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5 Distributed Activation Energy Modeling by the transmutation of different density functions

Abstract: This chapter incorporates the different perspective of modeling of activation energies through ingression of an additional parameter of distribution function to increase the flexibility and controlling ability of modeling by the linear mixing. The transmuted functions are adopted to bring flexibility in the numerical solution of multireaction models. A stochastic model is used to represent the activation energy function. Thus, the different activation energies can be represented by a density function to describe the pyrolysis process. The qualitative, as well as quantitative effects of the transmuted family of distribution on biomass pyrolysis, are carefully examined by the proposed mathematical solution. The nonlinear thermal history is implemented to demonstrate the approach.

Keywords: Biomass pyrolysis, transmuted function, kinetic parameters, thermal parameters, nonlinear ramping

Notation

" t "	Transmuted form	Dimensionless
W	Weight parameter for volatile content	Dimensionless
T	Temperature	K
α	Conversion	Dimensionless
A	Frequency factor	min^{-1}
E	Activation energy	kJ/mol
$p(E)$	Density function of activation energy	Dimensionless
τ	Shape parameter	Dimensionless
R	Universal gas constant	kJ/K mol
θ	Shape parameter for the Lindley distribution	Dimensionless
ψ	Shape parameter for the Lindley distribution	Dimensionless

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γ	Location parameter for the Lindley distribution	kJ/mol
β	Shape parameter for the Weibull distribution	Dimensionless
η	Scale parameter for the Weibull distribution	kJ/mol
γ	Location parameter of the Weibull distribution	kJ/mol
ρ	Shape parameter of the Frechet distribution	Dimensionless
δ	Scale parameter of the Frechet distribution	kJ/mol
μ	Location parameter of the Frechet distribution	kJ/mol
E_0	Mean value of the Gaussian distribution	kJ/mol
σ	Standard deviation of the Gaussian distribution	kJ/mol
ϕ	Location parameter of the Rayleigh distribution	kJ/mol
χ	Scale parameter of the Rayleigh distribution	kJ/mol
ε	Stochastic nature of regression model (error)	Dimensionless
a	Rate of change of heating rate	$^{\circ}\text{C}/\text{min}^2$
s	Instantaneous value of time interval	Min
m	<i>Heating rate</i>	$^{\circ}\text{C}/\text{min}$
T_0	Initial temperature	K
T_f	The maximum temperature	K
E_s	Central value of activation energy	kJ/mol
E_w	Step width	kJ/mol
$W(\kappa)$	Lambert W function	Dimensionless
κ	Time rescaling factor	Dimensionless
y^e	Maxima point	Dimensionless
y_s	Energy rescaling corresponding central value	Dimensionless
y_w	Energy rescaling factor for step width	Dimensionless
ω	Dimensionless number	Dimensionless
E_{∞}	Upper bound of activation energy	kJ/mol
f_1 and f_2	The components of the Lindley distribution	Dimensionless

5.1 Introduction

Modeling of a system is one of the most challenging tasks when you are dealing with the unit where multivariables are acting simultaneously within a system. One of such systems is a biological activity of constituents that have different chemical,

thermal, and physical properties, and it emerges out to be a reason of anomalies in the measurands. There are numerous ways of tackling such complicated problems, which need myriads of steps to evaluate them properly. Therefore, some assumptions, approximations, and advanced calculus are required to save three M's (men, machine, and money) from overexploitation.

Here, one of the thermochemical processes, namely pyrolysis, has been analyzed qualitatively and quantitatively of a given problem. The problem arises when the dynamical behavior of inflexion point of thermogravimetric (TG) variation of mass curve impedes the predicted stochastic modeling of activation energies to converge around the neighboring point of it. Many methodologies [1–7] have been adopted to fetch the best suitable prediction that can converge up to 90% of the measurand value.

Numerical solution of multireaction modeling of parallel reactions provides a better insight of parametric behavior and its effect on the natural phenomenon; thereafter, it becomes a lot easier to predict the outcome of solution than that of statistical linear models that merely rely on the linear regression of a straight line. There are various methods of modeling and evaluating kinetic parameters of pyrolysis process that can also be categorized as the single reaction model and the multi-reaction model [8–12].

The demarcation of modeling is based on the end results required by the user; therefore, it is necessary to understand the requirement of the given problem. In the same context, exploratory and application-based models are of the main concern [13]. The exploratory models require less computation resources and it is relatively fast and flexible, but the accuracy is highly compromised. On the other hand, the application-based models look for the concrete, robust, mature, and precise solution. It requires a little computer-based programming, but solution converges without reservation. In the real-time problems, the application-based modeling provides an accurate and sophisticated numerical solution which can be delineated graphically.

Hence, in this study the effect of one of such application-based models is considered to carry out the simulation process. Thermochemical parameters along with distribution pattern are examined through modeling of activation energies by the transmuted functions. Moreover, the dynamic behavior of stage decomposition is depicted through nonstationary maxima of curve with respect to time. The purpose of study is solely based on the application perspective of transmuted function, reducing the variation gap between Arrhenius parameters, and proposing the new concept for modeling activation energies, not to over-fitting of curves. Therefore, a new scheme has been proposed where the kinetic parameters are not influenced by the inflexion point of two different reaction phases, which is overlooked in the previous studies [1, 3, 14].

5.2 The transmuted function of activation energy $p(E)$

The idea of grouping the parallel reactions to analyze the mechanism of complex reactions is not the new scheme of comprehending the interrelationship between frequency factor and activation energy. For surface-catalyzed reactions, it had been envisaged that the surface has various sites that rely on distribution of activation energies among the competitive reactions [15]. The similar concept was adopted to measure irreversible changes in an electrical resistance while annealing the evaporated metal films [16]. This scheme was highly adopted by the coal pyrolysis community and the parallel reactions approach came into light in the 1960s [17, 18]. Later, Anthony and Howard (1976) proposed that the activation energy of the parallel reactions could be expressed as a density function of the normal distribution for coal pyrolysis [19]. However, there are some asymmetrical functions tested to validate the result for the loose biomass [20–22]. It is not that the derived results from other distribution functions have higher degree of entropy than the normal distribution. But the compensatory effect due to the mathematical mandate in the old theories that get drifted off through modification of the prevailing theorem [1].

Despite all those efforts for calculating multivariate function [1, 23], still there is a scope of assessing the nature of stochastic function as well as selection of appropriate thermal programming for pyrolysis reactions. Although it is difficult to interpret TG and derivative TG curves exactly, since (i) it is impossible to measure the sample temperature exactly through thermocouple, (ii) there is a time lag while formation of intermediate stages, (iii) interference of interactive atmosphere or cooling effect, and (iv) heat transfer limitation. Experimental curves have constraints and stagnation with time; overall, it reflects the gradual variation in property of material, which is related to alteration of thermal history. On the other hand, the attribute of mathematical model is based on the set protocol that overlooks the miscellaneous factors related to thermal decomposition. Transformation time between intermediate stage is almost Δt , which tends to zero for the mathematical model.

There are some methodologies developed to simulate the TG attribute effectively such as double-distributed activation energy model (2-DAEM) [5, 14]. The scheme manifests to mitigate uncertainties of distribution function to describe TG curves by introducing the weight parameter for volatile content “ w ” [24]. This proposition can be valid unless pyrolysis of biomass is carrying out in the unrealistic condition since it is not necessary that the role of volatile content ceases to act with the decreasing value of w . Lewellen et al. [25] stated that the residence time of volatile content has significant influence on pyrolysis of biomass. It decides the extent of secondary pyrolysis. Therefore, the weight factor and time factor cannot be correlated, as competitive pathways such as cracking, repolymerization can be inhibited through formation of some of light volatile gases. The

volatile content may initiate the autocatalytic reactions at elevated temperature. It accelerates the formation of the stable products content which would escape the biomass matrix to yield volatiles [25]. There are various key issues related to modeling of biomass that have been summarized in some of literatures [25–28]. It is complicating to find the exact mathematical solution to interpret the TG curves, but the discordance can be subdued to some extent. There are some other mathematical solutions used for condensed phase reactions – isoconversional and model fitting. Both are highly recommended for kinetic analysis [13, 29].

Regression-based modeling is very promising and time-saving, whether the estimated results are precise and exhibit the kinetic mechanism of pyrolysis. This must be investigated carefully. Isoconversional and model fitting are some of regression-based methods used for estimating the kinetic parameters. Isoconversional scheme or model-free kinetics does not imbibe the idea of fitting the experimental TG data to the phenomenological models, but it does not infer “free from assumption.” The basic tenets of scheme are that at any given extent of reaction, the same reactions occur in the same ratio at different heating rates and the reactions must be independent of temperature. However, this hypothesis can be easily nullified by a system of parallel independent reactions whose relative reactivity is proportional to temperature and it is varying due to different activation energies [30]. It is also possible that the overall reaction pathway of the competitive reactions with different activation energies is different at different temperature [31], as Lewellen et al. [25] suggested for pyrolysis of cellulose. Unlike isoconversional method, inconsistency for determining Arrhenius parameters is observed in the model-fitting method. It is mainly due to force-fitting of data to the hypothetical reaction model. The Arrhenius parameters are determined by the phenomenological model, which is already assumed. Moreover, both temperature and conversion consistently vary with time. This methodology is unable to demarcate separately the temperature dependence of rate constant and the conversion. Eventually, it causes drastic variation while determining the frequency factor and activation energies, and any phenomenological model can be claimed to describe the pyrolysis mechanism of biomass. Moreover, the existence of competitive reactions with different activation energies affects the overall decomposition rate, as these reactions are highly influenced by temperature and extent of conversion; therefore, the activation calculated from this method is a function of T and α [29]. This model is highly inaccurate and has been highly discouraged for kinetic analysis [32].

However, instrumental noise, response time, inabilities of thermocouples, and sensitivity of thermobalance cannot be incorporated in any advance integral model or regression schemes. One can filter data to remove suspicious values and reduce the gap between A and E variation. One may also adopt statistical testing scheme (Fisher’s exact test, Dixon Q ’s test, Bartlett’s test, etc.). But if your thermoanalytical data size is colossal, these probing schemes become time-consuming to analyze the sample size. Distribution in activation energies through conventional logistical distribution function [33] is not only the way to introduce a reactivity distribution, but

there are several other ways to solve DAEM, such as linear mixing of density function $p(E)$ of activation energy:

$$p^t(E) = (1 + \tau)p(E) - \tau (p(E))^2, \quad |\tau| \leq 1 \quad (5.1)$$

where E is the activation energy.

Unknown activation energy of pyrolysis reaction is said to be transmuted if it follows eq. (5.1). However, the same expression holds valid for cumulative distribution function of activation energy. Parametrization of well-established distribution reduces the effective computation time for deriving more robust and flexible families of distribution. Shaw and Buckle [34] were the leading researchers to explore distributional flexibility through introducing a new parameter to an existing distribution. They figured out that involvement of parameters did not make solution cumbersome but enhance the reproducibility of the modeling of natural process. The generated or transmuted family imbibes the parent distribution and impart more dynamical attribute to simulated results for various types of data than the conventional logistical approach. Implementation of transmuted family is very vast, and it encompasses all the natural phenomenon that demands the high degree of flexibility as the entropy of such systems is very high. One of such study is carried out for modeling the metrological data. The transmuted Gumbel distribution is found to be very effective for analyzing the snowfall data of a region [35]. The competitiveness of transmuted exponentiated Frechet distribution over exponentiated Frechet distribution for modeling wind speed data is performed to gather the statistical properties for a wind energy conversion system. The application indicates that the transmuted model's performance is relatively good to the parent model [36]. Another field of application of transmuted function is the mortality or failure of some system with respect to time. It is found that the reliable behavior of transmuted distribution functions is very useful for modeling reliability data in the manufacturing industries [37]. The application as well as modification of the conventional distributions is reported in the several literatures [38–40].

In the subsequent sections, the approximation techniques are adopted to simplify the classical DAEM and the conventional density variable from transmuted family of distribution, so that the distribution of reactivity can be introduced through the proposed scheme. However, interdependence of frequency factor (A) and E will still prevail in modeling of DAEM, but it is assumed that frequency factors (A) for all the competitive reactions are invariant and assumed to be constant. DAEM is represented through double integral equations for first-order reaction (eq. (5.2) [1]:

$$1 - \alpha = \int_0^{\infty} \exp \left\{ \left(- \int_0^t A e^{-\frac{E}{RT}} dt \right) \right\} p(E) dE \quad (5.2)$$

Density and cumulative functions of activation energy are illustrated in Table 5.1.

Table 5.1: Distribution functions and their corresponding parameters.

Distribution	Density function $p(E)$	Cumulative function $G(E)$	$\xi > 0$ Parameters
Lindley [41]	$\frac{\theta^2}{\theta + \psi} (1 + \psi(E - \gamma)) e^{-\theta(E - \gamma)}$	$\left\{ 1 - \left(1 + \frac{\theta\psi(E - \gamma)}{\theta + \psi} \right) e^{-\theta(E - \gamma)} \right\}$	θ, ψ, γ
Weibull [42]	$\frac{\beta}{\eta} \left(\frac{E - \gamma}{\eta} \right)^{(\beta - 1)} e^{-\left(\frac{E - \gamma}{\eta} \right)^\beta}$	$\left\{ 1 - e^{-\left(\frac{E - \gamma}{\eta} \right)^\beta} \right\}$	β, η, γ
Frechet [43]	$\frac{\rho}{\delta} \left(\frac{E - \mu}{\delta} \right)^{-(1 + \rho)} e^{-\left(\frac{E - \mu}{\delta} \right)^{-\rho}}$	$\left\{ e^{-\left(\frac{E - \mu}{\delta} \right)^{-\rho}} \right\}$	ρ, δ, μ
Gaussian [44]	$\frac{1}{\sqrt{2\pi}\sigma^2} e^{-\left(\frac{E - E_0}{\sqrt{2}\sigma} \right)^2}$	$\left\{ \frac{1}{2} \left(1 + \operatorname{erf} \left(\frac{E - E_0}{\sigma\sqrt{2}} \right) \right) \right\}$	E_0, σ
Rayleigh [45]	$2\chi(E - \phi) \exp \left\{ -\chi(E - \phi)^2 \right\}$	$1 - \exp \left\{ -\chi(E - \phi)^2 \right\}$	ϕ, χ

5.2.1 Distributed activation energy modeling

A complex material such as biomass or fossil fuel comprises several constituents whose thermal decomposition varies greatly with time and temperature. The different products are generated at different stages of decomposition. If the parallel reactions follow the complex pathways, it becomes more complicating to model such process, so it is possible that a simple mathematical distribution will not have flexibility to describe the reaction profile of some reactions. Copula-based modeling [1, 23] is recently adopted to illustrate the complexity of decomposition reactions and to some extent it is found to be very helpful; however, the validation of results for different thermal histories is not done yet. Discrete activation energy distributions schemes are developed to provide flexibility to the reaction model. One of such models was developed for petroleum generation, which was first published by Ungerer and Pelet [46]. This scheme is derived from the isoconversional methods, which is mainly designed for estimating the unique values of Arrhenius parameters, but later it was used to correlate activation energy variation with conversion. The detailed study of development of several other models is reported in the literature [47]. But it requires special attention for energy spacing between reaction channels, which may affect the validity of the model. Moreover, it is purely based on the non-linear regression and the numerical integration, which itself is stochastic in nature. A regression analysis is based on the relationship between study and explanatory

variables through the series of coefficients that decide the characteristics and role of independent variables in any event:

$$y = f(X_1, X_2, \dots, X_k, a_1, a_2, \dots, a_k) + \varepsilon \quad (5.3)$$

where ε represents the stochastic nature of regression model that can alter the solution if activation energy is not discretized evenly. However, this scheme is highly encouraged for estimating the kinetic properties of kerogen pyrolysis rates [13, 48]. A major drawback in discrete modeling is the derivation of the structure, that is, of the terms in the discrete-activation energy model. When the form of differential equation generating data is identified, one can estimate possible terms for the discrete model from numerical methods, but not necessarily the associated coefficients. A good structure design (i.e., the form of $f(X_1, X_2, \dots, X_k, a_1, a_2, \dots, a_k)$) gets the kinetic model-fitted data properly and provide the good predictive results. Redundant terms in a model, on the one hand, can lead to over fitting, whereas too few terms make model ineffective. There are some practical criteria considered for effective modeling. First, the model should be numerically stable. Second, the selected model makes the best predictions, which can be performed by testing the given data for different heating rates or thermal profile. Asymptotic behavior of model should comply with those of the data. Keep the demarcation of discrete and continuous models for abeyance and formulate the transmuted function-based scheme.

To demonstrate the scheme, eq. (5.2) is bifurcated for simplifying the mathematical expression of DAEM. It comprises two parts: double exponential term (DExp) and the continuous density function of activation energy. Laplace integral method is implemented to estimate the approximated form of DAEM. DExp terms are an implicit function of time and temperature history experienced by the sample. The second part is independent of time and depends on the distribution of reactivity. First, the behavior of implicit function is perused, and then approximations are derived for the nonlinear profile.

The ideal thermal histories are seldom implemented for the industrial applications; therefore, the computational algorithm is tested for the nonlinear thermal profile represented as follows (eq. (5.4)):

$$T(K) = as^2 + T_0(K) \quad (5.4)$$

where $a \left(\frac{^\circ\text{C}}{\text{min}^2} \right) = \frac{dm}{dt}$ and the value of “ a ” represents the rate of change of heating rate (m) with time.

$$\text{Let, } f(T) = -\frac{E}{RT}$$

$$\text{DExp} = \exp \left\{ \left(- \int_{T_0}^{T_f} \frac{A}{2a \sqrt{\left(\frac{T-T_0}{a} \right)}} \exp(f(T_f)) dT \right) \right\} \quad (5.5)$$

The ratio of $\frac{E}{R(as^2 + T_0)} \rightarrow \infty$ is assumed to be large; thus, the significant contribution of integral is at neighborhood of $T - T_f$ and $f(T_f) > 0$. This provides the asymptotic approximation to the temperature-dependent function:

$$D\text{Exp} \sim \exp\left(\frac{A}{2\sqrt{a(T_f - T_0)}} \frac{-\exp(f(T_f))}{f'(T_f)}\right) \quad (5.6)$$

Correlating the result with the central value and the step size of activation energies, eq. (5.6) can be rewritten as

$$D\text{Exp} \sim \exp\left\{-\exp\left(\frac{E_s - E}{E_w}\right)\right\} \quad (5.7)$$

Rather than arbitrarily spacing the activation energies, it is better to generate the form of function that relies on the explanatory variables of experiments, as the trend of activation energy variation with respect to conversion is highly indeterministic [29].

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

Asymptotic approximation results in a rapidly varying function as $\frac{E}{R(as^2 + T_0)} \rightarrow \infty$ and function varies from zero to one as E increases by E_w around E_s . To further simplify the function, $\left(\frac{E_s - E}{E_w}\right)$ is to be expanded by the Taylor series about $E = E_s$:

$$g(E) \sim g(E_s) + (E - E_s)g'(E_s) + L \dots \quad (5.8)$$

The initial condition for function $g(E)$ at E_s is defined as

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

Equating eqs. (5.6) and (5.7), we have

$$g(E) \equiv -f(T_f) + \ln\left(\frac{A}{2f'(T_f)\sqrt{a(T_f - T_0)}}\right) \quad (5.9)$$

After solving eqs. (5.8) and (5.9), we have

$$E_s = RT_f W(\kappa)$$

$$E_w = \frac{RE_s(T_f)}{E_s + RT_f}$$

where both E_s and E_w are implicit functions of time. W is a Lambert W function and the dimensionless group $\left(\frac{T_f A}{2at}\right)$ is denoted by κ .

Note: Lambert W function is defined as one of the real roots of equation of form

$$xe^x = W(x)$$

Approximations of Lambert W function for small and large values of “ x ” (correlated to short and long durations of time) can be represented as

$$W \sim x - x^2, \quad x = 1$$

$$W \sim \ln \left(\frac{x}{\ln \left(\frac{x}{\ln(x)} \right)} \right) \quad 1 = x$$

5.2.2 Characteristic of distribution function

It is observed from the approximated form of DExp, correlated with activation through energy spacing of step size E_w , that the function behaves like a smoothed step function. It rises swiftly from zero to one as the term $\left(\frac{A}{2\sqrt{a(T_f - T_0)}} \right)$ increases, or $\left(\frac{E - E_s}{E_w} \right) \rightarrow \infty$ and the peak is concentrated at the neighborhood of $T = T_f$. The DExp as implicit function E makes the whole integrand homogenous and it becomes easier to compute the complicated integral problem. But the fact that cannot be overshadowed is the relative significance of E_w to the standard deviation of activation energies from the average value of activation energy. In eq. (5.2), the DExp is multiplied with the density function of activation energy. The mean value as well as standard deviation of distribution function is constant; therefore, the shape of the whole integrand relies on the study variables E_w and E_s . There must be the limits that can modulate the form of the model through changing the location of maximum of the total integrand. Thus, it provides two different ways of solving DAEM. The first case: when the standard deviations of continuous distribution functions (listed in Table 5.1) are relatively wide to E_w of DExp, the total integrand is the distribution function, but as time increases it is progressively truncated from the left side by the sigmoid-like DExp. The location of maximum of the total integrand can significantly shifts toward the left side, and the shape of integrand gets skewed. On the other hand, the relatively narrow form of the continuous distribution function to the width of DExp makes the shape of total integrand like the distribution function, but the amplitude is drastically reduced by DExp as time proceeds. The nature (symmetrical or asymmetrical) of the distribution function remains unchanged; however, the global maxima of the whole integrands get shifted. Conversely, pyrolysis is not solely decomposition of the biomass, but the simultaneous degradation of various constituents (moisture content, hemicellulose, lignin, and cellulose). Therefore, it is difficult to describe pyrolysis through a single distribution function. It can also be an alternative to combine the two limits together for two distinct regions of experimental curve. But it is more important to look at the behavior of thermoanalytical data sets rather than applying “hit-and-trial” scheme. The data set is

highly unpredictable during devolatilization stage [29] and the reason is some fast-autocatalytic reactions that trigger the secondary pyrolysis, which is difficult to model through the conventional form without any transmutation, or variation of limit on σ (standard deviation), as the dependency of such reactions relies on the residence time of volatiles [25] inside the cellulose matrix; however, there are also some other factors, such as grain orientation, size of biomass particle, structural effect, and moisture content. Thus, the model must be robust enough to explain the transition states that depend on the residence time of volatile. Although the release of volatile content changes if heating rate varies from ramping to constant temperature cases, so there is no appreciable variation encountered in the amount of released volatile until the two parts of the DAEM integral overlap completely [3].

DExp as well as distribution together must be varied with time and temperature. Analysis is carried out for the relatively narrow distribution function ($\sigma \rightarrow 0$). The development in the subsequent sections pivoted around the method of the moving maximum for the Laplace integral problems (Refer Appendices). The behavior of the density function as well as DExp is examined at the interior points of activation energy domain ($p''(E) > 0$). The objective of implementing technique is to determine the moving maxima of the whole integrand as a function of time so that the TG data can be interpreted easily.

5.2.2.1 Asymptotic scheme

The postulation for the narrow distribution of the continuous distribution of types (Table 5.1) is taking standard deviation $\sigma = RT_1$, where T_1 denotes temperature at the inflexion point and follows the given thermal history. The local maxima y^e of corresponding functions ($M(y)$, $J(y)$, $U(y)$, and $H(y)$) of distribution functions is sought by finding the point where $M'(y)$, $J'(y)$, $U'(y)$, and $H'(y)$ are zeros. Asymptotes and shapes of transmuted function are decided by following the two limits [49].

Proposition 5.1. *The asymptotic of eq. (5.1) if $p(E) \rightarrow 0$ are*

$$(i) \mathbf{p}^t(\mathbf{E}) \sim (1 + \tau) \mathbf{p}(\mathbf{E})$$

$$(ii) \mathbf{G}^t(\mathbf{E}) \sim (1 + \tau) \mathbf{G}(\mathbf{E})$$

Proposition 5.2. *The asymptotic of eq. (5.1) as $E \rightarrow \infty$ are*

$$(i) \mathbf{p}^t(\mathbf{E}) \sim (1 - \tau) \mathbf{p}(\mathbf{E})$$

$$(ii) \mathbf{G}^t(\mathbf{E}) \sim (1 - \tau) \mathbf{G}(\mathbf{E})$$

Modeling and analyzing material properties in the field of engineering are very complicating and cumbersome. Sometimes, the data is too big to predict precisely through

the conventional distribution function, especially the life prediction of machine parts. The density functions are widely implemented for studying fatigue and endurance life of engineering device and materials. Despite the wide range of application of distribution function, sometimes it is unable to explain different types of data that has nonmonotonic attribute; for instance, conversion of material at different thermal histories. Therefore, it is required to develop a flexible parametric model that can appropriately be embedded into a large model by adding an additional shape parameter. A significant contribution has been carried out for transmutation of the conventional model, thus enhancing flexibility in modeling of various types of life prediction data of the engineering components. The new transmutation models are developed and comprehensively perused in some of literatures [35, 36, 38, 49]. Therefore, some of the distribution types are modified to predict the thermoanalytical data efficiently through activation energy modeling.

5.2.2.1.1 Case A: transmuted Lindley (refer Appendix A)

Invoking eq. (5.1) and replacing the distribution function with transmuted function $p^t(y_1)$ by proper transformation in eq. (5.2), we have

$$1 - \alpha \sim \int_0^{\infty} \gamma \exp \left\{ -\exp \left(\frac{y_s - y_1}{y_{w1}} \right) \right\} p^t(y_1) dy_1 \quad (5.10)$$

Putting the value of $p^t(y_1)$, we get

$$1 - \alpha \sim \gamma \left[\int_0^{\infty} \exp \left\{ -\exp \left(\frac{y_{s1} - y_1}{y_{w1}} \right) \right\} (k f_1(y_1) + (1 - k) f_2(y_1)) dy_1 \right] \quad (5.11)$$

Equation (5.11) can be written as a convex combination of functions $f_1(y_1)$ and $f_2(y_1)$:

$$1 - \alpha \sim \left[\int_0^{\infty} \exp \left\{ -\exp \left(\frac{y_s - y_1}{y_w} \right) \right\} \left(k \frac{\omega_1^2}{\theta} \psi(y_1 - 1) \exp \{ -\omega_1(y_1 - 1) \} + (1 - k) \omega_1 \theta \exp \{ -\omega_1(y - 1) \} \right) dy_1 \right] \quad (5.12)$$

where k is a mixing fraction.

Rewrite eq. (5.12) into two different parts and solve it for the same value of y_1 :

$$1 - \alpha = \{ (1 - \alpha_0) + (1 - \alpha_1) \} \quad (5.13)$$

Solve eq. (5.13) separately for $1 - \alpha$.

Let,

$$1 - \alpha_0 = \int_0^{\infty} \frac{k \omega_1^2}{\theta} \exp \left\{ -\exp \left(\frac{y_s - y_1}{y_w} \right) \right\} \psi(y_1 - 1) \exp \{ -\omega_1(y_1 - 1) \} dy_1 \quad (5.14)$$

Suppose that

$$V(y_1) = -\exp\left(\frac{y_s - y_1}{y_w}\right) - \omega_1(y_1 - 1) \quad (5.15)$$

The function $V(y_1)$ is at its extremum if $V'(y_1) = 0$.

Differentiating eq. (5.15) w.r.t y_1 , we get

$$V'(y_1^e) = \frac{\exp\left(\frac{y_{s1} - y_1^e}{y_{w1}}\right)}{y_{w1}} - \omega_1$$

Let the location of maximum is denoted by y_1^e , then

$$y_1^e = y_{s1} - y_{w1} \ln(\omega_1 y_{w1})$$

The second derivative of eq. (5.15) w.r.t. y_1 is given by

$$|V''(y_1^e)| = \frac{\omega_1}{y_{w1}}$$

Replacing $V(y_1)$ in eq. (5.15) by its Taylor expansion, we have

$$V(y_1) \sim V(y_1^e) + \frac{(y - y_1^e)^2}{2} V''(y_1^e) + \dots$$

After simplification, we get

$$(1 - \alpha_0) \sim 1.25(y_1^e - 1)k \left(\psi \frac{\omega_1}{\theta} \sqrt{y_{w1}\omega_1} \right) \left(\operatorname{erf}\left(y_1^e \sqrt{\frac{0.5\omega_1}{y_{w1}}}\right) + 1 \right) \exp\{-\omega_1(y_{w1} + y_1^e - 1)\} \quad (5.16)$$

Now consider the other term $(1 - \alpha_1)$

$$1 - \alpha_1 = \int_0^\infty \theta \omega_1 (1 - k) \exp\left\{-\exp\left(\frac{y_{s1} - y}{y_{w1}}\right)\right\} \theta \exp\{-\omega_1(y - 1)\} dy \quad (5.17)$$

Similarly, the required expression for $(1 - \alpha_1)$ is,

$$(1 - \alpha_1) \sim 1.25 \theta (1 - k) (\sqrt{y_{w1}\omega_1}) \left(\operatorname{erf}\left(y_1^e \sqrt{\frac{0.5\omega_1}{y_{w1}}}\right) + 1 \right) \exp\{-\omega_1(y_{w1} + y_1^e - 1)\} \quad (5.18)$$

Substituting eqs. (5.16) and (5.17) into eq. (5.13), we have the resultant solution for transmuted Lindley function at different limits

$$\lim_{p(E) \rightarrow 0} (1 - \alpha) \sim 1.25 (1 + \tau) (1 - k) \sqrt{y_{w1} \omega_1} \left(\operatorname{erf} \left(y_1^e \sqrt{\frac{0.5 \omega_1}{y_{w1}}} \right) + 1 \right) \exp \{ -\omega_1 (y_{w1} + y_1^e - 1) \} \{ \theta + \omega_1 (y_1^e - 1) \}$$

$$\lim_{E \rightarrow \infty} (1 - \alpha) \sim 1.25 (1 - \tau) (1 - k) \sqrt{y_{w1} \omega_1} \left(\operatorname{erf} \left(y_1^e \sqrt{\frac{0.5 \omega_1}{y_{w1}}} \right) + 1 \right) \exp \{ -\omega_1 (y_{w1} + y_1^e - 1) \} \{ \theta + \omega_1 (y_1^e - 1) \}$$

5.2.2.1.2 Case B: transmuted Weibull (refer Appendix B)

From eqs. (5.1) and (5.2), we get

$$1 - \alpha = \int_0^{\infty} y \exp \left\{ -\exp \left(\frac{y_s - y}{y_{w2}} \right) \right\} p^t(y_2) dy \quad (5.19)$$

Substituting the density ($p(y_2)$ from Table 5.1 into eq. (5.1) for the Weibull distribution, we have

$$1 - \alpha = (1 + \tau) \omega_2^\beta \beta \int_0^{\infty} (y_2 - 1)^{\beta-1} \exp \left\{ -\exp \left(\frac{y_{s2} - y_2}{y_{w2}} \right) - ((\omega_2 (y_2 - 1))^\beta) \right\} dy \quad (5.20)$$

The final expression after transmutation is expressed through eq. (5.20).

Assume that $M(y_2)$ is a function whose maxima is at $y_2 = y_2^e$, then

$$M(y_2) = -\exp \left(\frac{y_{s2} - y_2}{y_{w2}} \right) - ((\omega_2 (y_2 - 1))^\beta) \quad (5.21)$$

Find the first- and the second-order derivatives of eq. (5.21) and substitute its Taylor series expansion into eq. (5.20):

$$M'(y_2) = \frac{\exp \left(\frac{y_{s2} - y_2}{y_{w2}} \right)}{y_{w2}} - \beta \omega_2^\beta (y_2 - 1)^{\beta-1}$$

Equating $M'(y_2) = 0$, we get

$$y_2^e = 1 + (\beta - 1) y_{w2} W \left(\frac{1}{(\beta - 1) y_{w2}} \left(\frac{1}{\beta y_{w2} \omega_2^\beta} \right)^{\frac{1}{(\beta - 1)}} \exp \left\{ \frac{1}{(\beta - 1)} \left(\frac{y_{s2} - 1}{y_{w2}} \right) \right\} \right)$$

Likewise,

$$M''(y_2) = -\frac{\exp \left(\frac{y_{s2} - y_2}{y_{w2}} \right)}{y_{w2}^2} - \beta(\beta - 1) \omega_2^\beta (y_2 - 1)^{\beta-2} \quad (5.22)$$

$$M(y_2) \sim M(y_2^e) + \frac{(y - y_2^e)^2}{2} M''(y_2^e) + \dots \quad (5.23)$$

After substituting $M''(y_2)$ from eq. (5.22) into eq. (5.23) and replacing $M(y_2)$ by its expansion in eq. (5.20), we get the asymptotic expression for the Weibull distribution for different limits:

$$\begin{aligned} \lim_{p(E) \rightarrow 0} (1 - \alpha) &\sim (1 + \tau) \left(0.707 \sqrt{\frac{\pi \omega_2^\beta \beta (y_2^e - 1)^\beta}{\left\{ \left(\frac{y_2^e - 1}{y_{w2}} \right) + (\beta - 1) \right\}}} \right) (\text{erf}(y_2^e) + 1) \\ &\quad \exp \left\{ -\omega_2^\beta (y_2^e - 1)^{\beta-1} (y_2^e + \beta y_{w2} - 1) \right\} \\ \lim_{E \rightarrow \infty} (1 - \alpha) &\sim (1 - \tau) \left(0.707 \sqrt{\frac{\pi \omega_2^\beta \beta (y_2^e - 1)^\beta}{\left\{ \left(\frac{y_2^e - 1}{y_{w2}} \right) + (\beta - 1) \right\}}} \right) (\text{erf}(y_2^e) + 1) \\ &\quad \exp \left\{ -\omega_2^\beta (y_2^e - 1)^{\beta-1} (y_2^e + \beta y_{w2} - 1) \right\} \end{aligned}$$

5.2.2.1.3 Case C: Transmuted Gaussian (refer Appendix C)

Replacing the Gaussian distribution from eq. (5.2) with transmuted Gaussian function, we have

$$1 - \alpha = \int_0^\infty E_0 \exp \left\{ -\exp \left(\frac{y_s - y_3}{y_w} \right) \right\} p^t(y_3) dy_3 \quad (5.24)$$

After putting the value of the Gaussian distribution from Table 5.1 into eq. (5.1) and substituting into eq. (5.24), the transmuted form will be represented as

$$1 - \alpha = (1 + \tau) \sqrt{\frac{\omega_3}{\pi}} \int_0^\infty \exp \left\{ -\exp \left(\frac{y_s - y_3}{y_w} \right) - \omega_3 (y_3 - 1)^2 \right\} dy_3 \quad (5.25)$$

Suppose that

$$J(y_3) = -\exp \left(\frac{y_s - y}{y_w} \right) - \omega_3 (y_3 - 1)^2$$

The first and the second derivatives of $J(y_3)$ w.r.t “ y_3 ” are given by eqs. (5.26) and (5.27), respectively

$$J'(y_3^e) = \frac{\exp \left(\frac{y_s - y}{y_w} \right)}{y_w} - 2\omega_3 (y_3 - 1) \quad (5.26)$$

$$|J''(y)| = 2\omega_3 \left(\frac{y_3^e - 1}{y_w} + 1 \right) \quad (5.27)$$

The location of maximum of function $J(y_3)$ is obtained by $J'(y_3) = 0$. Hence

$$y_3^e = 1 + y_w W \left(\frac{1}{2\omega_3 y_w^2} \exp \left(\frac{y_s - 1}{y_w} \right) \right)$$

Substituting the values of $|J''(y_3^e)|$ in the Taylor series expansion of $J(y_3)$ about y_3^e , we have

$$J(y_3) \sim J(y_3^e) + \frac{(y - y_3^e)^2}{2} J''(y_3^e) + \dots$$

After simplification and rearrangement, the required solution of transmuted Gaussian function is expressed as

$$\lim_{p(E) \rightarrow 0} (1 - \alpha) \sim (1 + \tau) (\operatorname{erf}(y_3^e) + 1) \left\{ \frac{\exp \{ -\omega_3 (y_3^e - 1) (2y_w + y_3^e - 1) \}}{\sqrt{\left(\frac{y_3^e - 1}{y_w} + 1 \right)}} \right\} \text{ for } p(E) \rightarrow 0$$

$$\lim_{E \rightarrow \infty} (1 - \alpha) \sim (1 - \tau) (\operatorname{erf}(y_3^e) + 1) \left\{ \frac{\exp \{ -\omega_3 (y_3^e - 1) (2y_w + y_3^e - 1) \}}{\sqrt{\left(\frac{y_3^e - 1}{y_w} + 1 \right)}} \right\} \text{ for } E \rightarrow \infty$$

5.2.2.1.4 Case D: Transmuted Frechet (refer Appendix D)

The expression of transmuted Frechet is obtained after replacing density function from transmuted density function.

Equation (5.28) is the required expression which is subjected to investigation:

$$1 - \alpha \sim \int_0^\infty \mu \exp \left\{ -\exp \left(\frac{y_{s3} - y_4}{y_{w3}} \right) \right\} p^t(y_4) dy_4 \quad (5.28)$$

Replacing transmuted expression through substituting the value of density function from Table 5.1, we have

$$1 - \alpha \sim (1 + |\tau|) \int_0^\infty \exp \left[\left\{ -\exp \left(\frac{y_{s3} - y}{y_{w3}} \right) \right\} \rho \omega_4^{-\rho} (y_4 - 1)^{-(1+\rho)} e^{-\{\omega_4 (y_4 - 1)\}^{-\rho}} \right] dy_4 \quad (5.29)$$

To solve eq. (5.29), suppose that

$$U(y_4) = -\exp\left(\frac{y_s - y_4}{y_{w3}}\right) - \{\omega_4(y_4 - 1)\}^{|\rho|} \quad (5.30)$$

$$1 - \alpha \sim (1 + |\tau|) \int_0^\infty \exp(U(y_4)) dy_4 \quad (5.31)$$

Obtain the first- and the second-order derivatives of $U(y_4)$ as it is performed in the other cases:

$$U'(y_4^e) = \frac{\exp\left(\frac{y_s - y_4^e}{y_{w3}}\right)}{y_{w3}} - |\rho| \omega_4^{|\rho|} (y_4^e - 1)^{|\rho| - 1}$$

The location of maximum value is derived by $U'(y_4) = 0$.

$$y_4^e = 1 + y_{w3} W\left(\frac{1}{|\rho - 1| y_{w3}} \left(\frac{1}{y_{w3} |\rho| \omega_4^{|\rho|}}\right)^{\frac{1}{|\rho - 1|}} \exp\left(\frac{y_s - 1}{y_{w3}}\right)\right)$$

After simplifying the second-order derivative of eq. (5.30), we get

$$|U''(y_4^e)| = |\rho| (y_4^e - 1)^{|\rho| - 2} \omega_4^{|\rho|} \left(\frac{(y_4^e - 1)^{|\rho| - 1}}{y_{w3}} + |\rho - 1|\right)$$

Expand $U(y_4)$ with the Taylor series expression about $y_4 = y_4^e$,

$$U(y_4) \sim U(y_4^e) + \frac{(y - y_4^e)^2}{2} U''(y_4^e) + \dots \quad (5.32)$$

After replacing $U(y_4)$ from its Taylor expansion given by eq. (5.32), we get the solution for the transmuted Frechet as

$$\begin{aligned} \lim_{p(E) \rightarrow 0} (1 - \alpha) \sim (1 + \tau) 0.707 \sqrt{\frac{\pi (y_4^e - 1)^{|\rho|} \omega_4^{|\rho|}}{\left(\frac{(y_4^e - 1)^{|\rho| - 1}}{y_{w3}} + |\rho - 1|\right)}} (\text{erf}(y_4^e) + 1) \\ \left[\exp\left\{ -\omega_4^{|\rho|} (y_4^e - 1)^{|\rho| - 1} (y_{w3} |\rho| - (y_4^e - 1)) \right\} \right] \\ \lim_{E \rightarrow \infty} (1 - \alpha) \sim (1 - \tau) 0.707 (\text{erf}(y_4^e) + 1) \sqrt{\frac{|\rho| \pi (y_4^e - 1)^{|\rho|}}{\left(\frac{(y_4^e - 1)^{|\rho| - 1}}{y_{w3}} + |\rho - 1|\right)}} \\ \left[\exp\left\{ -\omega_4^{|\rho|} (y_4^e - 1)^{|\rho| - 1} (y_{w3} |\rho| - (y_4^e - 1)) \right\} \right] \end{aligned}$$

Note: Valid for the negative shape parameter ($\rho < 0$).

5.2.2.1.5 Case E: Transmuted Rayleigh distribution (refer Appendix E)

Two-parameter Rayleigh distribution is used for demonstrating the scheme. The transmuted distribution function is obtained by replacing the density function from its expression given in Table 5.1. Equation (5.33) is the transmuted expression for first-order chemical reactions:

$$1 - \alpha \sim \int_0^{\infty} \phi \exp \left\{ -\exp \left(\frac{y_{s4} - y}{y_{w4}} \right) \right\} p^t(y_5) dy \quad (5.33)$$

After obtaining $p^t(y_5)$ from eq. (5.1), we get the expression for the expected solution

$$1 - \alpha \sim \int_0^{\infty} \exp \left\{ -\exp \left(\frac{y_{s4} - y}{y_{w4}} \right) \right\} 2\omega_5(y - 1) \exp \left\{ -\omega_5(y - 1)^2 \right\} dy_5 \quad (5.34)$$

Assume that

$$H(y_5) = -\exp \left(\frac{y_{s4} - y}{y_{w4}} \right) - \omega_5(y - 1)^2$$

Then eq. (5.34) can be represented as

$$1 - \alpha \sim \int_0^{\infty} 2\omega_5 \phi(y - 1) \exp(H(y_5)) dy_5 \quad (5.35)$$

The first derivative of $H(y_5)$ w.r.t. “ y_5 ” is

$$H'(y_5^e) = \frac{\exp \left(\frac{y_{s4} - y}{y_{w4}} \right)}{y_{w4}} - 2\omega_5(y_5^e - 1)$$

For deriving the location of maximum, equate $H'(y_5) = 0$

$$y_5^e = 1 + y_{w4} W \left(\frac{1}{2\omega_5 y_{w4}^2} \exp \left(\frac{y_{s4} - 1}{y_{w4}} \right) \right)$$

“ y_5^e ” is the location where the function $H(y_5)$ attains its maximum.

Similarly, after simplification, the second derivation is obtained as

$$H''(y_5^e) = \left| 2\omega_5 \left(\frac{(y_5^e - 1)}{y_{w4}} + 1 \right) \right| \quad (5.36)$$

The Taylor series expansion of function $H(y_5)$ about y_5^e is given by

$$H(y_5) \sim H(y_5^e) + \frac{(y - y_5^e)^2}{2} H''(y_5^e) + \dots \quad (5.37)$$

After putting the value of $H''(y_5^e)$ from eq. (5.36) into eq. (5.37) and replacing $H(y_5)$ in eq. (5.35) with its Taylor series expansion (eq. (5.37)), we have the required expression for the transmuted Rayleigh distribution:

$$\lim_{p(E) \rightarrow 0} 1 - \alpha \sim (1 + \tau) \left(\sqrt{\frac{\omega_5 \pi}{2 \left(\frac{(y_5^e - 1)}{y_{w4}} + 1 \right)}} \right) (\text{erf}(y_5^e) + 1) \exp\{ -\omega_5 (y_5^e - 1) (2y_{w4} + y_5^e - 1) \}$$

$$\lim_{E \rightarrow \infty} 1 - \alpha \sim (1 - \tau) \left(\sqrt{\frac{\pi \omega_5}{2 \left(\frac{(y_5^e - 1)}{y_{w4}} + 1 \right)}} \right) (\text{erf}(y_5^e) + 1) \exp\{ -\omega_5 (y_5^e - 1) (2y_{w4} + y_5^e - 1) \}$$

5.3 Application and computation analysis of TG data

Elemental analysis of sample subjected to thermal degradation is conducted through CHNS-O analyzer. The CHNS-O analyzer (vario MACRO) is used to evaluate the chemical composition of pine needles. Before using the CHNS-O analyzer, the furnace is heated up to 1,473 K for 30 min. Once it gets heated, the capsule forms of sample are fed into a slot of rotating disk. The flow of oxygen maintains the catalytic combustion, whereas helium gas acts as a carrier gas stream so that the volatile gases with water (CO_2 , SO_2 , NO_2 , and H_2O) can be absorbed at different reduction columns. These tubes are in-between combustion chamber and detection unit (computer-based software), where the gas mixture is separated into its components through purge or trap chromatography. Thereafter, each component is separately detected by thermal conductivity detector (TCD). The gases CO_2 , H_2O , and SO_2 are absorbed in a sequence, whereas N_2 passes through all the three columns and it is finally detected by TCD. TCD generates the electrical signal that is proportional to the concentration of elementary components of biomass. The reference material is considered to be the powder of birch leaf. The bomb calorimeter at constant volume is used to measure the calorific value of pine needles. Thermal evaluation of pine waste is based on TG differential thermal analyzer (Diamond TG/DTA, Perkin Elmer, USA). The sample of 5.68 mg is placed in an electrobalance from 303 to 923 K. To avoid the measurement error due to buoyant effect at the high temperature, the horizontal differential-type balance is considered for experimentation. Thermocouple-type “R” is referred to measure the temperature inside the furnace. The volumetric flow of noninteractive gas is set at 200 mL min^{-1} . Indium and tin are used as reference materials for differential thermograms.

Table 5.2 illustrates the elemental characteristics and higher heating value of pine waste on the dry basis. TG data of pine sample is used to implement the transmutation of DAEM, so that qualitative assessment of different distribution functions can be performed. Computational as well as algorithm designing is carried out on MATLAB 2017b. The nonlinear thermal history is tested for narrow distribution nature of density functions. The different assigned values of parameters are repeatedly

Table 5.2: Elemental composition of pine needles.

C%	H%	N%	O%	S%	Ash content (%)	Higher heating value (MJ/kg)
53.7	6.48	0.56	36.13	0.10	2.92	22.23

examined in every iterative loop until it does not satisfy the given condition. If any parametric value does not validate the constraint, system searches for different values. Once the solution is obtained, the program terminates itself.

5.4 Results and discussion

The numerical solution of transmuted modeling of DAEM is performed by using the Laplace integral method. The proposed scheme is exhaustively examined for different distribution functions. The significant role of moving maximum with time on the energy distribution pattern of released volatile is illustrated graphically. There are three different limits imposed on each distribution case and the results are derived separately after transmutation.

5.4.1 Effect of transmutation on the Lindley distribution

The effect of transmuted Lindley distribution is shown in Figure 5.1(a)–(f). The sensitivity of the Lindley distribution with respect to time and temperature is relatively higher than that of other types of distribution functions analyzed for the energy modeling purpose. There is a steep increase in the conversion rate of biomass with variation of kinetic parameters in Figure 5.1(a)–(f). Elevation of frequency factor causes the remaining mass proportion curves to shift upward with relatively high (Table A.1) residual mass of biomass. However, the variation of residual mass of biomass is controlled to some extent through transmutation, but relative change in the residual mass of biomass is negligibly small. Transmutation of the Lindley distribution infers that the higher activation energy of 103 kJ/mol can be easily modeled through Lindley distribution. With increase in activation energy, the remaining mass fraction gets shifted down; however, there is no significant change in the attribute of $(1-\alpha)$ curves with the variation in the thermal history of sample. The maximum upper limit of activation should not be more than $E_{\infty} \leq 5.72 \times 10^3$ kJ/mol, while the average activation energy should not be more than 103. Comparative sketch of the transmuted Lindley distribution with the classical DAEM is shown in Figure 5.2. The fact concluded through the Lindley distribution is that Lindley distribution is not able to describe the pyrolysis mechanism more effectively than the other distribution types, despite having the

Figure 5.1: The effect of transmutation on the numerical solution of Lindley-based DAEM: (a)–(d) kinetic parameters; e and (f) characteristic of nonlinear thermal profile.

Figure 5.2: Comparative sketch of t-DAEM (Lindley) with the conventional DAEM form.

highest value of coefficient of regression. It may be possible that the Lindley distribution is not able to extrapolate pyrolysis effectively, and behavior is like the phenomenological models.

5.4.2 Effect of transmutation on the Weibull distribution

Unlike the Gaussian distribution, the Weibull distribution is abounded with different parameters, which is also one of the reasons of higher redundancy than the Gaussian. The effect of transmuted Weibull distribution is illustrated in Figure 5.3(a)–(f). The thermal decomposition of biomass takes some time to reach the critical temperature for initiating the process. The Weibull distribution is unable to distinguish the response time at different activation energies; therefore, all the curves are highly overlapped without any significant variation at the end states of pyrolysis (Figure 5.3(a)). The effect of different limit on the transmuted (Table B.1) Weibull distribution is depicted in Figure 5.3 (b)–(f). As the frequency factor increases, the remaining mass fraction curves get shifted upward, which results in shifting of critical decomposition temperature. Unlike the transmuted Gaussian distribution, the curves are converging for the lower range of activation energies, or the relative width between activation energies of parallel reaction must be narrow for the better simulation of pyrolysis through Weibull distribution. At the elevated heating rate with time, the devolatilization stage gets shifted to the left. The similar trend is obtained for the initial experimental

Figure 5.3: The effect of transmutation on the numerical solution of the Weibull-based DAEM: (a)–(d) kinetic parameters; (e) and (f) characteristic of nonlinear thermal profile.

temperature. Although the Weibull distribution is not able to interpolate the char formation stage effectively, despite the devolatilization stage effectively described the transmuted Weibull distribution. But the objective must not be overfitting of simulated solution to the thermoanalytical data, as unfamiliarity with the mechanism of autocatalytic reactions and the residence time of volatiles may provide erroneous solution. The maximum upper limit of activation energy for the transmuted Weibull distribution must not be more than 130 kJ/mol and the average activation energy (kJ/mol) should be within the domain of (69, 89] for the better convergent rate. Comparative demonstration of two different schemes is shown in Figure 5.4. The transmuted form of Weibull describes the devolatilization stage of decomposition of biomass efficiently, but the residence time of volatile content increases with temperature and the whole biomass is transformed into volatile gases (Figure 5.4). The char yield became asymptotic with temperature.

Figure 5.4: Comparative sketch of t-DAEM (Weibull) with the conventional DAEM form.

5.4.3 Effect of transmutation on the Gaussian distribution

The comprehensive effect of transmutation on the Gaussian DAEM is depicted graphically in Figure 5.5(a)–(f). At the initial stage of pyrolysis, the remaining mass fraction ($1-\alpha$) of biomass is always near to 1, unless there is interactive atmosphere or adsorption, or surface oxidation processes occur during thermal degradation of biomass. But the graphical representation of the classical DAEM (Figure 5.5(a)) is exactly 1, which is quite idealistic for pragmatic pyrolysis condition. As the frequency factor increases, there is an appreciable displacement of the upper segments of remaining mass fraction ($1-\alpha$) than that of lower halves at the constant rate of change

Figure 5.5: The effect of transmutation on the numerical solution of the Gaussian-based DAEM: (a)–(d) kinetic parameters; (e) and (f) characteristic of nonlinear thermal profile.

of heating rate with time. Despite drastic variation of distribution parameters, converging ability of the numerical solution is improved through transmutation. Thus, the homogeneity of shape is maintained throughout the process. The most important facet of transmutation is illustrated in Figure 5.5(b) and (c). The qualitative aspect of transmutation of distribution of activation energy is known through the characteristic of explanatory variable rather than the coefficient of regression analysis. The overlapping of curves happens if the density function of activation energy approaches zero, whereas the nonconvergent solution converges to solution, if activation energies spectrum is very broad for the Gaussian distribution; therefore, the Gaussian distribution can be the best fitting model for those reactions (Table C.1) where the activation energy variation among reactions is colossal. The effect of initial temperature gets devolatilization stage shifted to the right without any significant variation in “drying” as well as “char formation” stages. The residual mass obtained after simulating the pyrolysis process is approximately the same with $\pm 1.8\%$ difference. The effect of activation energy variation is depicted in Figure 5.5(d). The increase in the activation energy causes the intermediate stages to shift left. According to the analysis, the maximum upper bound of activation energy should not be more than $E_{\infty} \leq 185$ kJ/mol and the

maximum permissible limit for the average value of activation energy (kJ/mol) must lie in the domain of [120, 150). Inclusion of additional parameters supports the convergence rate of the numerical solution obtained by the Gaussian distribution. The effect of transmutation is mainly on the intermediate states of decomposition, which plays a pivotal role in the kinetic mechanism of pyrolysis. However, the influence of transmutation on the end stages of pyrolysis is difficult to interpolate, yet the variation gap and derivation of the classical DAEM from practical aspect of pyrolysis are overshadowed by transmutation and the form becomes more homogeneous than the classical form of DAEM. The nature of Arrhenius parameters and its effect on the thermal decomposition of biomass can be easily distinguished through transmutation. Comparative analysis of transmuted DAEM with classical DAEM is depicted in Figure 5.6. It clearly demarcated the controlling ability of transmutation to describe pyrolysis process far more effectively than the classical DAEM.

Figure 5.6: Comparative sketch of t-DAEM (Gaussian) with the conventional DAEM form.

5.4.4 Effect of transmutation on the Frechet distribution

Graphical representation of the transmuted Frechet distribution is illustrated in Figure 5.7 (a)–(f). The increase in the frequency factor increases the conversion rate, which results in residual mass approach to the experimental condition at the reduced timescale. However, the process is accelerated through introduction of linear mixing, and the remaining mass curves cause to shift upward as $E \rightarrow 0$. Therefore, the transmuted Frechet holds validation for set of reactions having relatively low variation of activation energies. The upper limit of activation energy is 190 kJ/mol, while the average activation energy (E kJ/mol) must not be more than $E_0 \leq 120$. Activation energy modeling through transmuted Frechet distribution provides good result only at lower initial temperature, and the variation of heating rate must not be very high. The

Figure 5.7: The effect of transmutation on the numerical solution of Frechet-based DAEM: (a)–(d) kinetic parameters; (e) and (f) characteristic of nonlinear thermal profile.

predicted transmuted DAEM solution with respect to the classical DAEM is shown in Figure 5.8. The transmuted Frechet distribution does not provide much better convergence than that of the Gaussian, the Weibull, and the Rayleigh distributions.

Figure 5.8: Comparative sketch of t-DAEM (Frechet) with the conventional DAEM form.

Comparative analysis of Laplace temperature with other numerical techniques is based on the attribute of numerical solution. However, the Copula distribution [1, 23] and 2-DAEM [5] are alternative forms of linear mixing of two different functions, but the emphasis is laid upon fitting of data rather than behavior of kinetic parameters with respect to time and the thermal history. Dynamic nature of inflexion points in the wide distribution case [21], and neglecting the time factor in the kinetic modeling, may provide a better fitting but the measured values would be quite far away from the pragmatic solution. Another way of solving the double integral of DAEM is through Simpson methods [21]. But without knowing the error component while spacing the activation energies leads to the fallacious inference. The concept of analyzing the thermal data is based on the stability of local maxima of curves and removing the inflexion point $H''(y_5^e) \neq 0$ out of the numerical solution. The derived solutions for the transmuted distributions rely upon the attribute of y^e with time. In the beginning, the moving maxima remains constant with temperature, but later it increases linearly as time proceeds. The narrow distribution is not able to interpolate the initial decomposition phase, as the Lambert W function is almost dormant in the beginning stage of simulation, while the Lindley distribution is related to the nature of logarithms. Therefore, spontaneity of reactions modeled through Lindley reactions is quite different from other transmuted forms. This problem can be tackled if the similar experiment is conducted at the complex thermal history. The obtained values of kinetic parameter for pine needles are homogenous with the isoconventional methods without any compensatory effect [29], which is a positive benchmark of the Laplace integral. However, the applicability of scheme is limited to only those functions that have the nonzero second derivatives and exhibit nonmonotonicity with time or temperature. The effect of proposed scheme is based on the significance of the whole integrand about its central value, which is overlooked in the previous studies [2, 21].

5.4.5 Effect of transmutation on the Rayleigh distribution

The effect of the transmutation on the activation energy modeling through the Rayleigh distribution is depicted in Figure 5.9(a)–(f). The resolution capacity of Rayleigh distribution with respect to variation of parameters is far more than that of the Gaussian and the Weibull distributions. One can observe a fine demarcation of behavioral variation of $(1-\alpha)$ with the frequency factor as illustrated in Figure 5.5(a). The increasing value of frequency increases the dehydration temperature and the $(1-\alpha)$ curves are deviated to the right side without any variation in the char formation temperature. However, the deviation of the remaining mass fraction is controlled through transmutation of Rayleigh distribution (Figure 5.9(b)–(f)). Likewise, the Gaussian distribution and the Rayleigh distribution support the reactions that occur at higher activation energies. There is no significant variation in the intermediate stages of decomposition except the time of initiation of reactions that increases with

Figure 5.9: The effect of transmutation on the numerical solution of Rayleigh-based DAEM: (a)–(d) kinetic parameters; (e) and (f) characteristic of nonlinear thermal profile.

increasing activation energies, which is obviously much practical. The upper bound of activation energy variation for the effective representation of pyrolysis reaction is 220 kJ/mol, whereas the feasible (Table E.1) boundary limits of variation in average activation energy (kJ mol⁻¹) is within the range of [96, 127]. Increasing the initial experimental temperature causes the remaining mass fraction curves $(1-\alpha)$ to shift upward with higher residual mass than that of lower initial temperature. Similarly, the decomposition temperature at the initial stage of pyrolysis is elevated with drastic variation of heating rate with time (Figure 5.9(e)). However, perturbation of Rayleigh distribution due to ingress of linear mixing does not affect the form of distribution drastically (Figure 5.10).

Figure 5.10: Comparative sketch of t-DAEM (Rayleigh) with the conventional DAEM form.

5.5 Conclusion

The narrow distribution of transmuted function is adopted to derive the numerical solution. Transmutation of the Gaussian distribution, the Weibull distribution, and the Rayleigh distribution provides the better results than that of transmutation form of Lindley and Frechet distributions. Every distribution function has its own unique attribute for representing the variation of activation energies. The Gaussian distribution and the Rayleigh distribution are found to be good for developing the model for higher activation energy reactions of maximum of 202 kJ/mol, while the Weibull distribution holds good relationship for the activation energy range of 80–130 kJ/mol. The modeling of activation energy through Frechet distribution is valid for the negative value of shape factor, whereas Lindley has anomaly with the measured value of pine needles from the isoconversional method. However, there is a likelihood of existence of those reactions whose activation energy is of 103 kJ/mol. The maximum value of activation energy for the transmuted Frechet distribution is found to be 190 kJ/mol. The frequency factor for all the cases is estimated to lie in domain of $103\text{--}1,013\text{ min}^{-1}$. The variation of activation energy with time, temperature, energy spacing, and thermal profile and the significant contribution of the whole integrand are investigated through knowing the attribute of moving maximum of the whole integrand. However, the computational effort of scheme is relatively high to other schemes [1, 23, 50], as algorithm evaluates the location of maximum with respect to time.

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Appendices

To demonstrate the scheme, the Laplace method of integration is chosen to simplify the DAEM problem of iterative computation of double integrals. This method is useful to solve the integral of the form

$$I = \int_a^b e^{-BQ(x)} s(x) dx$$

where a and b can be finite or infinite. Here $Q(x)$ and $s(x)$ are replaced by their local expansion when $x = x_0$. The same concept is used for approximating the integral form as mentioned earlier.

The general solution of Laplace method for interior points is given by

$$I = 1.7724 e^{-BQ(x_0)} s(x_0) \sqrt{\frac{1}{|BQ''(x_0)|}}$$

Note: $s(x_0) \neq 0$

However, $c(y_e) \ll 1$, so its contribution to integral is negligibly small for interval of $0 < y_e < 1$.

A. The Lindley (three-parameter) distribution

Table A.1: Kinetic parameters for the Lindley distribution functions.

Average activation energy (kJ/mol)	Frequency factor (min ⁻¹)		R^2	$(p(E) \rightarrow 0)$		$(E \rightarrow \infty)$	
				After transmutation		After transmutation	
				τ	R^2	τ	R^2
1.0543×10^4	A_1	2×10^{14}	0.95	0.0008	0.93	0.05	0.94
				0.02	0.94	0.04	0.95
1.4906×10^4	A_2	2×10^{20}	0.93	0.0008	0.94	0.05	0.94
				0.02	0.94	0.04	0.93
2.7733×10^3	A_3	2×10^3	0.96	0.0008	0.97	0.05	0.97
				0.02	0.97	0.04	0.98

$$p(E) = \frac{\theta^2}{\theta + \psi} (1 + \psi(E - \gamma)) e^{-\theta(E - \gamma)}, E > \gamma \geq 0, \theta + > 0 \quad (\text{A.1})$$

This can be solved through the convex combination of two different functions, but provided that $\forall f_1(E), f_2(E) \in C$ and $C \subseteq \mathbb{R}$

Equation (A.1) can be rewritten as

$$p(E) = kf_1(E) + (1-k)f_2(E) \quad (\text{A.2})$$

where k is the mixing fraction and φ is a scale parameter

$$k = \frac{\theta}{\theta + \psi} \quad \varphi = \frac{1}{\theta} \quad \text{and} \quad \omega_1 = \frac{\gamma}{\varphi}$$

The mean and the variance of the Lindley distribution are E_{01} and σ^2_{01} , respectively

$$E_{01} = \frac{\theta(1 + \gamma\theta) + \psi(2 + \gamma\theta)}{\theta(\theta + \psi)} \quad \sigma^2_{01} = \frac{[\{\theta(2 + \gamma\theta(2 + \gamma\theta)) + \psi(6 + \gamma\theta(4 + \beta\theta))\}]}{\theta^2(\theta + 6)}$$

Energy is rescaled as

$$y_1 = \frac{E}{\gamma}, \quad y_{s1} = \frac{E_s}{\gamma}, \quad \text{and} \quad y_{w1} = \frac{E_w}{\gamma}$$

The expressions for $f_1(E)$ and $f_2(E)$ functions are

$$f_1(E) = \theta\psi(E - \gamma)\exp\{-\theta(E - \gamma)\} \quad (\text{A.3})$$

$$f_2(E) = \theta^2\exp\{-\theta(E - \gamma)\} \quad (\text{A.4})$$

The simplified form obtained after incorporating the energy rescaling

$$f_1(y_1) = \omega_1\psi(y_1 - 1)\exp\{-\omega_1(y_1 - 1)\}$$

$$f_2(y_1) = \theta^2\exp\{-\omega_1(y_1 - 1)\}$$

The resultant form of density function in terms of energy rescaling factor is

$$p(y_1) = kf_1(y_1) + (1-k)f_2(y_1)$$

Note: The whole integral transforms into convex combination of Gamma functions

$$(\Gamma(\psi, \omega_1 y_1), \Gamma(\theta^2, \omega_1 y_1)) \quad \text{if} \quad \left(\frac{y_s - y_1}{y_w} \right) \rightarrow \infty$$

B. Weibull distribution (three parameters)

Table B.1: Kinetic parameters for the Weibull distribution functions.

Average activation energy (kJ/mol)	Frequency factor (min ⁻¹)		R^2	$(p(E) \rightarrow 0)$		$(E \rightarrow \infty)$	
				After transmutation		After transmutation	
				τ	R^2	τ	R^2
89	A_1	10^8	0.920	0.0008	0.94	0.05	0.90
				0.02	0.96	0.04	0.91
99	A_2	10^9	0.910	0.0008	0.94	0.05	0.89
				0.02	0.95	0.04	0.90
69	A_3	10^7	0.900	0.0008	0.93	0.05	0.88
				0.02	0.95	0.04	0.89

$$p(E) = \frac{\beta}{\eta} \left(\frac{E - \gamma}{\eta} \right)^{(\beta-1)} e^{-\left(\frac{E - \gamma}{\eta} \right)^\beta} \quad (\text{B.1})$$

This is the expression for the Weibull distribution function for three parameters.

Energy rescaling factor is given as follows:

$$y_2 = \frac{E}{\gamma}, \quad y_{s2} = \frac{E_s}{\gamma} \quad \text{and} \quad y_{w2} = \frac{E_w}{\gamma} \quad (\text{B.2})$$

After simplifying (B.1.), the required form of density function $p(y_2)$ is

$$p(y_2) = \frac{\beta}{\eta} \omega_2^{\beta-1} (y_2 - 1)^{\beta-1} e^{-\left(\omega_2 (y_2 - 1) \right)^\beta}$$

where

$$\omega_2 = \frac{\gamma}{\eta}$$

The mean and the variance of the Weibull distribution are E_{02} and σ^2_{02} , respectively:

$$E_{02} = \gamma + \eta \Gamma\left(\frac{1}{\beta} + 1\right) \quad \text{and} \quad \sigma^2_{02} = \eta^2 \left[\Gamma\left(\frac{2}{\beta} + 1\right) - \left\{ \Gamma\left(\frac{1}{\beta} + 1\right) \right\}^2 \right]$$

C. Gaussian distribution

Table C.1: Kinetic parameters for the Gaussian distribution functions.

Average activation energy (kJ/mol) E	Frequency factor (min ⁻¹) (A)		R^2	$(p(E) \rightarrow 0)$		$(E \rightarrow \infty)$	
				After transmutation		After transmutation	
				τ	R^2	τ	R^2
120	A_1	2×10^{10}	0.9315	0.0008	0.93	0.05	0.97
				0.02	0.92	0.04	0.94
119.6	A_2	2×10^7	0.9308	0.0008	0.93	0.05	0.94
				0.02	0.92	0.04	0.94
150	A_3	2×10^{13}	0.9307	0.0008	0.93	0.05	0.96
				0.02	0.92	0.04	0.95

The required expression for Gaussian distribution is given as follows:

$$p(E) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\left(\frac{E-E_0}{\sqrt{2\sigma}}\right)^2} \quad (\text{C.1})$$

The energy correction factor for the Gaussian distribution is expressed as

$$y_3 = \frac{E}{E_0}, \quad y_{s3} = \frac{E_s}{\gamma} \quad \text{and} \quad y_{w3} = \frac{E_w}{\gamma} \quad (\text{C.2})$$

Simplifying eq. (C.1) through incorporating energy factors, we have

$$p(y_3) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\left(\frac{E_0}{\sqrt{2\sigma}}\right)^2 (y_3 - 1)^2\right) \quad (\text{C.3})$$

Putting $\omega_3 = \left(\frac{E_0}{\sqrt{2\sigma}}\right)^2$ in eq. (C.3), the required form is

$$p(y_3) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\omega_3 (y_3 - 1)^2\right)$$

D. Frechet distribution

Table D.1: Kinetic parameters for the Frechet distribution function.

Average activation energy (kJ/mol)	Frequency factor (min ⁻¹)		R^2	$(p(E) \rightarrow 0)$ After transmutation		$(p(E) \rightarrow 0)$ After transmutation	
				τ	R^2	τ	R^2
119.6	A_1	2×10^{10}	0.94	0.008	0.93	0.05	0.96
				0.02	0.92	0.04	0.95
140	A_2	2×10^{12}	0.80	0.008	0.80	0.05	0.79
				0.02	0.81	0.04	0.80
171	A_3	2×10^{15}	0.15	0.008	0.16	0.05	0.13
				0.02	0.97	0.04	0.14

$$p(E) = \frac{\rho}{\delta} \left(\frac{E - \mu}{\delta} \right)^{-(1+\rho)} e^{-\left(\frac{E - \mu}{\delta} \right)^{-\rho}} \quad (D.1)$$

Equation (D.1) represents the density function of the Frechet distribution.

The energy factor for distribution is given by

$$y_4 = \frac{E}{\mu}, \quad y_{4s} = \frac{E_s}{\mu} \quad \text{and} \quad y_{4s} = \frac{E_w}{\mu} \quad (D.2)$$

Introducing the energy rescaling factors in eq. (D.1), we have

$$p(y_4) = \frac{\rho}{\delta} \left(\frac{\mu(y_4 - 1)}{\delta} \right)^{-(1+\rho)} e^{-\left(\frac{\mu(y_4 - 1)}{\delta} \right)^{-\rho}} \quad (D.3)$$

Putting $\omega_4 = \frac{\mu}{\delta}$ in eq. (D.3), the desired expression will be

$$p(y_4) = \frac{\rho}{\delta} \omega_4^{-(\rho+1)} (y_4 - 1)^{-(1+\rho)} e^{-\{\omega_4(y_4 - 1)\}^{-\rho}}$$

The mean and the variance of the Frechet distribution are E_{04} and σ^2_{4} , respectively,

$$E_{04} = \mu + \eta \Gamma \left(1 - \frac{1}{\rho} \right) (\rho > 1)$$

$$\sigma^2_4 = \eta^2 \left[\Gamma \left(1 - \frac{2}{\rho} \right) - \left\{ \Gamma \left(1 - \frac{1}{\rho} \right) \right\}^2 \right] (\rho > 2)$$

E. Rayleigh distribution

Table E.1: Kinetic parameters for the Rayleigh distribution functions.

Average activation energy (kJ/mol)	Frequency factor (min ⁻¹)		<i>R</i> ²	(p(<i>E</i>) → 0)		(E → ∞)	
				After transmutation		After transmutation	
				τ	<i>R</i> ²	τ	<i>R</i> ²
127	<i>A</i> ₁	2 × 10 ⁸	0.94	0.0008	0.940	0.05	0.95
				0.02	0.935	0.04	0.96
79	<i>A</i> ₂	2 × 10 ⁶	0.93	0.0008	0.941	0.05	0.94
				0.02	0.937	0.04	0.95
234	<i>A</i> ₃	2 × 10 ²¹	0.93	0.0008	0.930	0.05	0.95
				0.02	0.92	0.04	0.94

The density function of two parameters (2-P) is expressed as

$$p(E) = 2\chi(E - \phi)\exp\left\{-\chi(E - \phi)^2\right\} \quad (\text{E.1})$$

The energy factor for the Rayleigh distribution is expressed as

$$y_5 = \frac{E}{\phi} \quad y_{s5} = \frac{E_s}{\phi} \quad \text{and} \quad y_{w5} = \frac{E_w}{\phi}$$

Rearranging eq. (E.1), we will have the required form of density function:

$$p(y_5) = 2\frac{\omega_5}{\phi}(y_5 - 1)\exp\left\{-\omega_5(y_5 - 1)^2\right\} \quad (\text{E.2})$$

where

$$\omega_5 = \frac{\phi^2}{\sigma_{5}^2\left(1 - \frac{\pi}{4}\right)}$$

The mean and the variance of the Rayleigh distribution are *E*₀₅ and σ₅², respectively,

$$E_{05} = \phi + \frac{\sqrt{\pi}}{2\chi} \quad \text{and} \quad \sigma_5^2 = \frac{1}{\chi} - \frac{\pi}{4\chi}$$

where ϕ kJ/mol is the location parameter

The physical significance of location parameter is the minimum energy required to initiate the chemical reaction.