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# Determination of Kinetic Parameters for the Thermal Decomposition of *Parthenium hysterophorus*

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***Abstract* – A kinetic study of pyrolysis process of *Parthenium hysterophorous* is carried out by using thermogravimetric analysis (TGA) equipment. The present study investigates the thermal degradation and determination of the kinetic parameters such as activation *E* and the frequency factor *A* using model-free methods given by Flynn Wall and Ozawa (FWO), Kissinger-Akahira-Sonuse (KAS) and Kissinger, and model-fitting (Coats Redfern). The results derived from thermal decomposition process demarcate decomposition of *Parthenium hysterophorous* among the three main stages, such as dehydration, active and passive pyrolysis. It is shown through DTG thermograms that the increase in the heating rate caused temperature peaks at maximum weight loss rate to shift towards higher temperature regime. The results are compared with Coats Redfern (Integral method) and experimental results have shown that values of kinetic parameters obtained from model-free methods are in good agreement. Whereas the results obtained through Coats Redfern model at different heating rates are not promising, however, the diffusion models provided the good fitting with the experimental data.**

***Keywords* – Biomass pyrolysis; Coats Redfern method; kinetic parameters; model-free methods; non-isothermal**

| **Nomenclature** | | |
|---|---|---|
| $E$ | Activation energy | kJ/mol |
| $A$ | Frequency factor | $s^{-1}$ |
| $X$ | Conversion | |
| $t$ | Time | s |
| $k$ | Rate constant | |
| $T$ | Temperature | K |
| $m_0$ | Initial mass of sample | mg |
| $m_t$ | Instantaneous mass of sample | mg |
| $m_r$ | Residual mass of sample | mg |
| R | Gas constant | (kJ·K)/mol |
| $\theta$ | Heating rate | °C/min |
| $T_m$ | Peak temperature | °C |
| $\bar{T}$ | Mean temperature | °C |

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## 1. INTRODUCTION

*Parthenium hysterophorus*, an obnoxious, aggressive Asteraceous weed, has covered over millions of hectares of land in India. This erect, ephemeral weed is known for its prolific growth and high fecundity, especially in the summer season. It is also known as altamisa, carrot grass, bitter weed, star weed, white top, wild feverfew, the 'Scourge of India', and congress grass. It produces thousands of the small white capitula and each of them yields five seeds while reaching its maturity. It has invaded the wilderness of Africa, Asia, Australia and Pacific Islands and has become one of the world's seven most destructive and hazardous weeds. This noxious weed is often noticeable at under developing residential colonies sites, the side of metallic roads, railway tracks, drainage and irrigation canals, etc. The gardens, plantations and vegetable crops are easily overwhelmed by this weed [1]. A single plant can produce around 10 000 to 15 000 viable seeds and these seeds can disseminate and germinate to capture large areas. It is called hazardous as it causes allergic respiratory problems and contact dermatitis in humans and livestock [2], [3]. Productivity of crop is severely affected due to its allelopathy. Invasive species mainly change soil properties, such as moisture, temperature [3], [4], pH [5], [6] and soil organic matters [7]–[9]. Moreover, an aggressive expansion of this weed threatens biodiversity. Elimination of this unwanted weed by burning, chemical herbicides, eucalyptus oil and biological control by leaf feeding beetle, stem-galling moth, stem-boring weevil and fungi have turned out to be successful measures to some extent. However, many innovative uses of this notorious weed have also been discovered. *Parthenium hysterophorus* is utilised to remove heavy metals and dye from the environment, eradication of aquatic weeds, use as substrate for commercial enzyme production, additives in cattle manure for bio-gas production, as biopesticide, as green manure and compost are some of its potential ability.

In this study, *Parthenium hysterophorus* is used to evaluate its untapped thermal potential. As it is mentioned that this weed has a wide range of applications in biochemical, extraction and medical field, is now subjected to thermal decomposition so that its ability as an alternative fuel for thermochemical processes can be assessed. The contribution of bio-waste as an energy reservoir is likely to increases as per the statistics of the European energy policy report [10]. According to the Ministry of New Renewable Energy of India, around 32 % of total primary energy is derived from biomass and more than 70 % of the Indian population relies on it [11]. The total amount of biomass generation per year in India is 546.41 million ton and the major portion of biomass utilization comprises agricultural and forestry residues (around 54 %). Despite the wide application of biomass in the energy sector, there are still some complications which prevail due to the chemical and physical attributes, such as low thermal efficiency as it is highly fibrous, channelling and bridging, and transportation costs [12]. Torrefaction and pelletisation could be useful to solving these problems to some extent. But before proceeding to use a different kind of biomass, it is very essential to have comprehensive knowledge about its chemical and physical behaviour as well as the kinetics of the thermo-chemical process of the biomass.

The objective of this study is to evaluate the kinetics parameters for thermal decomposition of this notorious weed with the help of thermogravimetric analyser (TGA), as this technique is commonly applied for thermal analysis [13], [14]. This analytical method is not only valid for bio-waste but also for thermal decomposition of other materials, such as medical waste [15], waste tyre [16], printed circuit board [17] or sewage sludge [18]. Infestation of arable land is one of the important facets of this work, as in the Karakoram and the Himalayan (Greater, Trans and Lower) ranges of India the percentage of agricultural land is about 10 % in hills, while 90 % is fallow land. This weed

is a kind of a scourge to the hill states of India, so the work encompasses metamorphism and conversion of its side-effect into positive effect for the energy industries of India.

## 2. MATERIALS AND METHODS

### *2.1. Material*

A sample of weed (*Parthenium hysterophorus*) is investigated to obtain their activation energy ($E_X$) and pre-exponential factor ($A$) of Arrhenius equation values for thermal decomposition. The sample of pine needles and *Cedrus deodara* are also considered for comparative analysis with thermograms of weed samples. The chemical composition and higher heating values are obtained with the help of CHNO-S analyser (*Flash EA* 1112 series) and Dulong petit formula for calorific value estimation [19]. Table 1 shows chemical composition of *Parthenium hysterophorus* (dry-basis). Those sampled are pre-treated to assure homogeneity and reproducibility of the carried-out tests. The samples are grinded and dried so that ingression of moisture does not affect calculation.

TABLE 1. CHEMICAL COMPOSITION OF PARTHENIUM HYSTEROPHORUS SAMPLE ON DRY-BASIS

| C, % | H, % | N, % | O, % | S, % | H.H.V*, MJ/kg |
|---|---|---|---|---|---|
| 41.3 | 5.3 | 3.3 | 21.0 | 0 | 17.9 |

* Higher heating value

### *2.2. TG Method*

Each sample of 10.54 mg has undergone thermal decomposition at three different heating rates (5 °C min$^{-1}$, 10 °C min$^{-1}$, 20 °C min$^{-1}$) in a SII 6300 EXSTAR. A vertical TG/DTG holder is used. To obtain pyrolysis conditions, inert gases are commonly used. In this study, nitrogen atmosphere is used as the purge gas for protecting against possible ingression of pollutants. The volumetric rate is set to 200 mL min$^{-1}$ for the purge gas. $Al_2O_3$ crucibles are used. To measure the actual sample and furnace temperatures, thermocouple types R is considered.

### *2.3. Kinetic Models*

Kinetic analysis of solid state decomposition is mainly based on a one-step kinetic equation [20]:

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

where
$X = \frac{m_0 - m_t}{m_0 - m_r}$ is the extent of conversion;
$f(X)$ represents the reaction model.

The reaction model may be one of them illustrated in Table 2. Here $m_0$, $m_t$ and $m_r$ denote initial mass of sample, instantaneous mass and the residual mass respectively. The temperature dependent rate constant $k(T)$ can be replaced by Arrhenius equation, which gives us:

$$\frac{dX}{dt} = A\exp\left(\frac{-E_X}{RT}\right)f(X). \tag{2}$$

The right-hand side of Eq. (2) is also called as kinetic triplet. In case of non-isothermal conditions, the time dependence of conversion is replaced through temperature-time relation (Eq. (3)).

$$\frac{dX}{dT} = \frac{A}{\theta} \exp\left(\frac{-E_X}{RT}\right) f(X), \tag{3}$$

where
$\theta = \frac{dT}{dt}$ is the heating rate.

TABLE 2. SET OF REACTION MODELS REQUIRED TO DESCRIBE THERMAL DECOMPOSITION IN SOLIDS MODELS

| **Model No.** | **Nucleation models** | $\boldsymbol{g(X) = \int_0^X \frac{dX}{f(X)}}$ |
|---|---|---|
| 1 | Power law | $X^{\frac{1}{4}}$ |
| 2 | Power law | $X^{\frac{1}{3}}$ |
| 3 | Power law | $X^{\frac{1}{2}}$ |
| 4 | Avarami-Erofeev | $[-\ln(1-X)]^{\frac{1}{4}}$ |
| 5 | Avarami-Erofeev | $[-\ln(1-X)]^{\frac{2}{3}}$ |
| 6 | Avarami-Erofeev | $[-\ln(1-X)]^{\frac{1}{2}}$ |
| | **Diffusion models** | |
| 7 | 1-dimensional diffusion | $X^2$ |
| 8 | Diffusion control | $\left(1-(1-X)^{\frac{1}{3}}\right)^2$ |
| | **Reaction order and geometrical contraction models** | |
| 9 | Mampel (first order) | $-\ln(1-X)$ |
| 10 | Second order | $(1-X)^{-1}-1$ |
| 11 | Contracting Cylinder | $1-(1-X)^{\frac{1}{2}}$ |
| 12 | Contracting Sphere | $1-(1-X)^{\frac{1}{3}}$ |

There are two different mathematical schemes to evaluate kinetic parameters for thermal decomposition of biomass samples. The first one is model-free methods (iso-conversional technique), whereas the second approach is known as model based methods as it depends upon the different reaction models given in Table 2.

After rearrangement of Eq. (3), we have:

$$g(X) = \int_0^X \frac{dX}{f(X)} = \int_{T_0}^T \frac{A}{\theta} \exp\left(\frac{-E}{RT}\right) dT. \tag{4}$$

Eq. (4) can also be rewritten as:

$$g(X) = \int_0^X \frac{dX}{f(X)} = \frac{AE_a}{R\theta} I\left(\frac{E_a}{RT}\right). \quad (5)$$

The term $\left(\frac{E_a}{RT}\right)$ has no exact solution and it must be solved by the numerical approximations as in literature [14].

*2.3.1. Model-Free Methods*

The model-free methods are based on evaluating the Arrhenius parameters without relying upon the reaction order [21], [22]. Model-free method is also called isoconversional, as the reaction rate is a function of the temperature at constant extent of conversion [23]. Isoconversional methods are valid to analyse both isothermal and non-isothermal pyrolysis. In the 1960s, various isoconversional methods were proposed [24]–[26]. These methods involve the series of experiments performed at different heating rates.

2.3.1.1. Kissinger Method

The ASTM E698 method [27] shared a different perspective which lies between the model-based and model-free methods. Unlike other isoconversional models, there is no need to estimate $E_a$ for each conversion value. It takes a model-free approach for estimation of activation energy which is evaluated from Kissinger's plot of $ln\left(\frac{\theta}{{T_m}^2}\right)$ against $\left(\frac{1}{T_m}\right)$ [28], where $T_m$ is the temperature corresponding to the maximum of $\frac{dX}{dT}$. However, for both the non-isothermal and isothermal pyrolysis, pre-exponential factor is calculated on the assumption of first-order reaction as follows:

$$A = \frac{\theta E}{{RT_m}^2} \exp\left(\frac{E}{RT_m}\right). \quad (6)$$

The following equation is considered:

$$\ln\left(\frac{\theta}{{T_m}^2}\right) = \ln\left(\frac{AR}{E_X}\right) - \frac{E_X}{RT_m}. \quad (7)$$

Here, activation energy is estimated as a slope of the plot, which is equal to $\frac{-E_a}{R}$.

The value of $T_m$ can be computed from derivative of conversion ($X$) over Temperature ($T$) (illustrated in Fig. 4).

2.3.1.2. Flynn-Wall-Ozawa Method

The solution of Eq. (5) using Doyle's approximations (Eq. (8)) [29] provides the Flynn-Wall-Ozawa (FWO) method (Eq. (9)) [25], [26]:

$$I\left(\frac{E_X}{RT}\right) \cong -5.331 - 1.052\frac{E_X}{RT}, \quad (8)$$

$$\ln(\theta_i) = \ln\left(\frac{AE_{X_i}}{Rg(X_i)}\right) - 5.331 - 1.052\frac{E_{X_i}}{RT}. \quad (9)$$

Eq. (8) is valid only if $20 \leq \frac{E_a}{RT} \leq 60$ [25].

Here subscript '$X_i$' represents a fixed conversion with different heating rates. The plot of Eq. (9) is a straight line with the slope $-1.052\frac{E_{X_i}}{RT}$.

2.3.1.3. Kissinger-Akahira-Sunose

The Kissinger-Akahira-Sunose method (KAS) is derived by using approximation for $I\left(\frac{E_a}{RT}\right)$ (Eq. (10)), which is valid within interval of $20 \leq \frac{E_a}{RT} \leq 50$ [30]:

$$I\left(\frac{E_X}{RT}\right) \cong \frac{\exp\left(\frac{-E_X}{RT}\right)}{\left(\frac{E_X}{RT}\right)^2}. \tag{10}$$

In this method, the relation between the temperature and the heating rate is given by Eq. (11) [28]:

$$\ln\left(\frac{\theta_i}{{T_{X_i}}^2}\right) = \ln\left(\frac{A_X R}{g(X)E_X}\right) - \frac{E_X}{RT_{Xi}}. \tag{11}$$

The apparent activation energy can be estimated from a plot drawn between $ln\left(\frac{\theta_i}{{T_{Xi}}^2}\right)$ versus $\frac{1000}{T_{Xi}}$ for a fixed value of conversion *X*, where the slope is equal to $-\frac{E_X}{R}$.

*2.3.2. Model-Based Methods (Coats-Redfern Method)*

Coats-Redfern applied the asymptotic technique for approximating the exponential integral in Eq. (5) [31]:

$$\ln\left(\frac{g(X)}{T^2}\right) = \ln\left(\frac{AR}{\theta E_X}\left(1 - \frac{2R\bar{T}}{E_X}\right)\right) - \frac{E_X}{RT}. \tag{12}$$

If the term $\frac{2R\bar{T}}{E_X}$ is less than one, it can be ignored, and the right-hand side becomes constant.

Here $\bar{T}$ is the mean experimental temperature.

After plotting $ln\left(\frac{g(X)}{T^2}\right)$ against $\frac{1}{T}$, $E_X$ and *A* are obtained from slope and intercept respectively. However, it is to be checked for each model provided in Table 2. The model which provides the best fitting is selected as the chosen model. With the help of this model, a kinetic triplet can be evaluated from thermo-analytical date [32]. The value obtained for different reaction regimes at different heating rate is illustrated in Table 2.

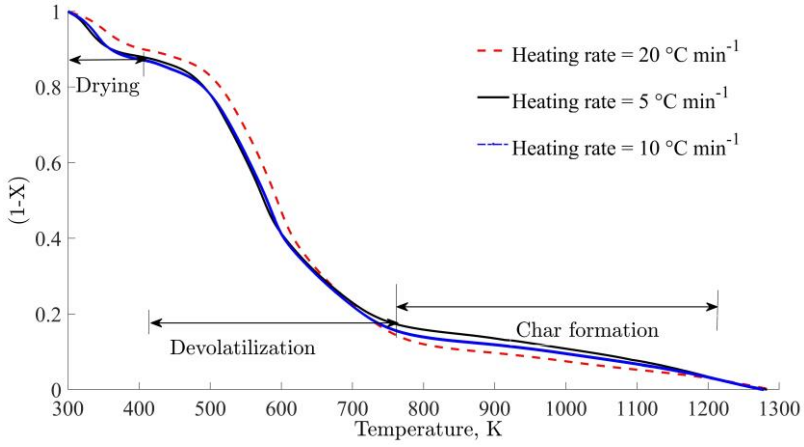
## 3. RESULTS AND DISCUSSIONS

### *3.1. Material Characteristic*

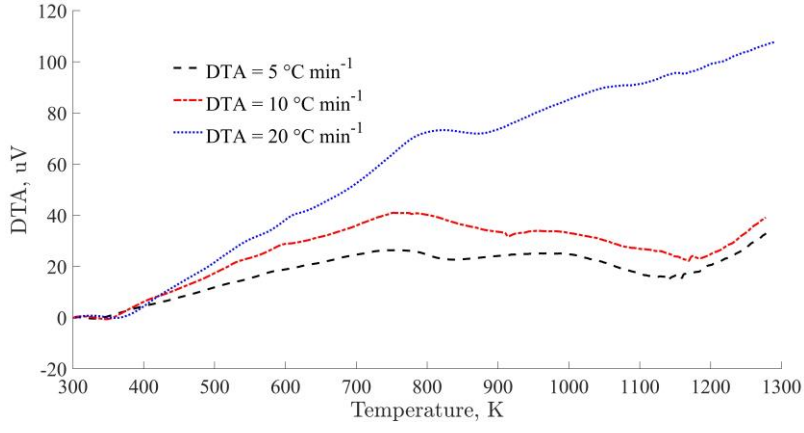
Unlike other forestry biomass [12], *Parthenium hysterophorus* contains a lesser percentage of carbon and hydrogen, therefore it has low higher heating value. This is due to the fact that energy content of carbon-carbon bond is higher than that of carbon-oxygen and carbon-hydrogen bonds. Through analytical chromatography of this weed, as depicted in Table 1, it has been observed that the percentage of sulphur and nitrogen is lower than another loose biomass used [12]. Therefore, it resulted in low greenhouse gas emissions. The gross calorific value of this weed is found to be 17.92 MJ/kg.

### *3.2. Thermal Analysis*

Assessment of *Parthenium hysterophorus* is carried out with the help of thermogravimetric (TG) and differential thermogravimetric (DTG) at three heating rates of 5 °C $min^{-1}$, 10 °C $min^{-1}$ and 20 °C $min^{-1}$ in a nitrogen atmosphere. The DTG curve is basically the first order derivative of TGA curve with respect to time or temperature. It depicts peak temperature at which maximum decomposition occurs in the TGA curves. The TG curves show the fraction of mass loss take place over a range of 300.82 K to 1300 K. It is clearly indicated from Fig. 1 that the most of volatile fraction is released within an interval of 400 K to 800 K. Pyrolysis of weed is divided into three different regimes, such as drying, devolatilization and char formation. The initial temperature for all the TGA experiments is fixed to be 300.82 K. Expelling out of moisture is accomplished in the temperature range of 300.82 K to 400 K. The devolatilization regime begins with formation of tar and volatile gases (CO, $CO_2$ and heavy hydro carbons) at 400 K and it lasts till 800 K. Further increase in the temperature led to conversion of the weed into solid, black residue (charcoal) char with the drastic falling off the content of volatile content.




(a)




(b)

Fig. 1. TG and DTA of *Parthenium hysterophorus* at different heating rates (a –TG; b – DTA).

Dhaundiyal, et al. [33] reported that the major devolatilization occurs in the range of 550 K to 670 K, which is termed as the region of active pyrolysis in Fig. 2 and Fig. 4, while the region at which the decomposition rate is the lowest is demarcated as region of passive pyrolysis in Fig. 2 and Fig. 4. In this region devolatilization ceases to act, that is the regime of char formation is initiated, thus obtained carbon and ash as the final solid residue. It is clearly noticeable at onset of char formation regime, there is an iota of increase in the mass of sample which is owing to cumulative increase in the char formation through simultaneous decomposition of lignin and hemicellulose, and as matter of fact, at end of devolatilization regime, volatile gases recombine with solid material, thus triggering autocatalytic secondary reactions. In Fig. 1(b) there is a drastic variation of change of temperature of *Parthenium hysterophorus* with respect to reference material as it shows anomality from similar kind of biomass, as after 800 K the nature of reaction becomes exothermic with increase in the heating rate. However, the nature of reaction depends on the direction of heat fluxes relative to the grain orientation of sample and increases the residence time of pyrolysis gases, which in turn triggers the secondary reactions.

The range of temperature from 410 K to 525 K representing the zone of decomposition of hemicellulose at low heating rate, while it is 430 K to 535 K for high heating rate. The first local maximum in Fig. 2 (local minimum in Fig. 4) corresponds to the time or temperature at which the maximum rate of decomposition of hemicellulose takes place. The global maximum (global minimum in Fig. 4) within given range of temperature indicates temperature at which the maximum decomposition rate of cellulose occurred varies from 575 K to 598 K. Degradation of lignin begins after 600 K and it keeps decomposition until it does not reach the final pyrolysis temperature of 1273 K, however decomposition of lignin takes places in both regions of active and passive pyrolysis without any characteristic peaks and it is difficult to distinguish from decomposition of cellulose and hemicellulose.

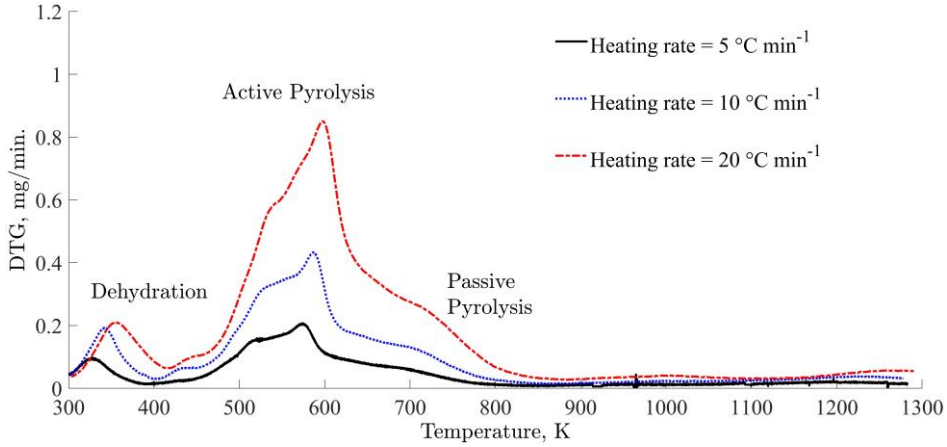



Fig. 2. DTG of *Parthenium hysterophorus* sample observed in the presence of nitrogen at different heating rates. Different stages are: dehydration, active and passive pyrolysis.

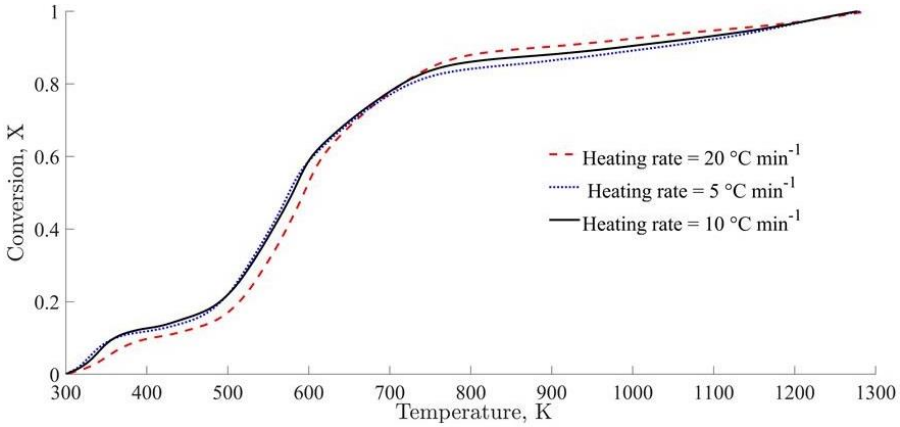



Fig. 3. Extent of conversion curves for the pyrolysis process of pine needles at different heating rate.

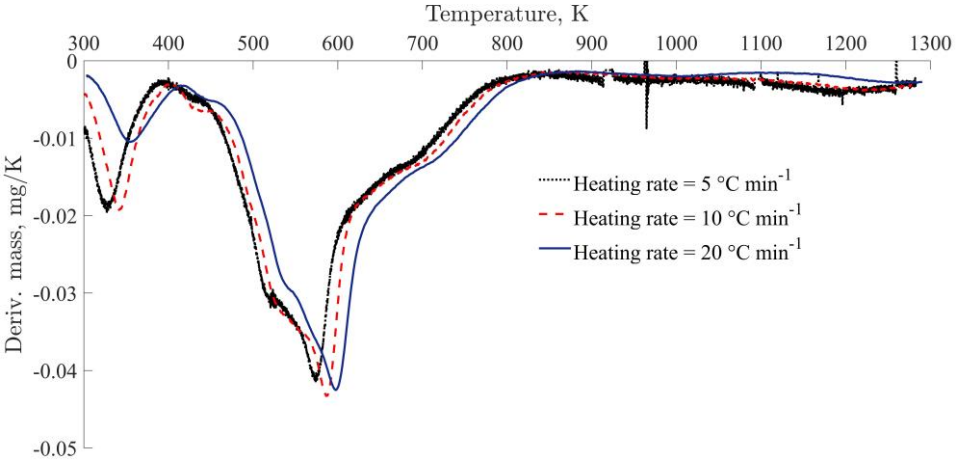



Fig. 4. DTG curves of *Parthenium hysterophorus* with respect to temperature at different heating rates.

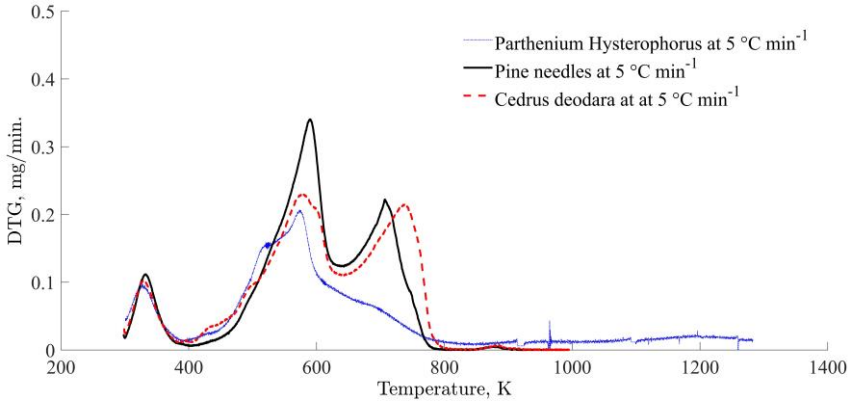



Fig. 5. Comparison of DTG curves of mass fraction as functions of temperature of coniferous species with *Parthenium hysterophorus* at heating rate of 5 °C min$^{-1}$.

The peak complexity is more visible at higher heating rates due to relatively high content of hemicelluloses decomposes at lower temperature than cellulose. The mass loss rate of cellulose significantly increases with temperature [34] and reached its maximum value at about 600 K, while it is 520 K and 710 K for hemicellulose and lignin respectively. The reason of shifting of the global minimum and the local minimum towards higher temperature regime within the same time interval is due to limitation of heat transfer, as at low heating rate a large instantaneous thermal energy is provided to the system and appreciable time is taken by purge gas, nitrogen, to attain equilibrium with the temperature of the sample. On the contrary, the same time scale has been reduced at high heating rate, thus reaction time decreases. Hence, at the same instant of time, temperature required to decompose the sample is also increased [35], [36]. This data is correlated with similar kinds of loose biomasses, pine needles and *Cedrus deodara* leaves and it validates that there is no shift in the global maximum at the same heating rate, as depicted in Fig. 5. The fine sample powder is used for analysis, therefore the thermal gradient between the furnace and the sample is negligibly small. The size and its contact with pan may affect its thermal stability and decomposition temperature. However, the larger size increases its sensitivity, but transition becomes sharp and causes spurious peaks as biomass heated. Thermal decomposition temperature increases as the particle size decreases and increase in heating rate [37].

### *3.3. Determination of Kinetic Parameters*

Estimation of kinetic parameters involves activation energy, and pre-exponential factor of the weed. The sample of weed has undergone non-isothermal temperature history in the presence of nitrogen Atmosphere. This study proposes different model-free methods and comparison of them with the integral method, i.e. Model based method (Coats-Redfern). Kissinger, FWO, KAS and Coats-Redfern methods are used to determine kinetic parameters. Pyrolysis of the weeds is demarcated by three different regions and kinetic analysis of each region is separately assessed. In the first method, the activation energy and pre-exponential factor is estimated with the help of Eq. (7), where $T_m$ indicates an onset temperature corresponding to the maximum mass loss peaks. The peak temperatures are derived from Fig. 4. The benefit of using the model-free method is non-forcible fitting of reaction model to prevailing problem. Kinetic parameters obtained from model-free method can be easily obtained without any presumption on reaction scheme.

#### *3.3.1. Kinetic Parameters Derived from Kissinger Method*

Kissinger method is model-free but not isoconversional, as the degree of conversion at the peak temperature ($T_m$) is constant at different heating rates, therefore provides a single set value of kinetic parameters for the whole process, but it is difficult to assess the complexity of reaction mechanism through this methodology [38].

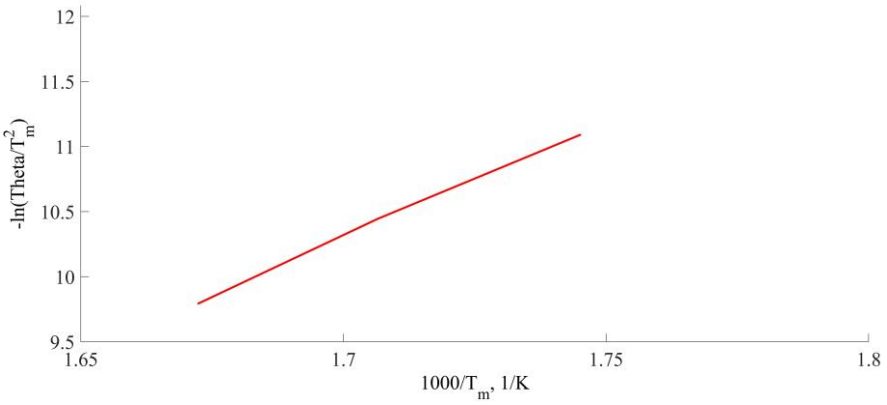



Fig. 6. Kissinger plot of *Parthenium hysterophorus*.

The slope and intercept are computed by plotting linear regression lines between $\ln\left(\frac{\theta}{{T_m}^2}\right)$ and $\frac{1}{T_m}\left(\frac{1}{K}\right)$, as shown in Fig. 6. Furthermore, 148.047 kJ/mol$^{-1}$ and $8.38 \cdot 10^{13}$ min$^{-1}$ are estimated as activation energy and pre-exponential factor respectively.

### *3.3.2. Kinetic Parameters Derived from FWO and KAS*

The kinetic parameters estimated from FWO and KAS methods are calculated at different values of conversion from Eq. (9) and Eq. (11) respectively. Variation in the conversion ($X$) at different heating rate with respect to temperature is shown in Fig. 3. To evaluate the kinetic parameters, the same value of conversion ($X$) is chosen for FWO and KAS with the corresponding temperatures at different heating rates. The comprehensive details of kinetic parameters along with coefficient of regression ($R^2$) at different degree of conversion are summarized in Table 3. The plot of apparent activation energies, obtained at the same conversion from FWO and KAS, is plotted against conversion, as shown in Fig. 7. It has been found that the apparent activation energy is a function of fractional conversion, as the most of pyrolysis reaction does not follow single step reaction and they rely on multi-step reaction which can also be recognized from Fig. 7 that apparent activation energies calculated from FWO and KAS at different conversion are not similar and exhibits the existence of complex multi-reaction mechanism within the solid matrix. The averaged activation energies and pre-exponential factors calculated from FWO and KAS are 145.81 kJ/mol and 145.44 kJ/mol, $4.77 \cdot 10^{24}$ kJ/mol and $3.16 \cdot 10^{24}$ kJ/mol respectively. The value of activation energy derived from Kissinger method (148.07 kJ/mol) is consistent with the values of activation energies derived from FWO and KAS. It is also at proximity of average values obtained from them. The value the pre-exponential factor is also in the domain of average values computed from FWO and KAS. However, the influence of ambient atmosphere used in TG analysis effect the computation of kinetic parameters, as Kumar, et al. [39] reported that the activation energy estimated in air is higher than $E_a$ in nitrogen atmosphere, therefore it becomes indispensable to examine the thermochemical process in the presence of inert atmosphere. For a similar kind of loose biomass, Dhaundiyal and Tewari [33] examined the thermal degradation of a similar kind of loose biomass by TG/DTA and applied multi reaction model to each constitutes species of biomass and they have found 152.0527 kJ/mol for the cellulose and 133.549 kJ/mol for hemicelluloses, which is found to be consistent with model-free methods. For comparative

evaluation of weed from another integral method than DAEM, Coats Redfern method is adopted to identity the reaction scheme suits to decomposition of weed.

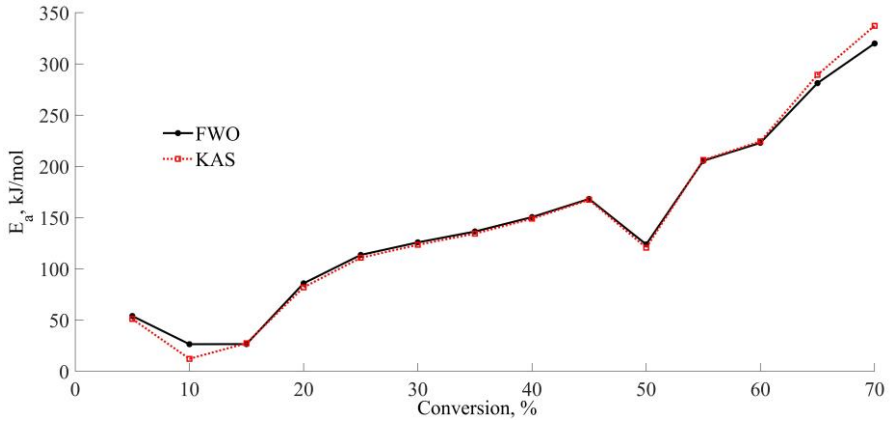



Fig. 7. Activation energy as a function of conversion.

Using simple numerical approximation, Cai and Liu [40] reported that 300 kJ/mol could be as activation energy for thermal decomposition of peanut-shell. In another experiment, Dhaundiyal and Singh [41] conducted experiments on *Cedrus deodara* leaves and estimated 39 kJ/mol as an activation energy for it. Lim and his co-worker [42] evaluated the averaged activation energy of 51.19 kJ/mol for rice husk using Kissinger-Akahira-Sunrose (KAS).

TABLE 3. KINETIC PARAMETERS OBTAINED BY MODEL-FREE METHODS

| Conversion ($X_i$) | FWO | | | KAS | | |
|---|---|---|---|---|---|---|
| | $E_a$, kJ/mol | $A$, min$^{-1}$ | $R^2$ | $E_a$, kJ/mol | $A$, min$^{-1}$ | $R^2$ |
| 0.05 | 53.99 | $9.40 \cdot 10^{6}$ | 0.92 | 51.13 | $2.11 \cdot 10^{6}$ | 0.99 |
| 0.10 | 26.51 | $5.31 \cdot 10^{3}$ | 0.72 | 12.26 | $3.30 \cdot 10^{4}$ | 0.99 |
| 0.15 | 26.62 | $2.14 \cdot 10^{2}$ | 0.99 | 27.50 | $8.70 \cdot 10^{3}$ | 0.60 |
| 0.20 | 85.92 | $1.32 \cdot 10^{8}$ | 0.80 | 82.04 | $3.50 \cdot 10^{7}$ | 0.80 |
| 0.25 | 113.62 | $4.94 \cdot 10^{10}$ | 0.81 | 110.86 | $2.16 \cdot 10^{10}$ | 0.80 |
| 0.30 | 125.86 | $4.60 \cdot 10^{11}$ | 0.87 | 123.49 | $2.35 \cdot 10^{11}$ | 0.84 |
| 0.35 | 136.46 | $2.78 \cdot 10^{12}$ | 0.87 | 134.42 | $1.59 \cdot 10^{12}$ | 0.86 |
| 0.40 | 150.53 | $3.47 \cdot 10^{13}$ | 0.88 | 149.00 | $2.32 \cdot 10^{13}$ | 0.86 |
| 0.45 | 168.27 | $1.07 \cdot 10^{14}$ | 0.90 | 167.46 | $7.20 \cdot 10^{14}$ | 0.90 |
| 0.50 | 123.89 | $5.48 \cdot 10^{10}$ | 0.99 | 120.71 | $2.30 \cdot 10^{10}$ | 0.99 |
| 0.55 | 205.47 | $6.80 \cdot 10^{17}$ | 0.88 | 206.23 | $7.68 \cdot 10^{17}$ | 0.88 |
| 0.60 | 223.00 | $1.14 \cdot 10^{18}$ | 0.70 | 224.43 | $1.21 \cdot 10^{19}$ | 0.70 |
| 0.65 | 281.28 | $2.29 \cdot 10^{23}$ | 0.71 | 289.41 | $4.44 \cdot 10^{23}$ | 0.70 |
| 0.70 | 320.00 | $6.65 \cdot 10^{25}$ | 1.00 | 337.24 | $4.37 \cdot 10^{25}$ | 0.70 |
| Average | 145.81 | $4.77 \cdot 10^{24}$ | | 145.4414 | $3.16 \cdot 10^{24}$ | |
| Kissinger | 148.047 kJ/mol | | | $8.38 \cdot 10^{23}$ min$^{-1}$ | | |

### *3.3.3. Kinetic Parameters Obtained from the Model-Based Method*

The Coats Redfern Eq. (12) is adopted to assess validity of model-free method and provide the most suitable reaction model for decomposition of weed. This model-based method relies on Arrhenius equation. Unlike model-free methods which are based on the degree of conversion, the Coats Redfern depends only on heating rates. Table 2 summarized different kinetic models which are tested to identity the reaction mechanism of pyrolysis of weed. Table 4 illustrates the kinetic parameters for weed evaluated from model based method at different heating rates. It can be observed that kinetic parameters computed at different heating rate for models has shown an appreciable variation from the model-free method, however, the diffusion mechanism has significantly influence the thermo-analytical date than that of the other reaction mechanisms. There are two main reasons for inconsistency between model-free and model based in case of non-isothermal runs. The first is a result of the force-fitting of non-isothermal data to hypothetical reaction model. Arrhenius parameters are determined by form of g($X$), which is already assumed. Moreover, both temperature and the conversion ($X$) are simultaneously varying with time. The model-based model is not able to distinguish separately temperature dependence of rate constant and the conversion. Consequently, any assumed model can be easily synchronised with thermoanalytical data at the expense of drastic variation between the assumed model and the true unknown model. Owing to this reason, the model based methods provide ambiguous values of Arrhenius parameters. Another main reason of disagreement is the existence of multi-reaction mechanisms with different activation energies, as contribution of these steps to the overall decomposition rate is influenced by temperature and extent of conversion, which implies activation energy calculated from the model based method is a function of $T$ and $X$. However, the calculated value of activation energy represents the average value for the overall process. This value is derived in such a way that it is invariant to the reaction mechanism and kinetics with change in temperature and degree of conversion, therefore, the isoconversional method is prefer to the model based scheme to overcome afore mentioned drawbacks [25], [26], as these models checks dependency of date with respect to conversion or temperature without prior judgement about assumed model.

TABLE 4. KINETIC PARAMETERS OBTAINED BY MEANS OF COATS-REDFERN METHOD

| Heating rate (non-isothermal) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 5 °C min$^{-1}$ | | | | 10 °C min$^{-1}$ | | | 20 °C min$^{-1}$ | | |
| Model No | $E_a$, kJ/mol | A, min$^{-1}$ | $R^2$ | $E_a$, kJ/mol | $A$, min$^{-1}$ | $R^2$ | $E_a$, kJ/mol | $A$, min$^{-1}$ | $R^2$ |
| 1 | 7.13 | $9.80 \cdot 10^{9}$ | 0.86 | 6.71 | $1.73 \cdot 10^{10}$ | 0.83 | 5.98 | $2.81 \cdot 10^{10}$ | 0.79 |
| 2 | 6.13 | $7.50 \cdot 10^{9}$ | 0.80 | 5.63 | $1.26 \cdot 10^{10}$ | 0.73 | 4.70 | $1.88 \cdot 10^{10}$ | 0.64 |
| 3 | 4.13 | $3.97 \cdot 10^{9}$ | 0.54 | 3.46 | $5.99 \cdot 10^{9}$ | 0.41 | 2.14 | $6.22 \cdot 10^{9}$ | 0.19 |
| 4 | 5.83 | $5.38 \cdot 10^{9}$ | 0.82 | 3.21 | $1.44 \cdot 10^{9}$ | 0.21 | 4.65 | $1.44 \cdot 10^{10}$ | 0.76 |
| 5 | 1.33 | $3.46 \cdot 10^{8}$ | 0.64 | 5.42 | $6.86 \cdot 10^{8}$ | 0.81 | 3.96 | $2.74 \cdot 10^{9}$ | 0.47 |
| 6 | 1.53 | $6.64 \cdot 10^{8}$ | 0.64 | 0.89 | $9.34 \cdot 10^{9}$ | 0.06 | 0.51 | $6.47 \cdot 10^{8}$ | 0.02 |
| 7 | 14.00 | $1.54 \cdot 10^{9}$ | 0.83 | 16.00 | $2.51 \cdot 10^{9}$ | 0.65 | 21.00 | $3.45 \cdot 10^{9}$ | 0.74 |
| 8 | 20.05 | $2.91 \cdot 10^{9}$ | 0.83 | 43.29 | $1.34 \cdot 10^{16}$ | 0.85 | 27.21 | $5.42 \cdot 10^{9}$ | 0.86 |
| 9 | 7.07 | $6.67 \cdot 10^{9}$ | 0.68 | 8.16 | $1.26 \cdot 10^{9}$ | 0.70 | 10.86 | $2.27 \cdot 10^{9}$ | 0.79 |
| 10 | 16.00 | $1.14 \cdot 10^{9}$ | 0.92 | 17.00 | $1.94 \cdot 10^{8}$ | 0.86 | 19.93 | $2.63 \cdot 10^{8}$ | 0.91 |
| 11 | 7.40 | $1.10 \cdot 10^{10}$ | 0.82 | 5.18 | $4.03 \cdot 10^{9}$ | 0.41 | 7.77 | $8.52 \cdot 10^{9}$ | 0.59 |
| 12 | 8.50 | $1.43 \cdot 10^{10}$ | 0.95 | 6.07 | $5.35 \cdot 10^{9}$ | 0.51 | 8.69 | $1.06 \cdot 10^{10}$ | 0.66 |

## 4. CONCLUSION

Thermal and kinetic behaviour of weed is investigated through thermogravimetric analysis performed at non-isothermal condition. Activation energy and pre-exponential factor are determined with the help of model-free and model-based methods. The activation energies estimated from Kissinger method is 148.047 kJ/mol, whereas the average values of activation energy derived from FWO and KAS are 145.81 kJ/mol and 145.44 kJ/mol respectively. The values obtained from FWO and KAS are consistent with Kissinger method, however, the values estimated with the help of the Coats-Redfern at different heating rates have shown an appreciable deviation from the expected values estimated from model-free methods. Moreover, apparent values of activation energies at different conversion have indicated the existence of the multi-reaction scheme. The inability of the model based method to correlate with the isoconversional methods is unable to demarcate variation of temperature and degree of conversion with respect to time. The results are also in good agreement with other literature works for similar sort of loose biomass.

Results furbish the significant thermal decomposition details about a weed that can be useful for developing pyrolysis plant and to comprehend mechanism of biomasses that come under purview of low bulk density biomass. In context of bulk density, this weed is relatively like pine needles, but the behavior is quite different. The release of energy per unit mass is more than that of pine needles at the same temperature. The nature of reaction is exothermic with increase in the heating rate as time proceeds, whereas it is mostly endothermic in different kind of biomass like wood, pine needles and *Cedrus deodara* leaves. It shows that residence time of volatile gases is relatively higher than the similar kind of forestry biomass and leads to increase in secondary pyrolysis reactions. This biomass can possibly be a good primary fuel for biofuel production. Temperature required for decomposition of the weed has a negative offset of 1 °C to 2 °C. While gasifying a biomass in a gasifier plant, the temperature required for drying the biomass is to be kept low, so that the heat loss can be minimised during computation of efficiency of gasifier plant. This weed needs less heat content as compare to other similar kind of forestry waste. Heat required for thermal decomposition may reduce the energy consumption for getting the same output. Exergy analysis of gasification process of this weed may provide a noteworthy outcome in context of plant modelling.

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