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CALCULATION OF KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION OF RESIDUAL WASTE OF CONIFEROUS SPECIES: CEDRUS DEODARA

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This paper deals with pyrolysis decomposition of *Cedrus deodara* leaves with the help of thermogravimetric analysis (TGA). Experiments are performed in the presence of inert atmosphere of nitrogen. Experiments are conducted at three different heating rates of 5 °C·min⁻¹, 10 °C·min⁻¹ and 15 °C·min⁻¹ within temperature range of 35 °C to 700 °C. Arrhenius parameters such as activation energy and frequency factor are estimated by Flynn Wall and Ozawa (FWO), Kissinger-Akahira-Sonuse (KAS) and Kissinger. The activation energy and frequency factor calculated by using Kissinger method are 67.63 kJ·mol⁻¹ and 15.06 × 10⁴ min⁻¹ respectively; whereas the averaged values of the same parameters through FWO and KAS methods are 89.59 kJ·mol⁻¹ and 84.748 kJ·mol⁻¹, 17.27 × 10⁸ min⁻¹ and 62.13 × 10⁷ min⁻¹ respectively. Results obtained through Kissinger method represent the actual values of kinetic parameters. Conversely, FWO and KAS methods reflect the apparent values of kinetic parameters, as they are highly influenced by the overlapping of competitive reactions occur during pyrolysis.

Keywords: thermogravimetric analysis (TGA); model-free methods; non-isothermal kinetics; biomass pyrolysis

Cedrus deodara is predominately found at the altitude of 2,000–3,200 m above the sea level in the Northern Himalayan region of India, Nepal and Afghanistan. According to Forest Survey of India, unlike *Pinus roxburghii* (Dhaundiyal and Tewari, 2016), the area covered by *Cedrus deodara* is 84932 hectares of total forest land in Uttarakhand state (ENVIS Centre, 2013).

Utilization of residual waste as the new renewable energy source can curtail the depletion level of conventional fuel resources. In addition to the use of residual waste for domestic or other medical purposes, deriving of some additional by-products, such as biofuel and producer gas from them, may also enhance the importance of forest waste in the field of energy sector. In order to obtain certain valuable secondary fuel, biochemical as well as thermo-chemical transformation is required; however, the scope of this paper is confined to the thermochemical process by which it is possible to obtain biofuel or other secondary gaseous fuel for running the power plant. Pyrolysis is one of such thermo-chemical processes, which converts the residual waste into volatile gases, char and tar through thermal decomposition. Pyrolysis usually takes place in the absence of oxygen or very less air, which involves simultaneous chemical as well as physical phase transformation. In broad sense, it is conversion of biomaterials into highly enriched-energy-secondary fuel, provided that the appropriate temperature and heating rate are reached. To obtain information about particular biomass, the most common methodology adopted by

various researchers is thermogravimetric analysis (TGA). During thermal composition, TGA analysis can be applied to different materials, such as plastic (Shakya, 2007), rubber derivative (Senneca et al., 2002), natural fibers (Yao et al., 2008), and the medical waste (Teng and Hsieh, 1999). There are various models to analysis of non-isothermal solid-state kinetic data from TGA (Simon, 2004; Sbirrazzuoli et al., 2009). These models can be categorized under two main headings: model fitting and model-free (isoconversional). Model fitting methods correlate different models with experimental data so that the statistical fit can be obtained. Model fitting approach is incapable of determining the reaction model uniquely and, therefore, it becomes difficult to reach a reliable mechanistic conclusion. On the other hand, model-free methods allow the dependence of activation energy on the extent of conversion, which in turn provides a reliable reaction rate prediction so that a mechanistic conclusion could be drawn. Isoconversional methods are also a part of model-free method, but not all the model-free methods are isoconversional, such as Kissinger method. Kissinger method does not evaluate kinetic parameters at the progressive values of conversion (X) (Khawam, 2007). The isoconversional methods estimate the apparent activation energy (E_a) without the modelistic assumptions, which is mainly done by grouping terms and reaction model into intercept of linear equation and using the slope of that equation to evaluate the kinetic parameters. Model-fitting methods are widely implemented for solid-state reaction for their ability to directly estimate the kinetic parameters at the single TGA measurement. There are several models which are statistically reliable, but the fitted kinetic parameters may differ by a large magnitude and, therefore, selecting an appropriate model becomes complicated.

The purpose of this study is to investigate the kinetics of thermal decomposition of *Cedrus deodara* sample. Devolatization of residual leaves of *Cedrus deodara* was done with the help of TGA/DTG curves obtained at different heating rates. Kissinger, FWO and KAS methods are implemented to estimate activation energy (E_a) and frequency factor (A). The effect of heating rate on the decomposition of *Cedrus deodara* residual leaves was also included in this study.

Material and methods

The residual waste of Cedrus deodara was collected from Danulti, Tehri district of Uttarakhand. A sample of Cedrus deodara leaves was mechanically grinded into powder form for performance of the TGA/DTA (SII EXSTAR 6300, Seiko Inc., Japan) experiments. The chemical composition and higher heating value of Cedrus deodara leaves is shown in Table 1 (Dhaundiyal and Singh, 2017). The experiments are performed at Institute Instrumentation Centre, Indian Institute of Technology, Roorkee. The elemental analysis of sample was done with help of CHNS-O analyzer (Flash EA1112 series, Thermofinnigan, Italy) at Sophisticated Analytical Instrumentation Facilities (SAIF), Indian Institute of Technology, Bombay. To attain pyrolysis conditions, an inert atmosphere was used. Nitrogen was used as protective gas to prevent the micro-balance from ingression of possible pollutants. The purge rate of nitrogen was set to 200 mL·min⁻¹. Thermogravimetric measurements are recorded at three different heating rates of 5 $^{\circ}C\cdot min^{-1}$, 10 °C·min⁻¹ and 15 °C·min⁻¹. Each sample underwent the same temperature range of 35 to 900 °C. Thermocouple type 'R' (87% Platinum/Platinum Rhodium – 13% by weight) was used to measure the furnace and sample temperatures. For computational purpose, Matlab R2017b was utilized.

Kinetic theory

The solid-state decomposition process can be expressed by the rate Eq. (1)

$$\frac{dX}{dt} = k(T) \cdot f(X) \tag{1}$$

where:

k(T) – the rate constant and 'X' represents conversion; it can be derived from mass loss data of decomposed sample. It can be stated as:

$$X = \frac{m_o - m_t}{m_o - m_r} \tag{2}$$

Here, m_0 is the initial mass of sample in mg, m_t is mass recorded at specific instant of time t, and m_r is the residual mass at the end of heating process.

Temperature dependence of rate constant k is obtained from Arrhenius Eq. (3)

$$k = A \exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

where:

 E_a – the apparent activation energy, kJ·mol⁻¹

T – the absolute temperature, K

R – the gas constant, 8.314 JK⁻¹·mol⁻¹

A – the frequency factor, min⁻¹

We obtained the basic expression of analytical method by putting the value of rate constant k in Eq. (1). Piloyan et al. (1966) suggested the kinetic analysis that follows Eq. (4).

$$\frac{dX}{dt} = A \cdot f(X) \cdot \exp\left(\frac{-E_a}{RT}\right) \tag{4}$$

Taking the natural logarithm of Eq. (4), we obtained Eq. (5)

$$ln\left(\frac{dX}{dt}\right) = ln(A) + ln(f(X)) - \frac{E_a}{RT}$$
(5)

Piloyan et al. (1966) suggested that the term ln(f(X)) could be neglected and thus the value of E and ln(A) are estimated by plotting $ln\left(\frac{da}{dt}\right)$ versus 1/T. It has been reported that the error rate encountered while estimating E values is around 15% to 20%. However, later on, this method has kept with group of methods, which evaluates the kinetic triplet at the single heating rate. Similarly, Criado and Ortega (1984) have also made conclusions on the drawbacks in their study and reported the detail calculation of the error in E occurred due to this assumption. In 1991, Flynn (1991) stated that f(X) follows a reaction model in which it varies according to n^{th} power of remaining mass fraction:

$$f(X) = (1 - X)^n$$
 (6)

where:

n – the reaction order

By substituting the expression (6) into expression (5):

$$\ln\left(\frac{dX}{dt}\right) = \ln(A) + n\ln(1-X) - \frac{E_a}{RT}$$
(7)

Eq. (7) can be rewritten for non-isothermal TGA experiments at linear ramp rate, $\theta = \frac{dT}{dt}$:

Tal	b	e 1	C	hemical	compositio	on of (Cedrus a	leodara	leaves
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С%	H%	N%	0%	S%	High heating value (MJ·kg ⁻¹)
47.68	7.67	2.02	32.51	0.00	21.31

ource: Dhaundiyal and Singh, 2017

$$\ln\left(\frac{dX}{dt}\right) = \ln\left(\frac{A}{\theta}\right) + n\ln(1-X) - \frac{E_a}{RT}$$
(8)

Eq. (8) expresses the fraction of material consumed with respect to temperature. The methods used to estimate kinetic parameters are model-free methods for nonisothermal condition.

Model-free methods

The terms 'model-free' and 'isoconversional' are sometimes used interchangeably, but not all model-free methods are isoconversional, Kissinger method is one of these exceptions as it does not allow to calculate E_a values at progressive X values, but assumes a constant apparent activation energy. Isoconversional approach can be implemented to analyze isothermal (where temperature changes) as well as non-isothermal (where the heating rate changes) data. In non-isothermal kinetics, several isoconversional methods are proposed in the 1960s (Friedman, 1964; Ozawa, 1965; Flynn and Wall, 1966a). Some of them are enlisted in the following sections.

Kissinger method

These methods allow estimating the kinetic parameters of a solid-state reaction without involving the reaction mechanism. Kissinger (1956) propounded a model-free method for non-isothermal condition, in which there is no need to estimate E_a for progressive value of conversion (X). This method gives the value of activation energy from a plot of $L_a(\theta)$ estimate 1.000/T.

of $ln\left(\frac{\theta}{T_m^2}\right)$ against 1,000/ T_m for a series of measurements recorded at different heating rates (θ), where T_m represents the temperature at which peak differential thermal analysis deflection takes place (shown in Fig. 3). Eq. (9) estimates the E_a and A:

$$ln\left(\frac{\theta}{T_m^2}\right) = ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_m}$$
(9)

The slope of Eq. (9) represents activation energy, which is equal to $-\frac{E_a}{R}$.

Flynn-Wall-Ozawa method

The FWO method (Ozawa, 1965; Flynn and Wall, 1966b) allows to calculate apparent activation energy by drawing a graph between natural logarithms of heating rates, $ln (\theta_i)$ and 1,000/ T_{xi} , which shows the linear relation with a different value of conversion at different heating rates. Differential and integral functions, f(X) and g(X), are expressed as:

$$g(X) = \int_{0}^{X} \frac{dx}{f(X)} = \frac{AE_{\chi_i}}{\theta_R} K(y)$$
(10)

where:

K(y) – the temperature integral, and $y = \frac{E}{RT}$. Therefore:

$$ln(g(X)) = ln\left(\frac{AE_{Xi}}{\theta_i R}\right) + lnK(y)$$
(11)

Using Doyle's approximation to temperature integral (Doyle, 1962):

$$ln(K(y)) = -5.331 - 1.052y$$

Replacing ln(K(y)) in Eq. (11) from Doyle's approximated value:

$$ln(\theta_{i}) = ln\left(\frac{A_{X}E_{Xi}}{g(X)R}\right) - 5.331 - 1.052\frac{E_{Xi}}{RT_{Xi}}$$
(12)

Eq. (12) is the required expression for FWO method. Subscript 'Xi' represents conversion at given heating rate.

Kissinger-Akahira-Sunose

The KAS method (Kissinger, 1956; Akahira and Sunose, 1971) is based on the following:

$$ln\left(\frac{\theta_{i}}{T_{xi}^{2}}\right) = ln\left(\frac{A_{x}R}{g(X)E_{x}}\right) - \frac{E_{x}}{RT_{xi}}$$
(13)

The apparent activation energy is evaluated from a plot of $ln\left(\frac{\theta_i}{T_{xi}^2}\right)$ versus $\frac{1,000}{T_{xi}}$ for a given value of conversion, *X*, where the slope is equal to $\frac{E_x}{R}$.

Results and discussion

Thermogravimetric analysis

Thermogravimetric graphs for residual leaves of *Cedrus deodara* are obtained at different heating rates, which are illustrated in Fig. 1(a). Thermo-analytical data show that the pyrolysis process started at about 400 K and the mass of sample has rapidly been decreased until the furnace temperature reached 836 K; consequently, the reduction in the remaining mass fraction (1-*X*) became nearly constant with temperature. The solid residue yield of 1.66% has been obtained for *Cedrus deodara* sample. Differential thermal analysis (DTA) curves at different heating rates are depicted in Fig. 1(b).

Derivative thermogravimetric (DTG) curves for devolatization of Cedrus deodara leaves at three different heating rates of 5 °C·min⁻¹, 10 °C·min⁻¹ and 15 °C·min⁻¹ under inert atmosphere of nitrogen are shown in Fig. 2. The three different stages have shown the range of temperature at which dehydration, active and passive pyrolysis has taken place. In the initial stage of pyrolysis, ranging from 300 to 400 K, drying or removing of moisture from the given sample has taken place. Primary pyrolysis reactions fall in between the range of 500 to 590 K at low heating rate; whereas in case of high heating rates, the same reactions took place at slightly high temperature range from 500 to 600 K. Furthermore, the two peaks (Strezov et al., 2003) give information about degradation of constituent components of Cedrus deodara sample, i.e. hemicelluloses and cellulose. On the other hand, degradation of lignin will be slowly taking place in both the areas of active and passive pyrolysis. The influence of heating rate on the thermo-analytical curves is shown in Figs 3, 4 and 5.



Fig. 1 TGA and DTA of residual leaves of Cedrus deodara



Fig. 2 DTG of residual leaves sample of *Cedrus deodara* at different heating rates

Variation of heating rate significantly affects locations of the maximum decomposition rate and the peak deflection temperature (T_m) in derivative thermogravimetric (DTG) plot. The differential thermogravimetric plot of *Cedrus deodara* leaves is shown in Fig. 3. As the heating rate increases, the temperature regime of active and passive pyrolysis shifted to the right (Figs 3 and 5). The position of evaporation stage is invariant to the heating rate for each analysis (Fig. 2). The locations of maxima in thermogravimetric (TG) plot and the minima of derivative thermogravimetric (DTG) curves get shifted to the high temperature range. This can be comprehended by considering the limitation of heat transfer. In case of low heating rate, an enormous amount of instantaneous thermal energy is available to the system and the flowing gas nitrogen requires a long time to attain equilibrium with the temperature of the sample. On the contrary, available time required to initiate reaction is reduced at high heating rate; therefore, the reaction time is also decreased (Quan et al., 2009).

To verify that the same heating rate causes a shift in the curve, comparative DTG plots of *Cedrus deodara* leaves and pine needles have been drawn at 5 °C·min⁻¹. As it can be validated from Fig. 6, the curves are not shifted with respect to each other.







Fig. 4 Extent of conversion curves for the pyrolysis process of residual leaves



Fig. 5 Conversion rate of residual leaves sample at different heating rate



Fig. 6 Comparative DTG plot of mass proportion as functions of temperature

Evaluation of kinetic parameters

Kinetic parameters for devolatization of *Cedrus deodara* sample are estimated by using model-free methods. Kissinger, FWO and KAS methods are used to calculate the activation energy (E_a) and the frequency factor (A). Eqs (9),

c		FWO		KAS			
Conversion	E_a (kJ·mol ⁻¹)	A (min ⁻¹)	R ²	<i>E_a</i> (kJ⋅mol ⁻¹)	A (min ⁻¹)	R ²	
0.05	28.213	46.926×10^{1}	0.900	23.395	10.277×10^{2}	0.840	
0.10	42.668	37.795×10^{2}	0.920	37.171	84.134×10^{1}	0.900	
0.15	77.299	74.709×10^{5}	0.977	72.922	15.647×10^{5}	0.970	
0.20	96.100	29.599×10^{7}	0.991	92.285	88.168×10^{6}	0.989	
0.25	110.168	37.810×10^{8}	0.997	106.751	13.925×10^{8}	0.997	
0.30	114.752	61.362×10^{8}	0.999	111.324	23.118×10^{8}	0.999	
0.35	115.858	50.702×10^{8}	0.999	112.239	18.497×10^{8}	0.999	
0.40	114.594	26.772×10^{8}	1.000	110.742	91.578×10^{7}	1.000	
0.45	117.913	36.456×10^{8}	1.000	113.984	12.689×10^{8}	1.000	
0.50	112.381	83.486×10^{7}	0.995	107.915	24.693×10^{7}	0.994	
0.55	90.568	73.489×10^{5}	0.985	84.553	12.836×10^{5}	0.981	
0.60	77.584	39.728×10^{4}	0.986	70.436	45.483×10^{3}	0.981	
0.70	66.567	31.843×10^{3}	0.991	58.006	31.666×10^{3}	0.986	
Average (Σ)	89.590	17.270×10^{8}	_	84.748	62.130×10^{7}	-	
St. deviation	29.623	2.238×10^{9}	-	30.492	8.268×10^{8}	-	
Variance	877.562	5.009×10^{18}	_	929.809	6.837 × 10 ¹⁷	-	
Kissinger	$E_a = 67.63 \text{ kJ} \cdot \text{mol}^{-1}$			$A = 15.0672 \times 10^4 \mathrm{min}^{-1}$			

 Table 2
 Kinetic parameters evaluated by mean of model-free methods

(12) and (13) are involved to estimate the activation energy and the frequency factor. For Kissinger model, the peak deflection temperature (T_m) corresponds to the maximum mass loss remove comma after peaks is found from differential thermal analysis (Fig. 3). In case of Kissinger, the graph is plotted between $In\left(\frac{\theta}{T_m^2}\right)$ and $\frac{1,000}{T}$ (K⁻¹) for decomposition of residual leaves (Fig. 7). The coefficient of correlation (R^2) is

of residual leaves (Fig. 7). The coefficient of correlation (R^2) is tabulated in Table 2.

The slope and the intercept of regression line represent the activation energy (E_a) and the frequency factor (A) respectively. The activation energy (E_a) and the frequency factor (A) obtained from Kissinger method are 67.63 kJ·mol⁻¹ and 15.0672 × 10⁴ min⁻¹ respectively. The effect of conversion on the thermoanalytical data at different heating rates is illustrated in Fig. 4. To carry out the computation procedure, the value of X is taken from 0.05 to 0.7 for all curves at different heating rates, and thus it is possible to obtain the corresponding temperature (T_{xi}). The apparent activation energies and the frequency factors at different conversion are presented in Table 2. The value of R^2 varies from 0.84 to 1 for all the methods.

For FWO and KAS, the variation of apparent activation energies with conversion is shown in Fig. 8. It is seen that the value of apparent activation energy for the devolatization of residual leaves sample is not the same for all the conversion (X), which insinuates the occurrence of complex multistep reactions, taking place in the solid state. It also implies that the reaction mechanism is not the same for the whole decomposition process and the activation energy is the function of conversion (X) and heating rate. The averaged values of apparent activation energy and the frequency factor for FWO and KAS are 89.5901 kJ·mol⁻¹ and 84.748 kJ·mol⁻¹, 17.27×10^8 min⁻¹ and 62.13×10^7 min⁻¹, respectively. The model-free approach helps to calculate activation energy as a function of conversion without assuming any reaction model and indicates the existence of multi-step kinetics.



Fig. 7 Kissinger plot of Cedrus deodara sample



Fig. 8 Variation of apparent activation energies as a function of conversion (*X*)

Conversely, Kissinger method gives a single value of E_a for the whole decomposition process and the mechanism is not known (Vyazovkin and Wight, 1999). Kinetic parameters calculated with the help of Kissinger method are independent of conversion. It does not differ from the range of values obtained from FWO and KAS methods. However, the results may vary in different ambience. The values of kinetic parameters obtained in air are higher than that of nitrogen atmosphere (Kumar et al., 2008). The range of activation energy obtained from asymptotic approximation of distributed activation energy model (DAEM) in isothermal condition is near to the value derived from Kissinger method (Dhaundiyal and Singh, 2017). The variation in kinetic parameters exhibits a complex nature of constitutes components of residual leaves of Cedrus deodara. Moreover, the difference in experimental condition and calculation procedure may cause the estimated kinetic parameters to differ in magnitude for the same class of biomass.

Conclusion

Thermogravimetric and kinetic analysis are performed in the nitrogen atmosphere at different heating rates of 5 °C·min⁻¹, 10 °C·min⁻¹ and 15 °C·min⁻¹. Thermal degradation of residual leaves of *Cedrus deodara* is differentiated by three stages: water evaporation, active pyrolysis and passive pyrolysis. Devolatization reactions occurred within the range of 400 to 900 K. The influence of heating rate on TG and DTG plots is also studied and it has been observed that the temperature needed to decompose biomass increases with increase in the heating rate. Calculation of kinetic parameters is carried out with the help of model-free models. Kinetic parameters derived from Kissinger method are constant for the whole pyrolysis process, whereas the kinetic parameters obtained from FWO and KAS methods are varying with conversion and show the existence of complex mechanism of reaction during pyrolysis process. The values 67.63 kJ·mol⁻¹ and 15.0672 \times 10⁴ min⁻¹ are the values of activation energy and frequency factor evaluated from Kissinger method respectively. While 89.59 kJ·mol⁻¹ and 17.27×10^8 min⁻¹, 84.748 kJ·mol⁻¹ and 62.13×10^7 min⁻¹ are the apparent average values of activation energy and frequency factor obtained from FWO and KAS respectively. It can be concluded from the experimental results that the model-free approach successfully described the complexity of pyrolysis process.

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