Calculation of Kinetic Parameters of Thermal Decomposition of Forest Waste using the Monte Carlo Technique

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Abstract – This paper deals with the pyrolysis of forest waste in the presence of an inert atmosphere. Experiments are carried out at different heating rates (5 °C, 10 °C and 15 °C) to determine derivative thermogravimetric behaviour of the material. Unlike the conventional scheme, the Monte Carlo technique is implemented to solve the distributed activation energy model (DAEM). DAEM is transformed into the inverse pyrolysis problem to determine the kinetic parameters of thermal degradation of forest waste. Activation energy, the preexponential factor and the distribution parameters are estimated by introducing the Monte Carlo Technique in the thermal conversion process.

Keywords – Biomass; distributed activation energy model; Monte Carlo technique; pyrolysis.

1. INTRODUCTION

Modelling scheme of biomass pyrolysis can be performed on the basis of single reaction and multi-reaction models. Comprehensive details of these models are reviewed in previous research [1]–[4]. The latest and up-to-date approach to describe biomass pyrolysis pivots around the distributed activation energy model [5]–[7]. The numerical solution of DAEM is used to estimate kinetic parameters. The DAEM is converted into an inverse problem, so that realistic results can be derived. As the trade-off relationship between material decomposition and mathematical model is fail to impart the robustness in the results, therefore the Monte Carlo scheme is adopted to make the solution more pragmatic. Some of the latest developments and the effect of various parameters on the single-reaction model are investigated by Brown [8]. Gune and Gune [9] reported the effect of miscellaneous parameters on the behaviour of first Order DAEM. Dhaundiyal et al. [10], [11] performed a comprehensive analysis of various density functions to predict the nature of thermal decomposition of biomass through DAEM.

In this study, kinetic parameters are determined by using the Monte Carlo scheme. The primary objective of this paper is to introduce a new method of solving in-exact integrals encountered while solving the solid-state kinetic models. It is assumed that the approximated solution forms an injective set. The Gaussian function is considered to be the initial distribution function. Only with the help of derivative thermogravimetric (DTG) analysis, the kinetic parameters of thermal degradation of forest waste is obtained.

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2. NON-ISOTHERMAL DAEM AND ITS NUMERICAL SOLUTION

DAEM is one of the multi-reaction models. The postulations, restriction and derivation of the non-isothermal n^{th} DAEM equations can be found in literature [12], [13]. Non-isothermal equations for the first order as well as n^{th} DAEM are given below:

$$(1-\alpha) = \int_0^\infty \exp\left(-\int_0^t \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) dt\right) f(E) dE, \quad (1)$$

$$(1-\alpha)_{n \neq 1} = \int_0^\infty \left[1 - (1-n) \left(\int_0^t \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) dt\right)\right]^{\frac{1}{1-n}} f(E) dE, \quad (2)$$

where

- E activation energy;
- α conversion of biomass;
- A frequency factor;
- R gas constant;
- t time;
- T temperature;
- N reaction order;

$f(E)$ density function of the activation energy of the volatile release. In this case, the function $f(E)$ represents density function of the Gaussian distribution.

The approximated solution of equations (1) and (2) can be done using the asymptotic technique. Therefore, the whole integral comprises two different kinds of density functions. The first term of DAEM is density function of temperature distribution, or temperature integral, whereas the density function of activation energy forms the second part of computational process. On the basis of these demarcations, the approximation is performed. The asymptotic form of the mean (E_s) and

the step width (E_w) of the temperature integral $\exp\left(\int_0^t \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) dt\right)$ is derived for the linear ramp

rate of temperature as mentioned in the study [13], thus, $E_s = RTY(\tau)$ and $E_w = \frac{E_s}{1+Y(\tau)}$, applying

the energy scaling and introducing the energy correction factor, we get

$$y_s = \frac{E_s}{E_0} \text{ and } y_w = \frac{E_w}{E_0}. \quad (3)$$

Therefore, the approximated form of temperature integral is:

$$\exp\left(\int_0^t \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) dt\right) \sim \exp\left(-\exp\left(\left(\frac{y_s - y}{y_w}\right)\right)\right), \quad (4)$$

where

- E_0 mean value of activation energy;
- $Y(\tau)$ Lambert W function;
- $\tau = A.t$ time-scale factor.

Equations (1) and (2) are simplified by incorporating functional expressions of the temperature integral and the distribution of activation energies.

$$(1-\alpha) \sim \int_0^{\infty} \exp\left(-\exp\left(-\exp\left(\left(\frac{y_s-y}{y_w}\right)\right)\right)\right) \exp\left(-\beta(y-1)^2\right) dy \quad (5)$$

Similarly, for n^{th} order reactions apply the binomial expansion on the equation (2):

$$(1-\alpha)_{n \neq 1} \sim \sqrt{\frac{\beta}{\pi}} \int_0^{\infty} \left[1 - \exp\left(\frac{y_s-y}{y_w}\right) + \left(\frac{n}{2}\right) \exp\left(2\left(\frac{y_s-y}{y_w}\right)\right) + \dots \right] \exp\left(-\beta(y-1)^2\right) dy, \quad (6)$$

where $\beta = \frac{E_0^2}{2\sigma^2}$ is a constant and σ is standard deviation of Gaussian distribution function.

Using the Laplace asymptotic scheme for the interior points of the integral ‘ dy ’ (Equation (5) and Equation (6)), we get a leading behaviour of the remaining mass fraction of the volatile $(1-\alpha)$ for the first and n^{th} order reactions.

$$(1-\alpha) \sim \frac{\exp\left(-\beta(y_e-1)(y_e+2y_w-1)\right)}{\sqrt{1+\left(\frac{y_e-1}{y_w}\right)}} \quad (7)$$

$$(1-\alpha)_{n \neq 1} \sim 1 - \frac{1}{\sqrt{2\beta}} \left[\exp\left(-\beta(y_{e,n}-1)(2y_s-y_{e,n}-1)\right) + \frac{n}{2} \exp\left(-2\beta(y_{e,n}-1)(y_s-y_{e,n})\right) \right] \quad (8)$$

Equations (7) and (8) are the desired expressions for the first and n^{th} order reactions. The values of y_e , and $y_{e,n}$ and $y'_{e,n}$ represent the points where the exponents of the exponential term in equations (5) and (6) attain maximum values, respectively.

$$y_e = 1 + y_w Y \left(\frac{1}{2\beta y_w^2} \exp\left(\frac{y_s-1}{y_w}\right) \right) \quad (9)$$

$$y_{e,n} = 1 - \frac{1}{2\beta y_w} \quad (10)$$

$$y'_{e,n} = 2y_{e,n} - 1 \quad (11)$$

3. MONTE-CARLO SCHEME

The Monte Carlo method is a computational technique used to obtain an unknown parameter. It is a fundamental tool to calculate and simulate a set of maps which are independent and identically distributed with the same distribution as the set of all maps [14]. Guo et al. [15] reported that the evolution of bonds in pyrolysis could be simulated by combining the Boltzmann-Monte-Carlo algorithm with the percolation theory. In pyrolysis problem of coal, the Monte Carlo algorithm delineates the bond formation by using coupling

or collision of radical fragment [15]. The concept of Monte-Carlo analysis is to understand the uncertainty in the system through random sampling. Random number generator assigns a random value to each variable within the demarcated limit. Thus, it helps to develop a robust scheme to solve the inverse problem. Mainly, the performance of any given model is carried out by the deterministic value of parameters, but Monte Carlo is very effective for those models that have no analytical solutions. However, sometimes deterministic approach may not be able to delineate the actual process, therefore it is necessary to enhance the decision ability of the model and the gap between numerical approximations and analytical solutions can be abridged. In this study, the area of the DTG curve is calculated by using the Monte-Carlo scheme. The MATLAB software is used to generate random particles of 17 to 20 million, so that the approximated area is nearly equal to the area bounded by the DTG plane. The area under the DTG curve is estimated by using binary logic matrices, which helps to determine the number of particles enclosed by the DTG curves, or the number of particles bombarded on the DTG plane. Programming for computing the area under the curve is performed on the MATLAB interface.

$$\left| \left(\frac{1}{(m_0 - m_r)} \beta \right) \int_{m_t}^{m_r} \left(\frac{dm}{dT} \right) dT \right| \sim \left(\frac{p}{n} \right) \cdot A \quad (12)$$

Here:

p inbound particles;

n total number of particles bombarded on the DTG plane;

A area under the DTG plane;

m_0 , m_t and m_r are the initial, instantaneous and residual mass of biomass respectively.

4. APPLICATION OF BIOMASS

Thermal degradation of pine waste is conducted in the presence of inert gas (Nitrogen) by using the thermogravimetry technique. The volumetric flow rate of the gas is 200 mL/min. The crucible holder of Alumina (Al_2O_3) is used to hold the sample inside the heating chamber. The thermocouple type 'R' is used to measure the temperature of the sample. The derivative thermogravimetric data is used to explore the kinetic parameters of thermal degradation of pine samples. The test is conducted at the heating rates of 5 °C/min, 10 °C/min and 15 °C/min. The chemical composition of the pine samples is shown in Table 1.

TABLE 1. CHEMICAL COMPOSITION OF PINE NEEDLES WITH HIGH HEATING VALUE (H.H.V)

C, %	H, %	N, %	O, %	Ash content, %	S, %	H.H.V, MJ/kg
54.28	6.55	0.61	35.50	2.92	0.11	20.65

5. RESULTS AND DISCUSSION

Mathematical computation of the kinetic model is performed by using the Monte Carlo simulation method. The given pyrolysis problem is converted into the inverse form assuming the non-surjective nature of the co-domain of kinetic parameters. The estimated range of variation of activation energy is distinguished by its integral limit. The Brownian movements of bombarded particles on the DTG plane at different heating rates are illustrated in Fig. 1,

Fig. 2, and Fig. 3. The number of inbound particles (p) is used to determine the area (Equation (12)) enclosed by DTG curves at the heating rates of 5 °C, 10 °C and 15 °C. The estimated areas under the DTG curve at different heating rates are shown in Table 2. It is assumed that the significant behaviour of total integrand (Equation (1) and (2)) is about the central value (E_s) of temperature integral, thus it reflects the activation energy required to initiate the thermal decomposition of the pine waste. The upper limits of activation energies are estimated to be 154.47 kJ/mol, 144.62 kJ/mol and 147.64 kJ/mol at the heating rates of 5 °C/min, 10 °C/min and 15 °C/min for first-order reactions, respectively, whereas the upper range of activation energies for n^{th} order reactions lies in the domain of 66.20 kJ/mol to 69.56 kJ/mol (Table 3).

Frequency factors calculated using the proposed scheme lie in between 10^4 and 10^7 min^{-1} . The activation energy distribution (on the basis of mean value) among the different stages of decomposition of pine needles is illustrated in Fig. 4. It is indicated that the energy required during the dehydration phase of pine needles vary from 25 kJ/mol to 50 kJ/mol, whereas the activation energy rises steadily until the char formation. The activation energy increases by 40 % till the end of 58 % conversion of pine waste. The activation energies of sigmoidal reactions get changed due to the variation of the heat of reactions (exothermic to endothermic). Unlike the drift in the activation energy at the end of dehydration of the pine needle sample, it is marginally very low at the onset of the char formation stage. The activation energies of pine needles during char formation gets increased by 9 %. The results are compared with different model-free methods and multi-component devolatilisation mechanisms, and it has been found that the derived solution provided the same solution with comprehensive details of the variation of activation energies caused by temperature integral, as well as the density function. The average variation of activation energy due to the density function varies from 66 kJ/mol to 76 kJ/mol, whereas the approximated solution of temperature integral has a significant role in deciding the overall activation energy of the pine-needles, as both the functions are intertwined in the distributed activation energy model, therefore it is necessary to demarcate the individual merit of them.

Fig. 1. Brownian motion of inbound and out bound particles on the DTG plane at 5 °C/min.

The significant contribution of the double exponential term to decide the shape and amplitude of the resultant curve is relatively high to the density function (the Gaussian distribution). Thus, the solution converges at the energy scaling factor (y) from 1.3 to 1.4.

The energy spacing of the temperature integral (or double exponential term), the kinetic parameters of n^{th} order and the variance of the Gaussian energy distribution are estimated in Table 4.

It can be concluded that the proposed scheme has good agreement with other statistical methods, where the solution is predicted by the trade-off relationship between experimental and mathematical models. However, Monte Carlo simulation is also an approximated methodology, yet it reduces the scope of multiple iterations through the direct correlation of experimental data with a mathematical solution.

Fig. 2. Brownian motion of inbound and out bound particles on the DTG plane at 10 °C/min.

Fig. 3. Brownian motion of inbound and out bound particles on the DTG plane at 15 °C/min.

Fig. 4. Energy distribution at different stages of decomposition of pine needles.

TABLE 2. CALCULATED AREA OF THE DTG CURVES FOR DIFFERENT HEATING RATES

Heating rate			
Area under curve (sq. Unit)	5 °C/min	10 °C/min	15 °C/min
$\left \left(\frac{1}{(m_0 - m_r)^\beta} \right) \int_{m_i}^{m_f} \left(\frac{dm}{dT} \right) dT \right = (1 - \alpha)$	52.4866	104.3758	153.6810

TABLE 3. PARAMETRIC INFORMATION OF THERMAL DECOMPOSITION OF PINE NEEDLES

Parameters	First order reactions			n^{th} order reactions ($n = 0.002$)		
	5 °C/min	10 °C/min	15 °C/min	5 °C/min	10 °C/min	15 °C/min
E_0 , kJ/mol	76	66.72	65.94	20	27	26
A , min^{-1}	$6.39 \cdot 10^7$	$3.10 \cdot 10^7$	$3.96 \cdot 10^4$	$5.44 \cdot 10^2$	$6.56 \cdot 10^2$	$7 \cdot 10^2$
σ^2 , kJ/mol	89.3	75.49	81.76	2	2.0670	2.29
E_s , kJ/mol	99.50	92.08	92.78	43.022	40.55	38
E_w , kJ/mol	4.95	4.91	4.98	4.64	4.59	4.64
Integral limit	$26.79 \leq E_\infty \leq 154.45$	$25.15 \leq E_\infty \leq 144.62$	$25.80 \leq E_\infty \leq 147.64$	$3.15 \leq E_\infty \leq 69.56$	$11.44 \leq E_\infty \leq 66.38$	$3.53 \leq E_\infty \leq 66.20$

TABLE 4. VALIDATION OF THE PROPOSED SCHEME WITH THE OTHER METHODOLOGIES

Activation Energy	Monte Carlo Technique	Model- free methods [16]			Multi-component devolatilization mechanism [17]
		FWO	KAS	Kissinger	
E , kJ/mol	92–100	82.38	74.83	132.77	90–132

6. CONCLUSION

The kinetic parameters of thermal decomposition of pine needles have been derived using the Monte Carlo technique. The variation of activation energy is demarcated on the basis of temperature integral, as the significant contribution of temperature integral governs the

integral problem of DAEM. The estimated value of activation energy varies between 92 kJ/mol and 100 kJ/mol, whereas the lower limit of activation energy changes from 25 kJ/mol to 26 kJ/mol. Similarly, the activation energy for the n^{th} reactions varies from 38 to 43 kJ/mol at the reaction order of 0.002. The obtained values are within the permissible limit of variation as mentioned in literature [16]–[19]. The proposed scheme is relatively robust and precise to other methodologies. By applying the inverse function to calculate the kinetic parameters, the computational burden gets lessened. Secondly, it demarcates the activation energy variation caused by temperature integral from the energy distribution introduced by the density function of the distribution function. However, the nature of the inverse function for the proposed scheme must be non-surjective in its validation. It implies that the conversion at a particular time cannot have two different activation energies at the given heating rate. So, the solution must be non-trivial in nature. Apart from precise calculation of kinetic parameters, the mathematically formulated solution demands one to one mapping of variables, thus the solution must be injective, and the kinetic parameters must have a single value at the given conversion (α). Furthermore, should the bombarded particles cover the DTG plane completely, the technique would be more effective.

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