Biocatalysis and Agricultural Biotechnology 21 (2019) 101315

Contents lists available at ScienceDirect

Biocatalysis and Agricultural Biotechnology

journal homepage: http://www.elsevier.com/locate/bab

Determination of kinetic and thermodynamic parameters of thermal degradation of different biomasses for pyrolysis

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ARTICLE INFO

Keywords:
Pyrolysis
Biomass
Thermogravimetric analysis
Kinetics
Thermodynamic parameter

ABSTRACT

In this work, we studied the kinetics and thermodynamics of thermal degradation of three different biomasses such as Kaner seed (*Thevetia Peruviana*), Flax seed (*Linum Usitatissimum* L.) residue, Microalgae (*Arthrospira Platensis*) using thermogravimetric analysis. Different kinetic parameters are determined using order based Mampel first-order model fitting method. The average activation energy for the different biomass are found to be 37.25 kJ/mol for kaner seed, 29.88 kJ/mol for flex seed residue and 23.55 kJ/mol for microalgae. The heating rate has an important role on the degradation pattern of the different biomasses and there is observable change in the kinetic and thermodynamic parameters with change in heating rate. The small increment in the thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS) and free energy change (ΔG) are observed with increase in the heating rate for all biomass. The values these parameters for the thermal degradation of different biomass are in the order of Kaner seed > flax seed residue > microalgae. The determination of the kinetic and thermodynamic parameters would provide valuable input to design more effective conversion systems.

1. Introduction

The world relies heavily on energy from fossil fuels (oil, natural gas, coal). Most (84%) of the world's energy demand is met from fossil fuels and demand will increase as world energy consumption is expected to increase 53% by 2035 as per EIA, 2011. As a substitute, other non-conventional fossil resources (tar sand oil, shale gas, arctic and deep-water oil) may become economically viable, but they are ultimately limited resource and carry risks to our health and environment. In addition, there has been concern for the environmental aspects due to extensive use of fossil fuel. Thus, biomass utilisation in mainstream energy uses is receiving great attention due to environmental considerations, government policies and programs to support renewable energy and the availability and renewability of large quantity of diversified biomass. However, effective conversion of biomass to energy will require the careful pairing of advanced conversion technologies with biomass feedstock optimized for the purpose.

The term biomass is used to describe any material of recent biological origin and includes plant materials such as trees, grasses and agricultural crops, as well as animal manure and municipal bio-solids (sewage). Biomass can be utilized to produce process heat, steam, motive power and electricity and can be converted by thermal or biological routes into a range of useful energy carriers such as liquid fuels and synthesis gas. Biomass has been used by mankind for a very long time to satisfy its energy needs. Apart from combustion which is a direct transformation of biomass into energy, there are several possible routes of biomass thermal processing like pyrolysis. Pyrolysis is a thermochemical process conducted in the absence of oxygen converting waste biomass into valuable chemicals of fuels. End products are carbon-rich char, condensable and non-condensable gases (Ounas et al., 2011). Slow pyrolysis is in use to produce solids (charcoal) whereas fast pyrolysis is carried out for production of gas or liquids (bio-oils). Fast pyrolysis represents an excellent way of utilizing lignocellulosic biomass that makes them highly attractive especially when concerning environmental issues during energy production. There are various studies on pyrolysis analysis of different biomasses, but biomass properties can significantly influence both heat transfer and reaction rates such that the optimal operating conditions are highly variable (Varma, and Mandol, 2016). Kinetic analysis is essential to design and establish efficient, safe and reasonable processes. Determination of thermo-kinetic behavior of biomass allows control of decomposition mechanism of biomass as a function of pressure, temperature and heating rate. Kinetic parameters of reaction are necessary for accurately prediction of reactions behavior

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https://doi.org/10.1016/j.bcab.2019.101315
Received 29 March 2019; Received in revised form 22 June 2019; Accepted 26 August 2019
Available online 28 August 2019

Nomenclature

A	Arrhenius factor
T	Temperature in Kelvin
Ea	Activation energy, KJ mol^{-1}
k	Rate constant, mol lit^{-1} sec^{-1}
W_0	Initial wt of the sample, mg
W_f	Final weight of the sample, mg
R	Universal gas constant (8.314 J/mol k^{-1})
X	Conversion of sample
β	Heat flow/heating rate

and optimization of the process towards products during the pyrolytic degradation (Hu et al., 2015). Thermogravimetric analysis (TGA) is a commonly adopted method for studying the thermal degradation behavior and kinetics of such reactions. The weight loss data obtained from TGA can be utilized to determine the kinetic parameters such as activation energy, pre-exponential factors, order of the reaction, and ignition temperature and reactivity index (the peak temperature where maximum degradation occurs) of the particular sample (Ghetti et al., 1996; Kumara et al., 2008).

There are numerous studies addressing the transformation kinetics of different kinds of materials such as natural fibers (Yao et al., 2008; Jiang et al., 2010), oil shale (Al-Harahsheh et al., 2011), sand bitumen (Ma and Li, 2012), scrap automobile tyres (Chen et al., 2001), municipal solid wastes (Sorum et al., 2001), oil sludge (Liu et al., 2009), coconut, and cashew nut shells (Tsamba et al., 2006), plastics and biomass blend (Parekh et al., 2009; Rotliwala and Parikh, 2011) etc. A. Agrawal and S. Chakraborty evaluated the kinetics of pyrolysis and combustion of microalgae *Chlorela Vulgaris* by using TGA at different heating rate ranging from 5 to 40 °C/min. They reported that the average activation energies required for the decomposition of protein and carbohydrate are comparatively less than that for decomposing the lipid in both pyrolysis and combustion process and showed that the biomass conversion in combustion process is higher than the pyrolysis (Agrawal, A. and Chakraborty, S. 2013). The pyrolysis of residues of two types of microalgae such as *Chlamudomonas* (*C. sp. JSC4*) and *Chlorella sorokiniana* (*C. Sorokiniana CY1*) was studied by means of thermogravimetric analyser and calculated the activation energy of the components, hemicellulose, cellulose, lignin, lipid and proteins of both the biomasses. The activation energy of hemicellulose, cellulose, lignin, lipid, protein for *Chlamudomonas* was found to be 115.12–117.12 kJ/mol, 181.67–198.30 kJ/mol,61.74–62.75 kJ/mol, 104.93–114.14 kJ/mol and 90.75–99.31 kJ/mol, respectively; and that for *C. Sorokiniana CY1* was 113.12–117.12 kJ/mol, 218.73–28.79 kJ/mol, 64.77–66.39 kJ/mol, 131.97–143.63 kJ/mol and108.03–118.13 kJ/mol, respectively (Bui et al., 2016). Q. Bach and W. Chen reported the pyrolysis characteristics of microalga *Chlorella vulgaris ESP-31* and modeled from thermogravimetric analysis. They projected that the three reaction model separates the decomposition of three main microalgal components (i.e. carbohydrate, protein and lipid) into three parallel reactions, the activation energy of protein is found to be 208.80 kJ/mol, that of carbohydrate is 40.36 kJ/mol, while its value for lipid is 48.46 kJ/mol (Bach and Chen, 2017). Non-isothermal thermogravimetric pyrolysis analysis of microalgae *Nannochloropsis oculata* (NO) and *Tetraselmis* sp. (TS) at different heating rates were carried out to understand the pyrolytic behavior and kinetics. The average activation energy and pre-exponential factor for pyrolysis of NO and TS were calculated by using distributed activation energy model. The highest activation energies were found as 152.20 and 334 kJ/mol for NO and TS, respectively, at different conversions. The pre-exponential factors for the corresponding activation energies were observed to be in the order of 10^8–10^{13} and 10^{12}–10^{25} s^{-1} for NO and TS respectively (Ceylan and Kazan, 2015). The thermal degradation behavior of rubber seed shell (RSS), high density polyethylene (HDPE), and the HDPE/RSS mixtures (0.2:0.8 wt ratio) by means of thermogravimetric analyzer under non-isothermal condition in argon atmosphere at flow rate of 100 $mlmin^{-1}$ under different heating rates 10,20,30 and 50 K min^{-1} in the temperature range of 323–1173 K. The kinetic parameters are generated based on first order rate of reaction. They reported that there are one, two, and three stages of decomposition occurring in HDPE, RSS, and HDPE/RSS mixtures respectively during the pyrolysis process. The remaining solid residue increases with an increase in heating rate regardless of the type of samples used. The activation energies for RSS, HDPE, HDPE/RSS mixtures are 46.94–63.21, 242.13–278.14, and 49.14–83.11 kJ/mol respectively for the range of heating rate studied (Chin et al., 2014).

The effect of heating rate on slow pyrolysis behavior of karanja seed cake was studied and the kinetic parameters at different heating rates of 5, 10, 20 °C/min using TGA by Isoconversional method was investigated. The calculated activation energies was found to be 118–124 kJ/mol at heating range of 5–20 °C/min. The experiments showed that the activation energy values increased with increasing heating rate (Muktham et al., 2016). Pradhan et al. examined the physicochemical properties of sal seeds and investigated the kinetics of pyrolysis of the seed at three different heating rates of 5, 20 and 40 K min^{-1} respectively. Non-isothermal methods were used to determine the activation energy and its value ranged from 297.3 to 517.07 kJ/mol (Pradhan et al., 2017). Kaur et al. used the castor seed residue to study its pyrolytic behavior and obtained the kinetics and thermodynamic parameters. The apparent activation energy calculated by FWO (167.10 kJ/mol) and KAS (165.86 kJ/mol) methods are slightly different. The resulted pre-exponential factor varies from 108 to 1018 and 107–1018 for FWO and KAS methods respectively. The average ΔG value of the reaction is found to be 152 kJ/mol (Kaur et al., 2018). The kinetic of thermal degradation of red pepper waste (RPW) was studied at three different heating rates, 5 °C/min, 7.5 °C/min and 10 °C/min in a thermogravimetric analyzer in oxidative atmosphere. The kinetic analysis was carried out applying the isoconversional model of Ozawa–Flynn–Wall. The activation energy observed was considerably low and varied from 29.49 to 147.25 kJ/mol. The Gibbs free energy varied from 71.77 kJ/mol to 207.03 kJ/mol and change in entropy is found negative varied for −8.31 J/mol to −249.52 J/mol (Maia and de Morais, 2016).

The present work reports a comparative analysis of thermal degradation behavior, kinetics and thermodynamics of pyrolysis of three different types of biomass such as a seed biomass: kaner seed, deoiled seed residue biomass: flax seed residue (after oil extraction), and a protein rich micoalgae *Arthrospira Platensis* by thermogravimetric analysis. The major content of these raw materials include lipid (fatty acids), carbohydrate, and proteins. Determination of kinetic parameters of all the three biomass would explore the possibility of effective degradation of different biomass together for the production of liquid and gaseous fuels.

2. Materials and methods

2.1. Biomass

Three different biomass samples are chosen for carrying out the pyrolysis experiment in the present study. They are Flax seed residue (*Linum Usitatissimum* L.), Microalgae *(Arthrospira Platensis)* and Kaner seed (*Thevetia Peruviana*). The black colored ripen fruits of the *Thevetia Peruviana* plant was collected from local areas of Burla, Odisha, India and subjected to sun drying for twenty days. The kernel inside the fruits are then taken out and crushed to about less than 1 mm size. The crushed kernel was then directly subjected to thermal treatment. The flax seed residue/remain chosen for this study was collected from the supercritical CO_2 fluid extraction industry, Gram-Tarang Foods, located at Parlakhemundi, Odisha, India. The dried seeds were pulverised and subjected to

extraction at 300 bar and 50 - 70 °C for 4 h, yielding 26 wt % oil. The seed residue was then used as feedstock directly in pyrolysis experiments.

The microalgae (*Arthrospira Platensis*) used in this study was obtained from the Algae culture collection facility of Biotechnology division of Aban Infrastructure Pvt. Ltd., Chennai, Tamilnadu, India. This alga was cultivated using seawater (Salinity: 30 ppt) in a 120 m^2 raceway pond (Capacity: 20,000 L) located in the poly house facility of Biotechnology division of Aban Infrastructure Pvt. Ltd, Chennai, India. The cultures were maintained in CFTRI medium with light intensity of 140 µmol photon m^{-2} $s^{-1}$and temperature of 25 ± 1 °C in the growth room.

2.2. Proximate and ultimate analysis of biomass

Proximate analysis of the biomass samples such as the percentage of moisture, volatile matter, fixed carbon and ash content has been carried out using prescribed standard methods ASTM D 4442, ASTM D 3172, ASTM D 3177 and ASTM D 3175 respectively on dry basis. Ultimate analysis of the raw material, which is used to determine the elemental composition (C,H,N,S,O) of the sample was carried out using a CHNS elemental analyzer (Variael CUBE, Germany).

2.3. Thermogravimetric/Differential thermal analysis (TG/DTA)

Thermo-gravimetric analysis of the seed samples was done using a DTG60 instrument. Definite weight of biomass sample was taken and heated to 900 °C for 1 min. TGA was performed in nitrogen atmosphere with flow rate 35 ml/min, at a desired heating rate.

2.4. Kinetic study by thermogravimetric analysis (TGA)

Thermal degradation of biomass being a complex reaction due to the presence of numerous components and their parallel and consecutive reaction. Thermal degradation of such reactions can be carried out by TGA and this has become the most commonly used methods to study the kinetics of thermal decomposition reaction.

The general non-isothermal heterogeneous solid state decomposition reaction rate can be expressed as:

$$\frac{dx}{dt} = k\ f(x)^n \tag{1}$$

where, f(x) = 1- x, x is the extent of conversion and is given by $x = \frac{w_o - w_t}{w_o - w_f}$ (w_o = initial weight, w_t = weight after time t and w_f = final weight)

Equation (1) can be written as,

$$\frac{dx}{dt} = k\quad (1 - x) \tag{2}$$

According to Arrhenius,

$$k = Ae^{-E_a/RT} \tag{3}$$

where k is the rate constant which depends on the temperature T.A is the frequency factorE_a is the activation energy and R is the universal gas constant.

Considering heating rateβ, which is equal to dT/dt or dt = dT/β.

We have,

$$(dx/dT)\ \beta = A\ e^{-Ea/\ RT}\ (1\text{-}x) \tag{4}$$

Integrating both sides we have,

$$\int dx/1 - x\ = \frac{A}{\beta}\int e^{-Ea/RT}dT$$

$$-\ \ln\ (1\text{-}x) = ART^2/\beta E_a\ e^{-E_a\ /\ RT}$$

Taking logarithm both sides we have

$$\ln\ (-\ln\ (1\text{-}x)) = \ln\ (ART^2/\ \beta E_a) - E_a/\ RT \tag{5}$$

Equation (5) is an equation of straight line with negative slope. On plotting a graph between ln (- ln (1-x)) and 1/T, a straight line is obtained with slope m = -E_a/R.

Therefore, activation energy can be calculated as,

$$E_a = -\ \text{slope x R} \tag{6}$$

Again, the Y intercept of the plot, c = ln ($ART^2/\beta E_a$).

The pre-exponential factor (A) can be calculated using equation (6).

$$A = \left(\frac{\beta E_a}{RT^2}\right)\ e^c \tag{7}$$

2.5. Thermodynamic parameter

Thermodynamic parameter such as change in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are determined from the theory of activated complex (transition state) of Eyring (Vlaev et al., 2008; Turmanova et al., 2008; Boonchom and Puttawong, 2010; Boonchom and Thongkam, 2010)using the following general equation:

$$A = \frac{e\chi K_B T_p}{h}\ \ Exp\ \left(\frac{\Delta S}{R}\right) \tag{8}$$

where e = 2.7183 is the Neper number, χ is the transition factor, which is unity for intergrated kinetic first order reactions, K_B is the Boltzmann constant, h is the Planck constant and T_p is thepeak temperature of DTG curve. The entropy at the formation of the activated complex from the reagent may be calculated using equation (9),

$$\Delta S = R\ \ \ln\frac{Ah}{e\chi K_B T_p} \tag{9}$$

And the enthalpy change of the reaction be calculated using equation (10)

$$\Delta H = E_a\text{- } RT_p \tag{10}$$

T_p is the peak temperature at corresponds to the highest rate of the process.

The changes of Gibbs free energy (ΔG) for the activated complex formation can be calculated, using well known thermodynamic equation (11),

$$\Delta G = \Delta H - T_p\Delta S \tag{11}$$

The values of ΔS, ΔH and ΔG are calculated the peak temperature (T_p).

Table-1
Characterization of biomass.

Proximate Analysis	Kaner seed	Flax seed residue	Microalgae
% Moisture	4.30	6.75	7.25
%Volatile Matter	89.62	77.016	74. 65
% Ash content	3.63	5.3	7.3
% Fixed Carbon	2.45	10.33	10.8
Ultimate Analysis			
% C	59.23	47.20	43.98
% H	1.34	3.21	6.76
% N	0.74	2.91	10.67
% S	0.49	0.11	0.71
% O	38.2	46.57	31.58
Gross calorific value (MJ/Kg)	15.18	11.92	18.95

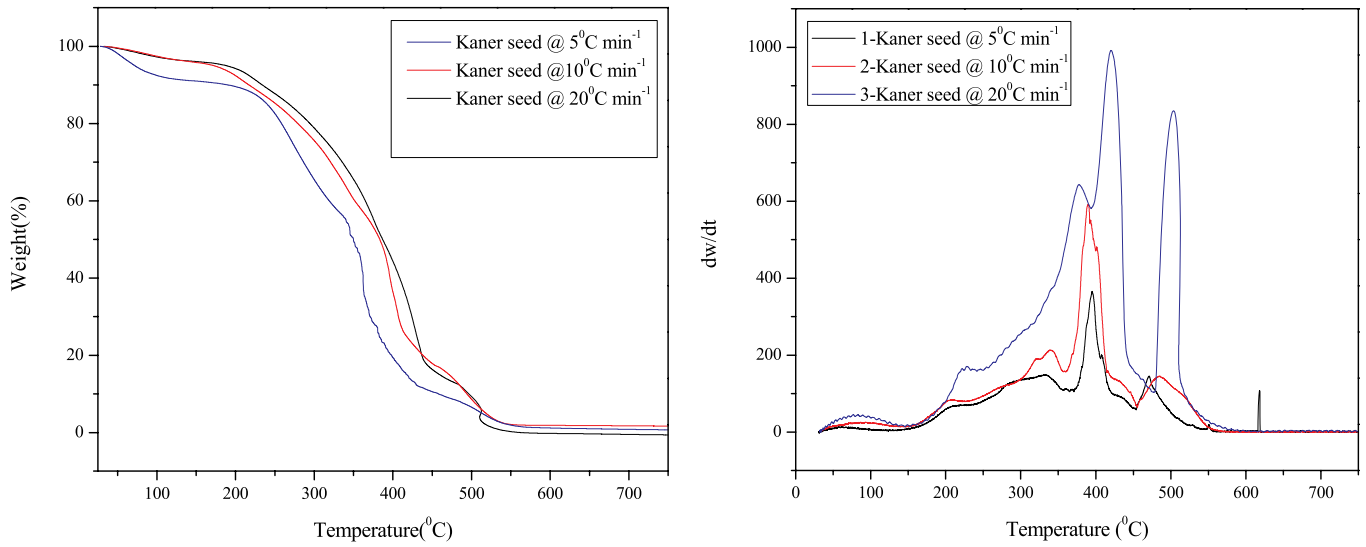

Fig. 1. a. TGA of Kaner seed. b. DTG thermograph of Kaner seed.

3. Results and discussion

3.1. Proximate and ultimate analysis of biomass

The proximate analysis (moisture, volatile matter, ash and fixed carbon) and ultimate analysis (elemental composition) of the three different biomass such as kaner seed, flax seed residue and microalgae on dry basis are summarized in Table 1. The result shows that kaner seed has lower moisture, fixed carbon and ash content with rich volatile matter content as compared to the other two biomasses. The low volatile matter and high fixed carbon of flax seed residue and microalgae is responsible for lowering the calorific value of both the biomasses. The major elements in all three samples include Carbon and Oxygen, with less percentage of nitrogen and hydrogen. The gross calorific values calculated based on the elemental composition are found lower for all the three biomass as compared to conventional fuels and follows the order: Kaner seed > Microalgae > Flex seed residue. The lower calorific value of all three biomass samples can be explained due to high oxygen content. So it should be converted to high energy content liquid and/or gaseous fuel through pyrolysis to make it more useful. Moreover, the nitrogen content in the microalgae is very high i.e.10.76% as compared to other two biomass owing to the presence of proteins and chlorophylls in it (Ounas et al., 2011). As the samples hold less moisture, and high volatile matter, they should yield more of pyrolysis oil and gas upon pyrolysis and thus suitable for pyrolysis. Similarly, flax seed residue and microalgae give high fixed carbon, yield char as one of the major products or could be suitably converted to char or activated carbon through slow pyrolysis. Very low Sulphur content of all the three samples make them suitable to be used as a fuel feedstock.

3.2. Thermal analysis (TG-DTG)

The thermogravimetric analysis of three different biomasses viz. Kaner seed, Flax seed residue and Microalgae is illustrated in terms of plot between weight percentage (wt%) versus temperature to understand the thermal degradation behavior of these biomasses. The thermal curves of kaner seed, flax seed residue and microalgae at three different heating rates (i.e. 5, 10 and 20 °C/min) of each are shown in Figs. 1a, 2a and 3a respectively. The different stages of thermal degradation with respect to temperature and the residual solid (char) percentage at different heating rates is shown in Table 2. It has been found that the residual weight in terms of wt% of the sample increases with the increase of heating rates. The graphs revealed that there are three stages of thermal degradation common to all heating rates. But there is a shift in conversion lines caused by various heating rates. At higher heating rates, individual conversions are reached at higher temperatures. In other

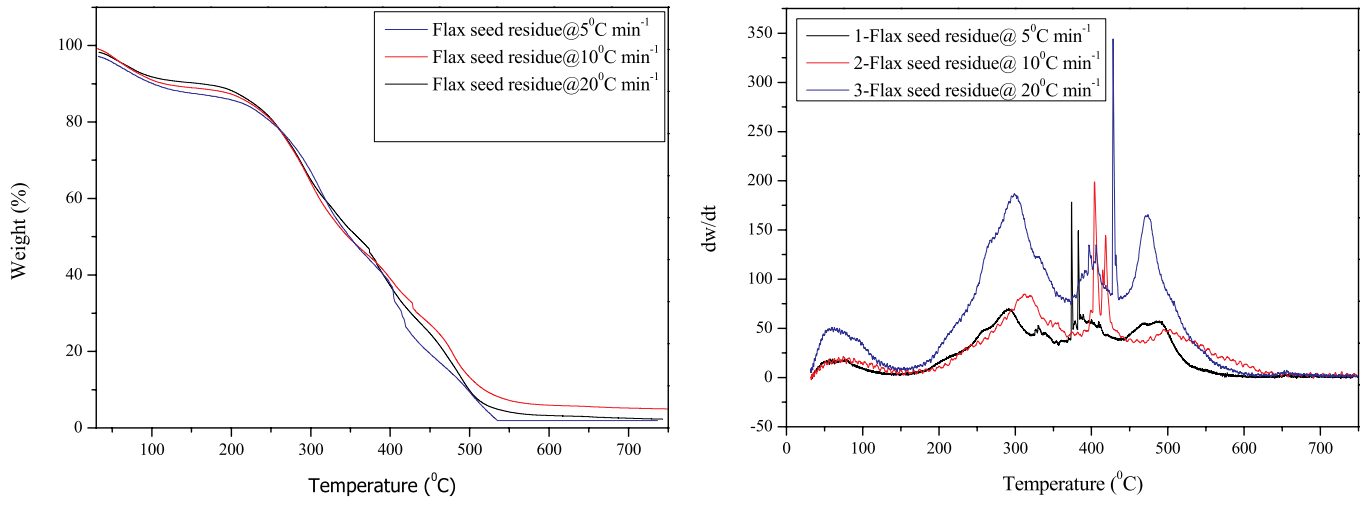

Fig. 2. a. TGA of Flax seed residue. b. DTG thermograph of Flax seed residue.

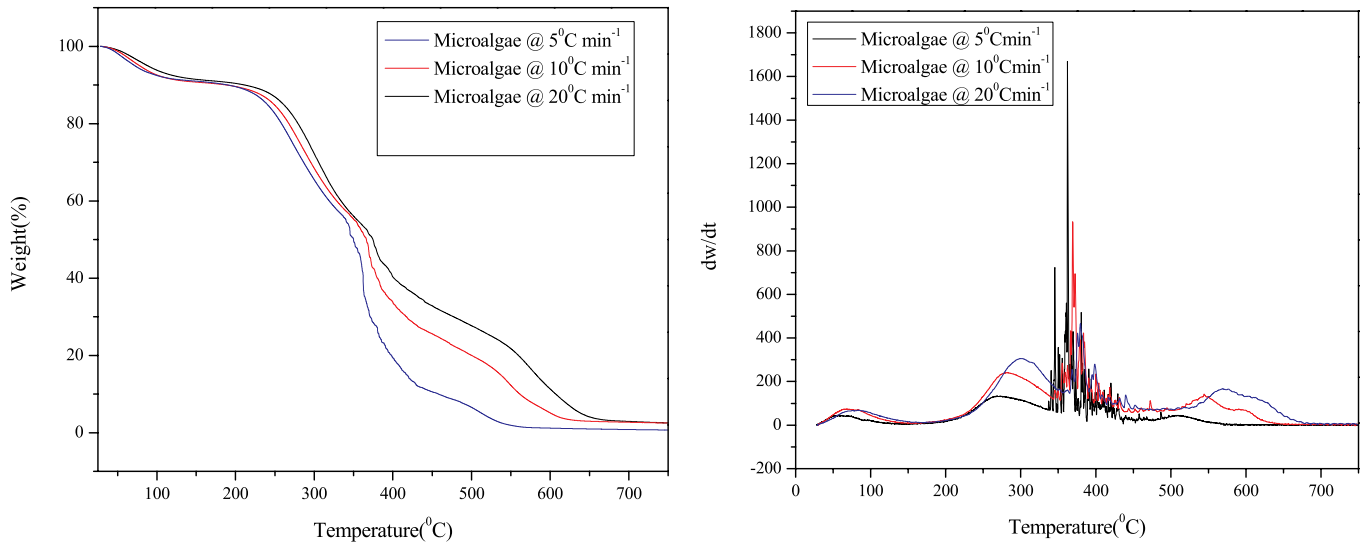

Fig. 3. a. TGA of microalgae. b. DTG thermograph of microalgae.

Table 2
Stages of thermal degradation with respect to temperature observed from DTG thermograph.

Biomass	β(°C min^{-1})	Temperature Range in °C at different stages			Remaining Char %
		1st Stage	2nd Stage	3rd Stage	
Kaner Seed	5	Up to 226	226–539	539–900	4.26
	10	Up to 190	190–535	535–900	4.26
	20	Up to 197	197–527	527–900	4.27
Flax Seed Residue	5	Up to 212	212–534	534–900	2.18
	10	Up to 201	201–530	530–900	2.69
	20	Up to 196	196–518	518–900	5.49
Micro-algae	5	Up to 230	230–539	539–900	4.26
	10	Up to 239	239–608	608–900	4.26
	20	Up to 249	249–645	645–900	4.26

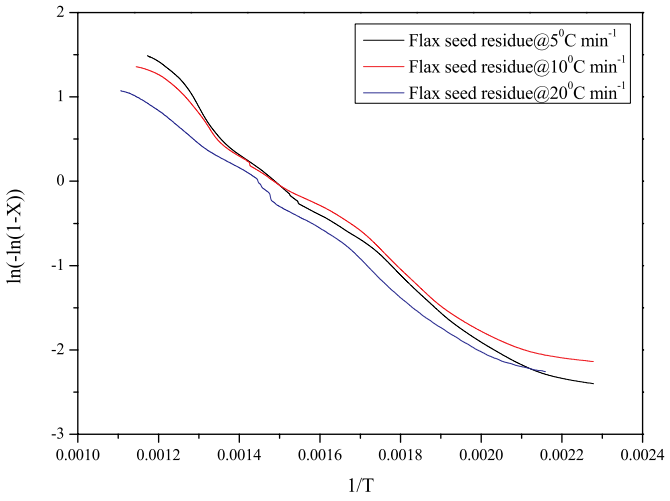

Fig. 4. Kinetic plots for thermal degradation of kaner seed.

word at higher heating rates, higher temperatures are required to achieve the same conversion level (Gomez-Rico et al., 2003; Sorum et al., 2001). The maximums of the decomposition rate are also slightly shifted towards higher temperatures. This fact can be a consequence of heat and mass transfer limitations. It means that temperature in the furnace space can be a little higher as the temperature of particle and the rate of devolatilization is higher than the release of volatilities. Because of the heat transfer limitation, temperature gradients may exist in the particle. Temperature in the core of a particle can be a bit lower than temperature on the surface, and different devolatilization processes or releasing rates can occur. At higher heating rate, the devolatilization process occurred sooner due to the increased rate of heat transfer between the reactor and the sample. The first stage weight loss occurring <250 °C found at higher temperature for microalgae at all heating rates and the relative weight loss percentage is maximum as well in case of microalgae (10.69%) as compared to kaner seed (6.79%) and flax seed residue (8.5%). The weight loss in this stage is due to loss of moisture and volatiles, also called dehydration stage.

The second stage is a sharp degradation stage where the mass loss is significant in all heating rates. This stage is known as devolatilization stage. The devolatilization includes the stepwise decomposition of the different bio-polymer fractions such as, protein, lipid, and lignocellulosic components. All the fractions present goes through the decomposition process at different temperatures. So it is considered as the active pyrolysis zone where de-volatilization and breaking of weaker chemical bonds releasing smaller molecules. All the three biomass degrade to >95% in this stage. The degradation temperature is different for three biomass types reported in Table 2 at different heating rates. In this stage, the flex seed residue shows maximum weight loss in comparison to other two biomasses which is due to the presence of high lipid/volatile fractions.

The third stage is the slow decomposition stage known as carbonisation step, and mass loss in this zone was attributed to char as well as inorganic ash decomposition.

The decomposition pattern of the biomass is supported by DTG plots shown in Figs. 1b, 2b and 3b for kaner seed, flax seed residue and microalgae respectively. A single small peak at the beginning of all the three plots indicates the first stage weight loss. The second stage of these plots consist of a number of peaks, infers the cumulative decomposition of different fractions leading to a very complex pyrolysis. Table 2 summarises the temperature ranges corresponds to the different stages of degradation. From the table it is observed that there is shift in the temperature to higher side with increase in heating rate.

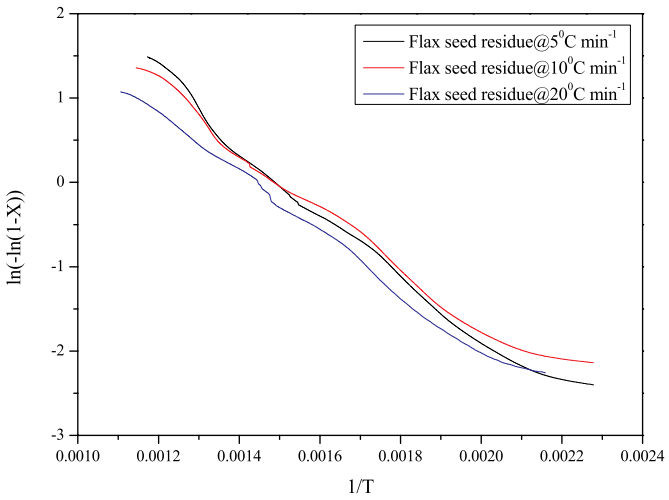

Fig. 5. Kinetic plots for thermal degradation of flax seed residue.

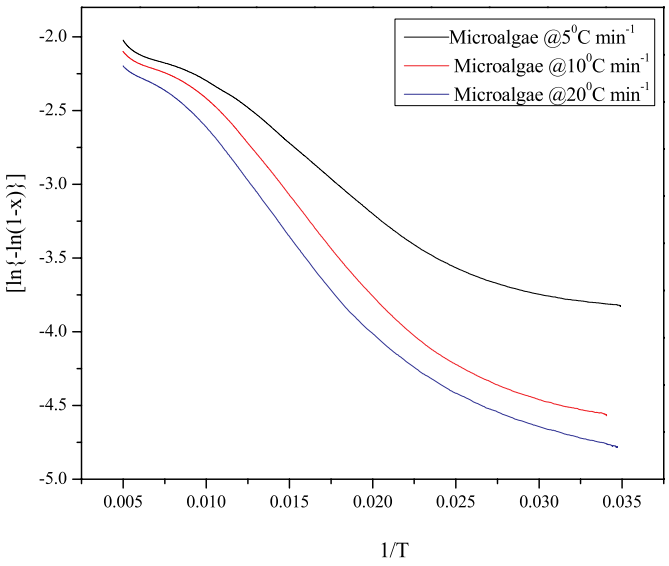

Fig. 6. Kinetic plots for thermal degradation of Microalgae.

3.3. Effect of heating rate in thermal degradation

The effect of heating rate on weight loss is visualized in Figs. 1a, 2a and 3a. The time of reaction decreases with increase in heating rate. At lower heating rate well degradation of contents occur. The pyrolytic curves of all the three samples confirm that rates of degradation are directly proportional to the heating rate. The rate of degradation also increases for different components with increase in heating rate as was evident from the DTG thermographs. The rise in the temperature with heating rate not only increases the rate of weight loss but also changed the temperature range for degradation.

3.4. Analysis of kinetic parameters

The value of activation energy of a reaction can be used to express ease or difficulty to start a reaction, while the frequency factor is a measure of effective collision of reactant molecules.

The apparent activation energy and average pre-exponential factor at different heating rate was calculated using the integral form of Arrhenius equation from the TGA data. The linear equations and R^2 values observed from the plots between ln (-ln (1 - X)) Vs (1/T) (Figs. 4–6) for each biomass samples are summarized in Table 3. The R^2 data in this table indicated that the equations are nearly linear in behavior, suggests that the kinetics of pyrolysis are not first order over the entire reaction temperature range.

The slope of the equations was used to calculate the activation energy while intercept provides the value of Arrhenius factor. The pyrolysis kinetic parameters of the three biomasses are compared in Table 3. The comparison study confirmed that the values of activation energy for all the biomasses at different heating rates are closer to each other. This may be caused heat transfer and mass transfer effect. The value of activation energy is in the order kaner seed (37.35 kJ/mol)> flax seed residue (29.88 kJ/mol)>microalgae (23.55 kJ/mol) and the difference in the value is attributed to the biochemical composition. The higher value of activation energy of kaner seed can be explained due to the presence of more volatile components including glycerides of fatty acids, protein and carbohydrates as compared to other two biomass. The trend of activation energy can also be explained in terms of elemental composition of the biomass. Kaner seed with higher carbon content, low oxygen and nitrogen content must carry more stable C–C bonds as compared to weak C–O and C–N bonds. In contrast, microalgae with very high nitrogen content must have more C–N bonds make it easier for thermal degradation (McKendry, 2002).

3.5. Thermodynamic parameter

The thermodynamic parameters such as enthalpy change, entropy change and Gibb's free energy change has been calculated at different heating rates and summarized in Table 3. The values of different

Table 3
Kinetics and thermodynamics Parameters.

Sample	Heating Rate (°C/min)	Linear Equation (Y = mx + C)	T_{av} (K)	T_p(K)	R^2	E_a (KJ/mol)	A	ΔS (J/K.mol)	ΔH (J/mol)	ΔG (J/mol)
Kaner Seed	5	Y = −4417.898x+6.673	782	669	0.984	36.730	1588.298	−198.670	31.168×10^3	16.407×10^4
	10	Y = −4447.6936x+ 6.633	781	661	0.986	36.978	1567.943	−198.677	31.482×10^3	16.280×10^4
	20	Y = −4611.983x+6.832	796	693	0.982	38.344	1976.211	−197.146	32.582×10^3	16.920×10^4
	Average					37.35	1710.81	−198.16	31.74×10^3	16.53×10^4
Flax seed Residue	5	Y = −3478.705 x + 5.292	661	658	0.986	28.921	447.6933	−209.059	23.451×10^3	16.101×10^4
	10	Y = −3497.295x + 5.008	664	678	0.996	29.076	452.3334	−211.300	23.439×10^3	16.670×10^4
	20	Y = -3806.730x + 5.785	675	701	0.986	31.649	541.489	−222.566	25.821×10^3	16.782×10^4
	Average					29.88	480.50	−214. 31	24.23×10^3	16.51×10^4
Microalgae	5	Y = −2812.26x+4.310	589	633	0.960	23.381	167.6171	−216.905	18.118×10^3	15.541×10^4
	10	Y = −2841.765x+ 4.183	600	641	0.962	23.626	186.3541	−216.727	18.128×10^3	15.637×10^4
	20	Y = −2844.776x+4.505	611	653	0.953	23.651	202.4753	−215.593	18.222×10^3	15.900×10^4
	Average					23.5	185.48	−216.40	18.15×10^3	15.69×10^4

thermodynamic parameters follow the order kaner seed > microalgae > flax seed residue. As large amount of heat is required for the degradation process, the process is endothermic and thus the value of ΔH is positive and the average value is 31.74×10^3 $Jmol^{-1}$for Kaner seed, $24.23 \times 10^3 Jmol^{-1}$ for flax seed residue and from 18.48×10^3 $Jmol^{-1}$for microalgae at different heating rates from 5°$Cmin^{-1}$ to 20°$Cmin^{-1}$. The higher heat requirement for thermal degradation in case of kaner seed can be explained due to presence of more numbers of strong C–C bonds as compared to C–O and C–N bonds (McKendry, 2002). The higher ΔH for kaner seed may also be due to higher lipid and volatile concentration.

The value of entropy show small increment, with few exceptions, with increase in heating rate. This is due to the fact that the transformation of more organized structure to less organized with increase in heating rate (Turmanova et al., 2011). The negative values of ΔS obtained would indicate that the formation of the activated complex is connected with a decrease of entropy, that is the activated complex is a "more organized" structure compared to the initial substance as entropy is usually a measure of randomness i.e. the sample (reactant) has undergone some chemical or physical aging processes due to thermal application, and then finally reached to thermodynamic equilibrium state (Kim et al., 2010; Xiang et al., 2017; Sokoto et al., 2016). Entropy change of pyrolysis of kaner seed is found more (−198.16 J/K.mol) as compared to that of other two biomasses. It means, in case of kaner seed, decrease of disorderness of products from the reactant required more energy as compared to other two. There is obviously a relationship between the values of E_a, A and ΔS. Higher values of A correspond to higher values of E_a and less negative values of ΔS (Sharma and Rajeswara Rao, 1999). The value of ΔG for the reaction was found to be positive which indicate that the reaction don't proceed spontaneously. Obviously the thermal degradation process is a non-spontaneous process and here entropy is negative and Gibb's free energy is positive (https://www.chem.fsu.edu/chemlab/chm1046course/gibbs.html). Moreover, the free energy has quite similar value at different heating rates for different biomasses.

4. Conclusions

The TGA experiment of three different types of biomass samples such as seed, seed residue an microalgae showed that the heating rate has an important role on the degradation reaction. The kinetic parameters of three different biomasses using TGA were determined using Coats Redfern method. Different biomasses are found to give different kinetic and thermodynamic parameters. These parameters are slightly affected by the change in heating rates. The average value of activation energy of the thermal degradation is found to be 37.35 kJ/mol for kaner seed, 29.88 kJ/mol for flax seed residue and 23.55 kJ/mol for microalgae. The order of the different thermodynamic parameters are Kaner seed > flax seed residue > microalgae. The average value of ΔH, ΔS and ΔG are found to be 31.74 J/mol, −198.16 J/K.mol and 16.4×10^4 J/mol for kaner seed, 24.23×10^3 J/mol, −214. 31 J/K.mol and 16.51×10^4 J/mol. for flax seed residue and 18.15×10^3 J/mol, −216.40 J/K.mol, 15.69×10^4 J/mol respectively. The determination of the kinetic and thermodynamic parameters would provide information to design more effective conversion systems.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.bcab.2019.101315.

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