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PARAMETRIC STUDY OF n^{TH} ORDER DISTRIBUTED ACTIVATION ENERGY MODEL FOR ISOTHERMAL PYROLYSIS OF FOREST WASTE USING GAUSSIAN DISTRIBUTION

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This paper deals with the influence of some factors relevant to isothermal pyrolysis of residual leaves of *Cedrus deodara* on the asymptotic solution of the non-isothermal n^{th} order distributed activation energy model (DAEM) using Gaussian distribution. Frequency factor, integral upper limit, the reaction order and the variance of Gaussian distribution are the parameters taken under purview of this study. In order to determine the kinetic parameters of the isothermal n^{th} order Gaussian DAEM from thermoanalytical data of loose biomass pyrolysis, the variation of these factors has been considered. The obtained results show that the predicted results for n^{th} order DAEM hold good at upper limit of dE , $E_{\infty} = 39 \text{ kJ mol}^{-1}$.

Keywords: pyrolysis; mathematical modelling; distribution function; kinetic parameters

Cedrus deodara is mainly found at altitude of 1200 to 3000 m above the sea level in the Northern Himalayan region of India, Pakistan, Nepal and Afghanistan. It is a large evergreen deciduous tree, tall up to 65 m and has sharp-pointed acicular structure with silvery stiff leaves. Unlike pine needles (Dhaundiyal and Tewari, 2015; Dhaundiyal and Tewari, 2016), *Cedrus deodara* forest covers 2.24 lakh hectares of forest land, constituting 64.79% of total forest area in Uttarakhand (Tewari et al., 2010). Forestry waste can be considered an excellent substrate for synthesizing of the biofuel. A large amount of forest waste is available in the form of litter which have enormous amount of energy potential. Non-utilization of residual leaves and keeping them as waste on forest floor is unethical and uneconomical. Moreover, a higher level of utilization of residual forest waste as a new renewable energy source can rather mitigate the depletion of conventional fuel resources.

Besides tapping the residual waste, extracting of useful by-products from it, such as biofuel and producer gas for power generation, is also equally important. One of the main thermochemical transformations is pyrolysis. It is basically a thermal degradation of substrate at very elevated temperature in the absence of oxygen or at the presence of very little amount of air. It involves simultaneous chemical, as well as physical phase transformations. The significant part of any analysis is to peruse its chemical kinetics in the presence of inert ambience. There are various models which are able to simulate the biomass pyrolysis mathematically. These models can be classified as following: the single-reaction and the multi-reaction models (Capart et al., 2004; Conesa et al., 1995; Conesa et al., 2001; Pysiak et al., 2004; Mysyk et al., 2005). The most accurate and well defined

approach for the modelling of biomass pyrolysis is to use the distributed activation energy model (DAEM) (Burnham and Braun, 1999; Burnham et al., 1995; Galgano and Biase, 2003; Ferdous et al., 2002). The DAEM is also applicable to the pyrolysis of various materials, including medical waste (Teng and Hiseh, 1999), resin (Zhu et al., 2009) and chars (Otero et al., 2008). However, solutions of this model may require several computational steps, involving rapidly varying function and thus creating significant numerical complexity. While solving DAEM for various temperature histories, another bottleneck situation arises due to the double exponential term (D_{Exp}). In order to handle the numerical complications, asymptotic methodology is used to make accurate approximations to the integrals and hence perform rapid evaluation of DAEM solution.

The asymptotic solutions of the kinetic models are used to perform the evaluation of kinetic parameters. In order to obtain good approximation, the parameters affecting the numerical results of the model equation must be known. The effect of various parameters on the numerical results of single reaction model is stated in literature (Lakshmanan and White, 1994).

The present paper sheds some light on the parametric values relevant to pyrolysis of *Cedrus deodara* leaves. The numerical solution of DAEM involves iterative evaluation of a double integral and therefore causes numerical difficulties. In order to tackle it, asymptotic technique has been implemented to make an accurate approximation to DAEM as well as examined the effect of various kinetic parameters on the numerical solution of isothermal pyrolysis of n^{th} order DAEM.

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Material and methods

Isothermal pyrolysis of *Cedrus deodara* using the Gaussian distribution

The model postulates that the decomposition mechanism takes a large number of independent, parallel and the first order chemical reactions with different activation energies showing variation in the bond strength of various constituent components of biomass. In this section, first order, as well as n^{th} order DAEM is discussed, the derivation of the same can be found in literature (Brown, 1988). Isothermal n^{th} order DAEM is expressed below:

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

where:

- E – the activation energy
- θ – the heating rate
- A – the frequency factor
- R – the ideal gas constant
- n – the reaction order
- T – absolute temperature
- T_0 – the initial temperature
- $(1-X)$ – represents remaining mass fraction
- $f(E)$ – the initial distribution function of activation energies

The Gaussian distribution is applied to describe the distribution of activation energies, as the integral curve of biomass pyrolysis decomposition is similar to the Gauss function. The integrand in Eq. (1) contains two parts. The first term is double exponential term (DExp) which depends on time, whereas the second part is independent of time but it depends on the distribution of activation energy of constituent species. In the following section, systematic simplification of DExp has been discussed and thereafter a useful approximation is derived. The isothermal temperature regime is observed along with initial distribution of volatile content of biomass.

Simplification of double exponential term (DExp)

Niksa and Lau (1993) were the first to derive the analytical approximation to the DAEM for temperature undergoing linear and exponential ramping. The approach adopted here is similar to that of Niksa and Lau, but it is different in the sense that more systematic method and accurate approximation is used:

$$DExp = \exp\left(-\int_0^t A e^{\frac{-E}{RT(t)}} dt\right) \quad (2)$$

where:

- $T(t)$ – specified temperature
- E – can take any positive value

To demonstrate the approach, it is very important to assume some typical values of parameters and functions on which Eq. (2) depends.

The frequency factors are typically in the range of $10^{10} \text{ s}^{-1} \leq A \leq 10^{13} \text{ s}^{-1}$, while the activation energies usually lie in domain from 100 kJ mol^{-1} to 300 kJ mol^{-1} . The temperature range depends on the particular condition of experiment, but in this case, the temperature remains constant. However, the same approach can also apply to combustion problem where the temperature range can be appreciably very higher than any other applications. In order to carry out the stepwise simplification of the DExp, the isothermal conditions are imposed, taking a typical values $\frac{E}{RT} \approx 10$ and $tA \approx 10^{10}$. The large size of both of these parameters makes the function vary rapidly with E . To motivate and demonstrate the simplification technique, the case of constant temperature (when the integral is particularly simple) is assumed first. Taking $T(t) = T_0$, DExp becomes:

$$DExp \equiv \exp\left(-tA e^{\frac{-E}{RT_0}}\right) \quad (3)$$

Equation (3) can also be written as follows:

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

where:

- E_s – the mean value
- E_w – the width of double exponential term

As E increases with width size of E_w around E_s , the function varies rapidly from zero to one and this can be approximated as follows:

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

then Eq. (4) can be expressed as:

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

where:

$$g(E) \equiv -\ln(tA) - \frac{E}{RT_0} \quad (5)$$

As behaviour of function at vicinity of E_s is of interest, $g(E)$ expanded with the help of Taylor series expansion about $E = E_s$ is:

$$g(E) \sim g(E_s) + (E - E_s) g'(E_s) + \dots \quad (6)$$

Using Eq. (6), the definition of $g(E)$, E_s and E_w are chosen in such a manner that:

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

After solving Eq. (5) and (6), we get:

$$E_s \equiv RT_0 \ln(tA)$$

$$E_w \equiv RT_0$$

Asymptotic expansion

Double exponential term in Eq. (2) is observed to vary like a smooth step-function, rising rapidly from zero to one in a range of activation energies of width size E_w around the value $E = E_s$, where both E_s and E_w vary with time. In Eq. (1), $D\text{Exp}$ is multiplied by the initial Gaussian distribution $f(E)$. In this paper, we used the limit where the relatively wide initial distribution $f(E)$ as compared to width of $D\text{Exp}$ is adopted. The shape of the total integrand changes with respect to time, and thus depends on the limit applied to the problem. The initial distribution is assumed to be relatively wide in comparison to E_w .

Assuming that the initial distribution function $f(E)$ is normal distribution (Gaussian) function that can be expressed in terms of activation energy as:

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \int_0^\infty e^{-\frac{(E-E_0)^2}{2\sigma^2}}$$

where:

E – activation energy

E_0 – the mean activation energy and σ^2 denotes variance of distribution function. Putting the value of $f(E)$ in Eq. (1), we get:

$$1 - X = \frac{1}{\sigma\sqrt{2\pi}} \int_0^\infty \exp(h(E)) dE \quad (7)$$

where:

$$h(E) = -\exp\left(\frac{E_s - E}{E_w}\right) - \left(\frac{(E - E_0)^2}{2\sigma^2}\right)$$

Rescaling factor 'y' is introduced to rescale energy as:

$$y = \frac{E}{E_0}, \quad y_s = \frac{E_s}{E_0}, \quad y_w = \frac{E_w}{E_0}$$

The problem is further simplified as:

$$1 - X = \frac{1}{\sigma\sqrt{2\pi}} \int_0^\infty \exp\left[-\exp\left(\frac{y_s - y}{y_w}\right) - \beta(y - 1)^2\right] dy \quad (8)$$

where:

$$\text{the constant parameter } \beta = \frac{E_0^2}{2\sigma^2}$$

In practical approach, the value of $\beta \gg 1$.

For isothermal pyrolysis $T(t) = T_0$; corresponding rescaling factor for E_s and E_w is expressed as:

$$y_s = \frac{RT_0 \ln(\tau)}{E_0}, \quad y_w = \frac{RT_0}{E_0}$$

where time has been rescaled as $\tau = At$

Wide distribution

In order to adopt the wide distribution case, the limit $y_w \sqrt{\beta} \ll 1$ is taken. As it is known, $D\text{Exp}$ jumps from zero to one at neighbourhood of $y = y_w$ by the step-function in such a manner that has been reported in literature (Vand, 1943; Pitt, 1962; Howard, 1981; Suuberg, 1983):

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

Equation (8) can be re-written as:

$$1 - X = \sqrt{\frac{\beta}{\pi}} \int_0^\infty \left[\exp\left(-\exp\left(\frac{y_s - y}{y_w}\right)\right) - U(y - y_s) \right] e^{(-\beta(y-1)^2)} dy + \sqrt{\frac{\beta}{\pi}} \int_{y_s}^\infty e^{(-\beta(y-1)^2)} dy \quad (9)$$

The second integral term in Eq. (9) is a complementary error function, and therefore it can be easily computed. The integrand in the first integral contains a function which is negligibly small everywhere except at neighbourhood of $y = y_s$. Therefore, this can be approximated easily by expanding the initial distribution term as a Taylor series about $y = y_s$ giving:

$$R.H.S. = \sqrt{\frac{\beta}{\pi}} \int_0^\infty \left[\exp\left(-\exp\left(\frac{y_s - y}{y_w}\right)\right) - U(y - y_s) \right] \left(1 + 2\beta(y_s - 1)(y - y_s) + \frac{2\beta(1 + 2\beta(y_s - 1))(y - y_s)^2}{2!} + \dots \right) e^{(-\beta(y-1)^2)} dy + \frac{1}{2} \text{erfc}(\sqrt{\beta}(y_s - 1)) \quad (10)$$

where:

R.H.S – Right Hand Side

Each of the integral terms derived from the Taylor series expansion can be separately integrated to yield:

$$1 - X = \sqrt{\frac{\beta}{\pi}} y_w e^{(-\beta(y_s - 1)^2)} \left[\alpha_0 - 2\beta y_w (y_s - 1) \alpha_1 + \beta y_w^2 \{2\beta(y_s - 1)^2 - 1\} \alpha_2 + \frac{2}{3} y_w^3 \beta^2 \{2(y_s - 1) + 2\beta(y_s - 1)^3 + 1\} \alpha_3 \right] + \frac{1}{2} \text{erfc}(\sqrt{\beta}(y_s - 1)) \quad (11)$$

The values of α_i need to be evaluated once, as they are invariably independent of any other parameters:

$$\alpha_0 \approx -0.5772, \quad \alpha_1 \approx -0.98906, \quad \alpha_2 \approx -1.81496, \\ \alpha_3 \approx -5.89037, \quad \alpha_4 \approx -7.3969$$

The remaining integrals to be evaluated are represented by:

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

Equation (11) is the required expression for the first order reaction.

Similarly, by using the Eq. (1), the expression for n^{th} order reaction can be obtained as:

$$1 - X_n = \sqrt{\frac{\beta}{\pi}} \int_0^\infty \exp(-\beta(y - 1)^2) - \sqrt{\frac{\beta}{\pi}} \int_0^\infty \exp\left(\left(\frac{y_s - y}{y_w}\right) - \beta(y - 1)^2\right) + \frac{n}{2} \left(\int_0^\infty \exp\left(2\left(\frac{y_s - y}{y_w}\right) - \beta(y - 1)^2\right) \right) \quad (12)$$

$$\begin{aligned}
 (1 - X_n) = & \sqrt{\frac{\beta}{\pi}} \int_0^\infty \exp(-\beta(y-1)^2) - \frac{1}{2} \operatorname{erfc}(\sqrt{\beta}(y_s-1)) + y_w e^{(-\beta(y_s-1)^2)} \\
 & \sqrt{\frac{\beta}{\pi}} \left[B_0 - 2y_w \beta(y_s-1) B_1 + \beta y_w^2 (2\beta(y_s-1)^2 - 1) B_2 - \frac{2}{3} y_w^3 \beta^2 (y_s-1) \right. \\
 & \left. B_3 \left((2\beta(y_s-1)^2 - 3) \right) \right] + \frac{n}{2} \left[\frac{1}{2} \operatorname{erfc}(\sqrt{\beta}(y_s-1)) - \frac{1}{2} y_w e^{(-\beta(y_s-1)^2)} \right. \\
 & \left. \sqrt{\frac{\beta}{\pi}} \left[C_0 - 2y_w \beta(y_s-1) C_1 + \beta y_w^2 (2\beta(y_s-1)^2 - 1) C_2 - \frac{2}{3} y_w^3 \beta^2 (y_s-1) \right. \right. \\
 & \left. \left. C_3 \left((2\beta(y_s-1)^2 - 3) \right) \right] \right] \quad (12)
 \end{aligned}$$

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

$$\begin{aligned}
 \beta_0 & \approx -0.36788, \beta_1 \approx -0.23576, \beta_2 \approx -0.17273, \beta_3 \approx -0.13607 \\
 C_0 & \approx -0.56767, C_1 \approx -0.35150, C_2 \approx -0.25250, C_3 \approx -0.19642
 \end{aligned}$$

The remaining integral terms can be represented as:

$$\begin{aligned}
 B_i &= \int_{-\infty}^{\infty} x^i (e^{-x} - U(x)) dx \\
 C_i &= \int_{-\infty}^{\infty} x^i (e^{-2x} - U(x)) dx
 \end{aligned}$$

Application of biomass and computational algorithm

The sample of *Cedrus deodara* underwent TGA/DTA (Exstar 6300) analysis. Elemental composition is obtained with the help of Elemental analyser (Flash EA 1112) and the calorific value is derived with the help of Dulong's formula. Thermogravimetric analysis is performed in the presence of nitrogen 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 are implemented to simulate the n^{th} order Gaussian DAEM prediction. Table 1 shows the chemical characteristic of dried leaf sample of *Cedrus deodara*. To simplify the calculation, algorithm has been designed in order to evaluate the appropriate value of kinetic parameters. For calculating the kinetic parameters, the root mean square of error (R.M.S.E.) is minimized in each iterative loop so that we can obtain the values which can satisfy the Eq. (1) and Eq. (12). In each iterative loop, the

resultant square of R.M.S.E must satisfy the end condition to terminate the loop, i.e. $R.M.S.E. \leq \varepsilon_{\max}$.

Table 1 Chemical characteristic of dried leaves of *Cedrus deodara*

C in %	H in %	N in %	O in %	S in %	HHV* in MJ kg ⁻¹
47.68	7.6765	2.0285	32.511	0.000	21.318

* higher heating value

Thermogravimetric tests were conducted at Indian Institute of Technology, Roorkee, India. Elemental analysis was performed at Sophisticated Analytical Instrumentation Facility (S.A.I.F.).

Result and discussion

After using the asymptotic technique and rescaling the energy (y) on Eq. (10), the outer ' dE ' integration upper limit is determined. The influence of frequency factor (A) on the numerical results of the isothermal n^{th} order DAEM is depicted in Fig. 1. At the beginning of pyrolysis reaction, the remaining mass fraction ($1 - X$) must be close to one. Whereas in Fig. 1, it is observed that ($1 - X$) is less than one for all values of $A < 0.4 \text{ s}^{-1}$. As the frequency factor approaches 0.609 s^{-1} , the obtained results are more precise and closely proximate to each other. Although, in case of ($1 - X_n$) curves, all the curves are exactly equal to one, yet the conversion rate (X) is finished at less than 60% of whole reaction. It implies that n^{th} order curves for $1 < n$ are not precisely simulating the biomass pyrolysis, which can also be observed with attribute of curves obtained in Fig. 1 (b), Fig. 2 (b) and Fig. 3 (b). However, the simulated results provided good fit with thermoanalytical data at $n = 2.8$, so this value is chosen to be reaction order of kinetic model, Eq. (1). With the increase of E_∞ in Fig. 2, the conversion rate is rather fast as compared to the lower values of upper limit. The results are found to be more suitable because the values lie in domain of $37 \text{ kJ mol}^{-1} \leq E_\infty < 40 \text{ kJ mol}^{-1}$. As time proceeds, the ($1 - X$) curves shift to the right side with increase in the values of variance (σ^2) in Fig. 3. Furthermore, the shifting of inflexion point is observed with the increase

Figure 1 The effect of frequency factor on the numerical results ($T_0 = 564 \text{ K}$, $E_\infty = 37.63 \text{ kJ mol}^{-1}$, $\sigma^2 = 21.8 \text{ kJ mol}^{-1}$) (a) first order reaction; (b) n^{th} order ($n = 2.8$)

Figure 2 The effect of upper limit (E_{∞}) of dE integral on the numerical results ($T_0 = 564$ K, $A = 10$ s $^{-1}$, $\sigma^2 = 21.8$ kJ mol $^{-1}$) (a) first order reaction; (b) n^{th} order ($n = 2.8$)

Figure 3 The effect of variance (σ^2) on the numerical results ($T_0 = 564$ K, $A = 10$ s $^{-1}$, $E_{\infty} = 37.63$ kJ mol $^{-1}$) (a) first order reaction; (b) n^{th} order ($n = 2.8$)

Figure 4 The effect of reaction order (n) on the numerical solution ($T_0 = 564$ K, $A = 10$ s $^{-1}$, $E_{\infty} = 37.63$ kJ mol $^{-1}$)

in the values of σ^2 . The main reason of shifting at the higher values is decrease in the value of β and therefore the error function increases in the interpolation range of $(0, y_s)$. The effect of remaining mass fraction curves on numerical results with reaction

order is illustrated in Fig. 4. It can be seen that with increase in reaction order, the $(1 - X)$ drastically shifted up with time scale and hence imperfect simulation has been obtained. Comparison of thermoanalytical data with simulated results is shown in Fig.

5. The asymptotic technique accurately predicts the behaviour of experimental data at the beginning and the end of biomass pyrolysis.

Dhaundiyal and Singh (2016) have performed the experiment under the non-isothermal condition for pine needle sample and it has been reported that the effect of variation of reaction order on the numerical results is not as much as in the isothermal condition. Moreover, the range of variation of activation energies in pine needles is wider than that of *Cedrus deodara*. The results may differ as the temperature distribution for isothermal condition is independent of time and therefore it depends solely on the single fixed temperature (T_0). Unlike non-isothermal condition, after inflexion point, the slope of $(1 - X)$ curves becomes constant with time. Although both pine needles and *Cedrus deodara* are the part of loose biomass class, yet

Figure 5 Comparison between experimental data and the n^{th} - order Gaussian DAEM prediction

they exhibit different behaviour with change in the experimental condition.

Conclusion

The main aim of this article is to investigate the parametric influence on biomass pyrolysis with the help of asymptotic solution of DAEM. The value $E_{\infty} = 39 \text{ kJ mol}^{-1}$ can be used as the upper limit of the outer dE integral. The influence of variance, frequency factor and the reaction order merely affect the shape of the mass fraction curves. The results are beneficial for getting the information of kinetic parameters of the isothermal n^{th} order Gaussian DAEM from thermoanalytical data of *Cedrus deodara* leaves. According to mathematical prediction, unlike non-isothermal condition, where time correlates with temperature, it has been found that first order reaction provided the best simulation with experimental data. The behaviour of experimentally found isothermal curve is considered to be more logarithmic rather than exponential. At the initial stage of pyrolysis, the predicted $(1 - X)$ curves behave as similar as exponential complementary error function, whereas after the inflexion point, the behaviour puts up logarithmic nature at end of pyrolysis reaction.

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