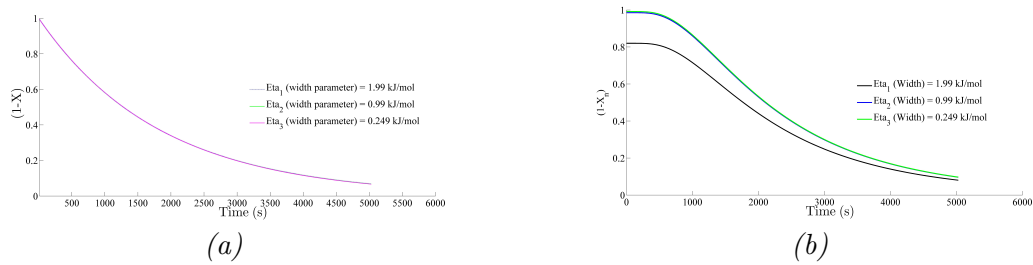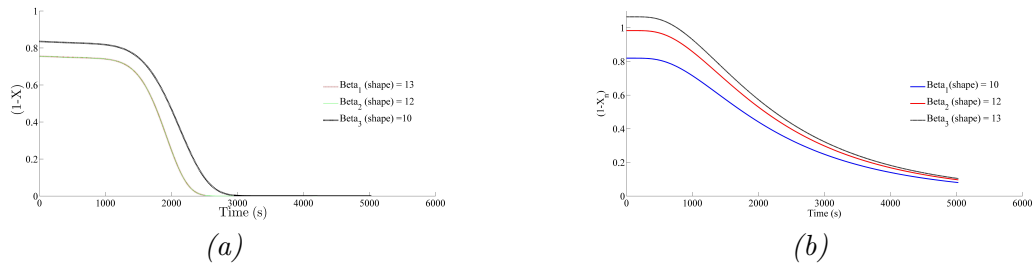

FIGURE 4. The effect of width parameter (η) of the Weibull distribution on the numerical solution ($T_0 = 564\,\mathrm{K}$, $E_\infty = 8.42\,\mathrm{kJ/mol}$, $Y = 4.4\,\mathrm{kJ/mol}$, $A = 1.4\mathrm{s}^{-1}$, $\beta = 2$ and $n = 2.2$ (a- first order reaction, b- n^{th} order reaction)

FIGURE 5. The effect of shape parameter (β) of the Weibull distribution on the numerical solution ($T_0 = 564\,\mathrm{K}$, $E_\infty = 8.42\,\mathrm{kJ/mol}$, $Y = 4.4\,\mathrm{kJ/mol}$, $A = 1.4\,\mathrm{s}^{-1}$ $\eta = 785.85\,\mathrm{kJ/mol}$ and $n = 2.2$ (a- first order reaction, b- n^{th} order reaction)

the remaining mass proportion $(1 - X)$ must be at vicinity of one. While it has been observed, with the increase in the upper limit, the remaining fraction is less than 1 for $19.26\ \mathrm{kJmol}^{-1} \leq E_\infty$. With the increase in the upper limit, the location of the inflexion point and toe of curves has shifted to the right side. The conversion rate gets catalyzed as the upper limit increases, thus the temperature of sample reaches the given isothermal temperature at the reduced time scale. When less than $9.261\ \mathrm{kJmol}^{-1}$ are used for E_∞, the result is more accurate and closely proximate to each other. Therefore, $8.42\ \mathrm{kJmol}^{-1}$ can be used as the upper limit of the dE integral. The behaviour of $(1 - X)$ curves with
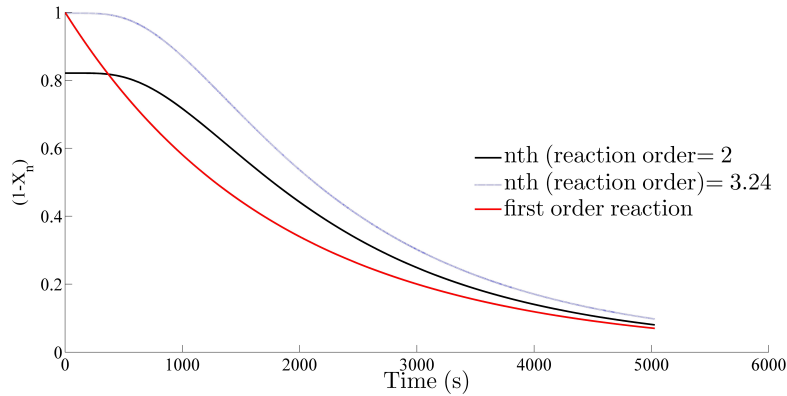
FIGURE 6. The effect of frequency factors (n) on the numerical solution is illustrated ($T_0 = 564\,\mathrm{K}$, $E_\infty = 8.42\,\mathrm{kJ/mol}$, $Y = 4.4\,\mathrm{kJ/mol}$, $A = 1.4\,\mathrm{s}^{-1}$ and $\eta = 785.85\,\mathrm{kJ/mol}$)
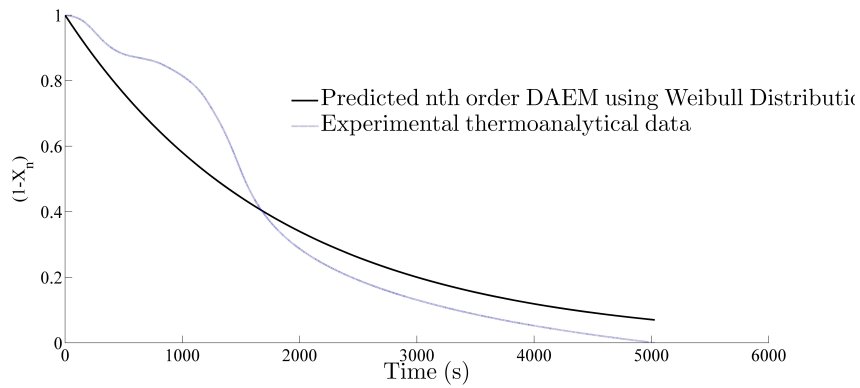

FIGURE 7. Comparison between experimental and predicted n^{th} order DAEM (Weibull)

frequency factor (A) is illustrated in figure 2. According to these curves, increase in A values deviates $(1 - X)$ curves to the right direction and becomes constant for $n = 2.2$ (Figure 2(b)). The effect of location parameter (Y) is shown in figure 3, where it is observe that the remaining mass proportion curves shifted up the time scale as the value of location parameter decreases.

The effect of the width parameter (η) and shape parameters values on the numerical results is depicted in figures 4 and 5, from which it is seen that increase in value of ¿η' and ¿β' reduces the slope of the remaining mass fraction and therefore the conversion rate (X) decreases progressively with time. The effect of the reaction order (n) values on the numerical results is illustrated in figure 6. As it is clearly visible that the reaction order changes the shape of the remaining mass fraction curves, the toe of the curves shifted to the right direction for $2 \leq n$. The behaviour of experimentally found data (in case of isothermal pyrolysis) exhibit logarithm nature as time proceeds, therefore the first order reaction provides the good agreement with thermo analytical data. Moreover, the shoulder of the remaining mass fraction curves get shifted down with the increase in the reaction order increase till $n = 2$. Thereafter, it again approaches to one as reaction order increases.

4. Conclusion

The numerical solutions of the isothermal n^{th}- order DAEM using Weibull distribution is approximated with the help of asymptotic expansion. The parametric values as the attribute of pyrolysis of loose biomass, 8.42 kJ/mol can be used for the upper limit of the outer dE integral. With increase in the activation energies, the time scale decreases, thus the temperature of sample reaches the isothermal temperature of furnace at the beginning of pyroylsis. Variation of the frequency factor, the reaction order, and the shape, scale and location parameters merely affect the contour of remaining mass fraction curves. The results are found to be very promising in order to compute the kinetic parameters of the isothermal n^{th}- order Weibull DAEM from TGA/DTG data of biomass pyrolysis. Dhaundiyal and Singh [23] reported that the behaviour of another coniferous species, pine needles convergence for all the value of n (reaction order) greater than one. Therefore, it can be concluded that the experimental condition sets boundary conditions for the numerical solution of DAEM, which provides different values to kinetic parameters for every changed boundary conditions.

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