Experimental investigation of kinetic parameters of bamboo and bamboo biochar using thermogravimetric analysis under non-isothermal conditions

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Research Article

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Experimental investigation of kinetic parameters of bamboo and bamboo biochar using thermogravimetric analysis under non-isothermal conditions

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Abstract

The subject of this research is the thermogravimetric analysis of bamboo and bamboo biochar in an inert environment at 10, 20, and 30 °C/min. The physicochemical characterizations of bamboo and bamboo biochar were carried out as per the standard methods. Vacuum pyrolysis was used for the bamboo biochar. The FWO (Flynn-Wall-Ozawa) and KAS (Kissinger–Akahira–Sunose), methods determined thermodynamic and kinetic parameters within the active pyrolysis zone. Thermal degradation bamboo biomass undergoes several steps of loss of mass, including moisture loss, passive and active pyrolysis. Between 180 °C and 395 °C, the active pyrolysis zone accounted for 50 to 55 percent of the mass loss. For FWO and KAS models, bamboo biochar had lower activation energy values (99.23 and 96.07 kJ/mol) than bamboo biomass (262.5303 and 266.62 kJ/mol). The findings of the study for bamboo and its biochar revealed a significant opportunity in the agro industry for designing and building pyrolysis reactors for long-term biofuel generation**.**

Keywords: Bamboo, pyrolysis, biochar, kinetics, TG/DTG evaluation, activation energy

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1. Introduction

Fossil fuel energy is valuable for economic and long-term growth [1]. On the other hand, increased population and industrialization have played a significant role in inflating global energy demand, resulting in uncontrolled energy use. Moreover, the release of hazardous gases (CO_2, SO_x, NO_x) due to the indiscriminate burning of fossil fuel reserves has a negative impact on the environment [2]. Therefore, the use of renewable energy increases as the global energy demand rises [3]. Among the various sustainable energy sources like solar, biomass, hydropower, and wind, biomass is an environmentally friendly and carbon-neutral energy sources [4]. It's also been proven that biomass releases fewer gaseous pollutants during combustion [5]. Many countries have large forests and agricultural areas where biomass resources provide about 40–50% of the required energy in many developing countries [6].

Biomass production in India ranges from 450 to 500 million tonnes. Biomass accounts for 32 percent of the country's overall primary energy consumption [7]. Biomass has the potential to supplement coal to the tune of 260 million tonnes. Every year, this could result in a savings of around Rs. 250 billion [8]. There are mainly two processes for biomass conversion: biological and thermochemical conversion processes [9]. In thermochemical conversion, pyrolysis is the most feasible process that extracts energy from biomass into various products like biochar, bio-oil, and syngas [10]. Biomass carbonization is influenced by reaction conditions such as heating rate, biomass composition, biomass particle size, pressure, and residence time. The application of these biomass technologies for energy generation necessitates a thorough knowledge of biomass thermal decomposition properties (such as cellulose, hemicelluloses, and lignin) and reaction kinetics, which are important for better understanding and improving pyrolytic conversion. Thermogravimetric analysis is one of the most common methods for examining pyrolysis reactions' kinetic and thermodynamic parameters [11]. Thermogravimetric investigations, which are required for estimating the kinetic factors of solid-state processes, record variations in mass loss as a function of temperature and time. The two most common methods for quantitatively describing biomass pyrolytic kinetics are model-free (iso-conversional) and model-fitting [12]. Model-free techniques are the most widely used in kinetics analysis because the kinetic parameters are obtained from data gathered at various heating rates,

making them more reliable, ideal, and accurate for kinetic analysis than single heating rate or model-fitting methods [13]. As a result, iso-conversional methods, FWO and KAS are frequently used to estimate the thermodynamic and kinetic parameters of the pyrolysis process of various biomass like activation energy, enthalpy frequency factor, Gibbs free energy, entropy and reaction order etc. [14] [15].

Compared to woody biomass, bamboo has a high yield and a short growth cycle, making it a promising renewable biomass [16]. Bamboo is used for various applications like making bamboo houses, mats, knives, activated carbon, papermaking, and many others [17]. In recent times, a new approach of employing bamboo as an alternative energy source to replace fossil fuels that have gone out of stock has been introduced to the list [18]. Bamboo can potentially be used to generate energy in the future [16]. This new approach must be thoroughly investigated to maximize the use of bamboo biomass while avoiding or minimising any potential risks to mankind and the environment. However, the range of research on bamboo (woody biomass) is relatively restricted. As a result, studying bamboo's pyrolysis properties is extremely beneficial to comprehension the process conversion and utilizing bamboo as a biofuel. The main components of bamboo biomass are cellulose, hemicellulose, and lignin, with 35–45 percent, 15–20 percent, and 15–25 percent, respectively. Chen et al. studied the effects of rate of heating at 5, 10, 20, and 30^0C/min on the product properties of moso bamboo. They observed that the pyrolysis technique can be broken down into several steps and is similar to that of other biomasses. Hemicelluloses, cellulose, and lignin decompose at temperatures ranging from 200 to 380 degrees Celsius, 250 to 380 degrees Celsius, and 180-900 degrees Celsius, respectively [19]. There are some researchers examined kinetics analyses of bamboo wasete. Mallick et al. examined the kinetic analysis of bamboo waste where the E_α (average activation energies) values for the FWO and KAS methods were found to be 181.973 kJ/mol and 183.113 kJ/mol for the degree of conversion 0.1–0.9 [20]. In addition to this, Poletto et al. investigated the average activation energy of pine and eucalyptus wood. They found that the values for FWO for the rate of conversion 0.1–0.8 were 191 and 208 kJ/mol, respectively [21].

The present study investigated the thermal degradation of bamboo and bamboo biochar produced from vacuum pyrolysis by using thermogravimetric. The bamboo and bamboo biochar were thermally degraded at 10, 20 and 30 °C/min. The KAS (Kissinger-Akahira-Sunose) and FWO (Flynn-Wall-Ozawa method) are two iso-conversional methods used to calculate Ea

(activation energy) at 0.1 to 0.9 conversion rate. In addition, Thermodynamic variables such as enthalpy, entropy, and Gibbs free energy were also calculated using iso-conversional models.

2. Methodology

2.1 Feedstock preparation

The bamboo (B) was acquired from the experimental learning field of MPUAT, Udaipur, India. Bamboo wood can be cut into 2-5 cm pieces to produce biochar. The bamboo pieces were dried in a solar dryer for 24 hours to remove excess moisture. For physicochemical properties and thermogravimetric analysis, the materials are crushed and sieved to acquire particle sizes of less than 100 microns.

2.2 Biochar production

Two kilograms of biomass feedstock were pyrolyzed at 600 °C for 60 minutes under reduced pressure of 18–25 kPa in a vacuum pyrolysis reactor. It was found that the bamboo biomass (B) was carbonised and turned into bamboo biochar (BB). Both samples were ground in a grinder to obtain the smallest particle size possible. The powdered B and BB samples were kept in an airtight container to prevent further moisture attained.

2.3 Physicochemical properties

The moisture, ash, and volatile matter of bamboo and bamboo biochar samples were determined using ASTM D3174, ASTM D3173, and ASTM D3175 standard procedures, respectively [22]. The HHV (higher heating value) of B and BB was obtained using a bomb calorimeter. The cellulose, hemicellulose, and lignin percentages in B feedstock were obtained from TGA using the DTG curve. Using an elemental analyser, the available carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) content in B and BB were examined. To achieve the average value, all of the abovementioned tests were performed three times using the standard error experiment.

2.4 Thermo-gravimetric analysis

The produced B and BB material were analysed in a thermogravimetric analyzer, (Hitachi STA7300) obtain a thermal decomposition pattern of feedstock. In TG analysis, temperature from 30 to 900 °C, the finely ground material is heated at 10, 20, and 30 °C/min. To avoid undesired oxidation reactions inside the pyrolysis zone, nitrogen (N2) gas was provided at 80 ml/min flow rate in all experimental runs. With the help of TG data, the differential thermo gravimetric values (DTG) were updated using Origin Pro software.

2.5 Kinetic analysis

The kinetic analysis of feedstock gives crucial data for developing and optimizing biofuel generation systems. Using non-isothermal iso-conversional methods, the kinetic analysis of bamboo and its biochar obtained from vacuum pyrolysis was carried out. Biomass pyrolysis is a thermochemical conversion process that can be described by equation 1:

$$\text{Feedstock(Bamboo)} \xrightarrow{k\,(T)} \text{Soild biochar} + \text{Volatiles (Gas + Tar)} \qquad (1)$$

Where, k- constant rate

Under non-isothermal conditions, the conversion rate from solid (biochar) state to volatile (Gas+ liquid) product following reaction can be used to described [23].

$$\frac{d\alpha}{dt} = k\,(T)\, f\,(\alpha) \qquad (2)$$

Where, α (degree of conversion) can determined by the mass-loss given as follows, [24]:

$$\alpha = \frac{m_0 - m_T}{m_0 - m_f} \qquad (3)$$

Constant rate depend on temperature 'T' which is given by Arrhenius equation

$$k(T) = Ae^{-\left(\frac{E_a}{RT}\right)} \qquad (4)$$

Combining Equations (2) and (4) gives

$$k(T) = Ae^{-\left(\frac{E_a}{RT}\right)} f(\alpha) \qquad (5)$$

Where,

m_0, m_f - Initial and final mass

m_T - Instantaneous mass

T - Temperature, K

A - Pre-exponential factor (s^{-1});

Ea - the apparent activation energy, $kJ.mol^{-1}$;

R - Gas constant, $J.mol^{-1}.K^{-1}$.

According to Apaydin-Varol et al., the f (α) (expression of the function) is used to describe (n) order of reactions and is directly proportional to the concentration of non-degraded material [25]. As a result, expression of the function is mathematically expressed as follows:

$$f(\alpha) = (1 - \alpha)^n \qquad (6)$$

Substituting equation (6) for equation (5) yields the following equation.

$$k(T) = Ae^{-\left(\frac{E_a}{RT}\right)} f(1-\alpha)^n \qquad (7)$$

During the non-isothermal method, the β (heating rate) remains linear to increase the temperature.

$$T = T_0 + \beta_t \qquad (8)$$

$$dT = \beta dt \qquad (9)$$

Where, T_0, are initial temperature.

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\,\frac{1}{\beta} \qquad (10)$$

Where; dt/dT = (1/β) and dα/dt = isothermal reaction rate, and dα/dT = non-isothermal rate of reaction. Equation (7) can be substituted into Equation (10) to obtain formula of the rate law for non-isothermal conditions:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\left(\frac{E_a}{RT}\right)} f(1-\alpha)^n \qquad (11)$$

This Equation (11) refers to the biomass decomposition. The kinetic parameters of the are calculated using this expression and was integrated

$$g(\alpha) = \int_0^a \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\int_{T0}^{T} e^{-\frac{E_a}{RT}}\, dT \qquad (12)$$

$$g(\alpha) = \frac{AE_a}{\beta R}\int_X^{\infty} u^{-2}e^{-u}\, du = \frac{AE_a}{\beta R}\, P(X) \qquad (13)$$

Where, P(x) and Ea/RT are the exponential integral.

2.6 Iso-conversional methods

For non-isothermal thermogravimetric analysis, fitting models or free models can be used to evaluate kinetic parameters. As a function of temperature or conversion, the kinetic parameters are determined. In the iso-conversional method, reaction rate is solely determined by thermogravimetric data and temperature, and it required minimum three different heating rates [26].

Complex processes involving a series of chemical reactions are described using iso-conversional approaches. Their exact reaction mechanism, however, is unknown. Therefore, differential or integral approaches can be used to describe iso-conversional methods. The current research examined kinetic parameters from two iso-conversional methods: FWO (Flynn–wall–Ozawa) and KAS (Kissinger–Akahira–Sunose).

2.6.1 Flynn–Wall–Ozawa (FWO) method

The Flynn–Wall–Ozawa is a model-free iso-conversional method. For obtains the activation energy (E_α) the ploting ln β_i versus 1/Tαi for a given value of conversion (α) at different heating rates (β),

$$\ln\left(\beta_i\right) = \ln\left(\frac{AE\alpha}{RG(\alpha)}\right) - 5.331 - 1.052\frac{E\alpha}{RT\alpha i} \quad (14)$$

Where βi and αi the rate of heating for a given value of i and g (α) is constant. The slope $1.052\frac{E\alpha}{RT\alpha i}$ is used to estimate Eα (activation energy).

2.6.2 Kissinger–Akahira–Sunose (KAS) method

KAS is also model free iso-conversional method for calculating the Eα (activation energy) as given as follows.

$$\ln\frac{\beta i}{T^2\,\alpha i} = \left(\frac{AR}{E\alpha\, G(\alpha)}\right) - \frac{E\alpha}{RT\alpha i} \quad (15)$$

The activation energy calculated using the slope of the equation derived from $\ln\frac{\beta i}{T^2\,\alpha i}$ verses $\frac{1}{T\alpha i}$. The slope of the straight line (Eα/R) using for calculated activation energy. In comparison to FWO, it provides more precise or exact activation energy estimates [27].

2.6.3 Thermodynamic parameters

FWO and KAS models have been used to estimate E_α (activation energy), and also used to calculate thermodynamic parameters such as A (pre-exponential factor), ΔH (enthalpy), ΔG (Gibbs energy), and ΔS (entropy) etc. listed by below equation 16,17,18 and 19, respectively [15].

$$A = \beta E_\alpha \exp\frac{\left(\frac{E\alpha}{RTm}\right)}{RT_m{}^2} \quad (16)$$

$$\Delta H = E_\alpha - RT_\alpha \quad (17)$$

$$\Delta G = E_\alpha + RT_m \ln\left(\frac{T_m k_B}{hA}\right) \quad (18)$$

$$\Delta S = \left(\frac{\Delta H - \Delta G}{T_m}\right) \quad (19)$$

Where, Tm, kB and h are the peak temperature, Boltzmann constant and plank constant, in DTG curve respectively.

3. Results and discussions

3.1 Characteristics of bamboo and bamboo biochar

Biomass characterization is crucial in determining its physico-chemical properties, which are significant in deciding its ability as a source of fuel. Table 1 summarises the physico-chemical and calorific values of B and BB determined in the current study. Bamboo has a moisture content of 5.26 percent, which is less than 10% and makes it acceptable for thermal processing [28]. According to Table 1, bamboo biomass has lower ash content and a higher volatile matter content than other agricultural residues, 2.18% and 77.12%, respectively. Biomass fuels with low ash and high volatile matter are more suitable for thermochemical conversion [29]. When feedstock has a higher ash percentage, it usually has an inverse proportional with biochar heating value of the biochar produced [30]. It also slows down the burning process and causes aggregation and fouling [20]. The heating value of bamboo biomass is 18.50 MJ/kg. Bamboo has a C (carbon) 45.05%, H (hydrogen) 5.57 %, N (nitrogen) 0.56 %, and an O (oxygen) 39.42 %. The low percentage of nitrogen in bamboo means it produces fewer nitrogen oxide emissions during combustion. [20]. Compared to raw bamboo biomass, bamboo biochar has contained less percentage of ash and volatile matter content. Therefore, thermochemical conversion might be able to remove some of the oxygen-based chemical groups in organic waste [31]. The produced biochar had a heating value of 28.25 MJ/kg, greater than the other biochar sample produced from agro-waste [32].

As shown in Table 2, the combined hemicellulose and cellulose content of bamboo biomass is around 67.96 percent, with hemicelluloses and cellulose accounting for 45.34 percent and 22.62 percent, respectively, and a lower lignin content of 21.83 percent. Endothermic reactions are involved in the decomposition of biomass with high lignin content [33].

Table 1: Physico-chemicals properties of bamboo and its biochar

Analysis	Bamboo (present study)	Moso bamboo [34]	Bamboo Biochar (Present study)	Moso bamboo Biochar [19]
Proximate analysis				
Moisture content	5.26	8.67	1.3	-
Volatile matter	77.12	74.81	6.29	5.27
Ash content	2.18	2.56	5.36	4.89
Fixed carbon	15.44	13.96	87.05	89.84
HHV (MJ/kg)	18.50	-	27.8	28.25
Ultimate analysis				
C	45.05	44.87	88.34	89.71
H	5.57	5.73	2.01	1.19
O (by difference)	39.42	38.32	8.33	7.91
N	0.56	0.71	1.2	1.05
S	0.03	0.01	0.12	0.14

Table 2: Lignocellulosic percentages of bamboo

Cellulose	Hemicellulose	Lignin	Extractives	References
45.34	22.62	21.83	10.21	Present study
46.45 ± 3.0	19.23 ± 3.0	18.17 ± 2.0	-	[20]

3.2 Thermogravimetric analysis of bamboo and bamboo biochar

The thermal behaviour of bamboo and its biochar was evaluated in a thermogravimetry furnace at rate of heating of 10, 20, and 30 ^{0}C/min was shown in Fig 1 and Fig 2 respectively. In the TG analyzer's thermal performance, bamboo and bamboo biochar go through three different phases: moisture removal, devolatilization, and biochar formation. Biomass mainly consists of, cellulose, hemicellulose, and lignin. During pyrolysis, they respond differently at specific temperatures and heating rates. Hemicelluloses, cellulose, and lignin decompose at temperatures ranging from 200 to 380 degrees Celsius, 250 to 380 degrees Celsius, and 180-900 degrees Celsius, respectively [19]. Thermal decomposition of bamboo mainly occurs in three different temperature stages, viz., drying, devolatilization, and char formation. At temperatures below 200°C, the physically and externally bound moisture from bamboo and its biochar is removed in the initial phase. The second stage entails of pyrolysis, hemicellulose, and cellulose thermally decompose, with the decomposition rate reaching its maximum. The second phase is divided into

two parts: left and right sides. Left side indicates the decomposition of hemicelluloses. At moderate temperatures, biochar degrades more slowly; this could be due to the char's low volatile component content [35]., The bamboo biochar indicates the highest temperature of degradation in the second region As shown in Fig. 2, which was possible due to the biochar's low volatile content and high availability of fixed carbon, which causes decomposition to occur at a higher temperature [36].

This research looked into how the temperature range in the bamboo pyrolysis process and the mass loss rate were influenced by the heating rate according to the DTG and TG curves represented in Fig 1 and Fig. 2, respectively. Furthermore, increasing the heating rate may cause the DTG and TG curves very as the temperature rises, but the total mass loss remains constant. Due to the low thermal conductivity of biomass, the effects of heat and mass transfer increase as the pyrolysis rate increases [37]. As a result, the TG curves shifted to a higher temperature. Overlapping curves indicate a complex composition of hemicellulose, cellulose, and lignin in bamboo biomass [38]. **Table 3** summarises the intensity of decomposition and the corresponding temperatures for the various heating rates of bamboo. The first degradation peak in the DTG curve is depicted in Fig. 1, which is separated into three stages: Stage I (30 to 180 ^{0}C) is dehydration stage in this stage some moisture and extractives are released, Stage II (180 ^{0}C to 395 ^{0}C) about 50 to 55 % of mass loss occurred this is the active pyrolysis zone where hemicellulose and cellulose decompose, with hemicellulose decomposition causing the first peak of left side, and Stage III (395^{0}C to 579 ^{0}C), lignin degradation occurred in this zone, as well as some endothermic and exothermic reactions takes placed between organic compounds. Lignin degradation begins at 420 ^{0}C and reaches a broad peak before slowing down to a closing carbonization temperature of 580 ^{0}C. Lignin has better heat stability requires a higher temperature (100–900 ^{0}C) to degrade completely of the slower rate of reaction [39] [40] [41]. The rate of devolatilization was almost stable after 600 ^{0}C, indicating that the pyrolysis had completed this stage, indicating the biochar's formation. This means that the devolatilization process has completely stopped after 600 ^{0}C. The most mass degradation occurred in second stage of the curve. As a result, stage II is considered active pyrolysis for determining the kinetics, and stages I and III are considered passive pyrolysis zones [42].

Thermal performance of bamboo biochar was accomplished at 10, 20, and 30 °C/min with the help of a thermogravimetric analyser. Fig. 2 shows that the first peak shows at the

temperature of 40 to 60 ^{0}C at which biochar is released with moisture. At temperatures of 170 to 390 ^{0}C, the peak totally disappeared when it was compared with raw bamboo. The least mass loss (1.5-2%) was observed at temperatures ranging from 390 to 480 ^{0}C, indicating the highest thermal stability of obtained biochar [43]. When the temperature was raised from 480 to 740 °C, the maximum weight loss was observed, which is about 75–78%, whereas there was no loss of mass in the bamboo biochar when the temperature was raised above 740 °C. These studies indicate that the pyrolysis process had no effect on the characteristics of biochar after a period of time [44]. A similar graph pattern was found by [45] in their kinetic and thermal study.

Table 3: Pyrolysis parameters relevant to heating rates for bamboo biomass

Bamboo					
Parameters →	**β, ◦C/min**	**Ti,^{0}C** (Initial temperature)	**Tf, ^{0}C** (final temperature)	**Tm, ◦C** (Temperature at max decomposition)	**DTG max, %/min** (max decomposition rate)
Stage I	10	30	171	52	1.33
	20	30	175	63	3.09
	30	30	180	67	4.69
Stage II	10	171	380	335	6.79
	20	175	385	340	20.79
	30	180	395	344	38.49
Stage II	10	380	565	482	2.19
	20	385	570	483	6.60
	30	395	579	493	13.14

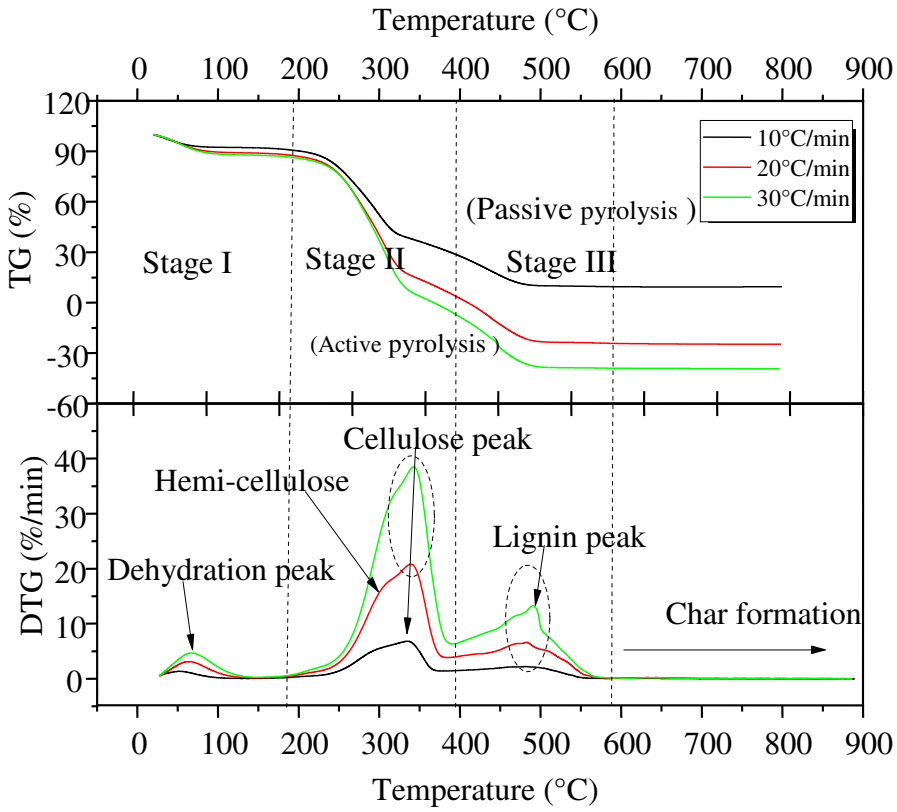

Fig. 1 Thermal decomposition behaviour of raw bamboo at heating rate of 10 ^{0}C/ min, 20 ^{0}C/min and 30 ^{0}C/min showing different peak of dehydration, devolatilization, and biochar formation.

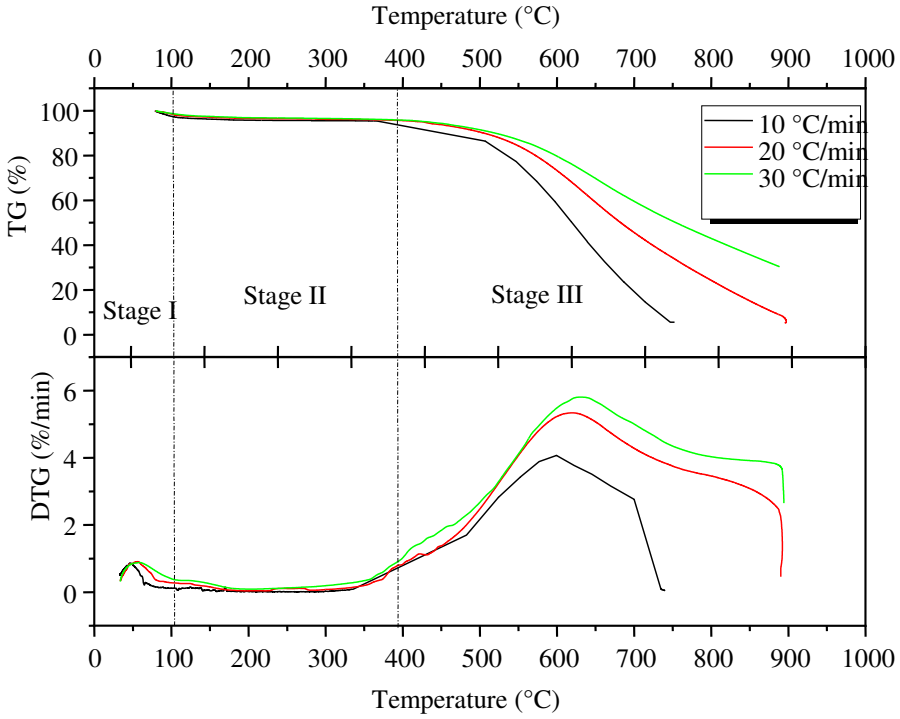

Fig. 2 Thermal decomposition behaviour of bamboo biochar at heating rate of 10 ^{0}C/ min, 20 ^{0}C/min and 30 ^{0}C/min for analyzing the mass loss at different stages.

3.2 Kinetic analysis

Iso-conversional methods were used to determine the kinetic parameters of bamboo and bamboo biochar such as A (pre-exponential factor) and E_α (activation energy). The apparent activation energy of bamboo and bamboo biochar determined with FWO and KAS were shown in the Fig. 3(a & b) and Fig 4 (a & b), respectively. Fig 3 (a & b) and Fig 4 (a & b) shows all lines are nearly parallel, indicating that the apparent activation energy can be closed and possibly indicating single reaction mechanisms [46]. As per, the FWO model, E_α can be evaluated from the slope at increasing degrees of conversion estimated from the linear plots of $ln(\beta/T_2)$ versus 1/T as appear in Fig. 3 (a & b), using equation(14). In the KAS method E_α was calculated using the and eq (15), Fig 4(a & b) depict the linear plots of $ln(T)$ versus 1/T. The activation energies for bamboo were determined to be within the range of 183 –327 kJ/mol using the FWO and KAS models of 0.1–0.9 in the conversion range, respectively. The average activation energies for bamboo using the Flynn–wall–Ozawa and Kissinger–Akahira–Sunose models were observed to be 262.5303 and 266.62 (KJ/mol) respectively. The difference in all average values of activation

energy noted is less than 5%, which justifies its reliability and accuracy [47]. The activation energy values obtained in this study were found to be very close to timber, which was determined by FWO and Starink models to be 300-222 KJ/mol respectively [48] and higher side to those of bamboo subfamily (200-225 KJ/mol), and bamboo waste (181.97- 183 KJ/mol) Flynn–wall–Ozawa and Kissinger–Akahira–Sunose models, respectively [34] [20]. Several factors influenced the activation energy values, including the different kinetics models, heating rate, type of biomass, and particle size [49]. The model-free methods' E_α (activation energy) differ due to estimates and calculations used to solve the temperature integral. These findings suggest that bamboo could be used as a feedstock for biomass thermal conversion to bioenergy.

Table 4 illustrate that as the activation energy increased as the degree of conversion rate (α) increased from 0.1 to 0.9, the, indicating that the complex reaction may have occurred at a higher temperature [50], thermal cracking and devolatization of wood components occur at this stage, implying a series of reaction [51]. The E_α values increased from 189 to 326 KJ/mol and from 189 to 335 KJ/mol for FWO and KAS, shown in Fig 5 (a & b). The linear correlation coefficients for determining the activation energy ranged from 0.88 to 0.99, which was nearly suitable for liner plots.

The FWO and KAS methods were used to compute the activation energy values for bamboo biochar generated at 600 °C in order to estimate its thermal potential for energy generation via combustion. As shown in Table 5, the average values E_α bamboo biochar of for the FWO and KAS models were 99.23 and 96.07 kJ/mol, respectively. Bamboo biochar had a lower E_α value than raw bamboo, indicating that the biochar produced from the biomass can easily react with the low energy requirement shown in Fig 5b. As biochar has high carbon contain, higher heating value, higher lignin composition, and higher aromaticity, it easily reacts with a low-energy supply [47] . Fig 5 (a & b) shows the activation energy change for bamboo and bamboo biochar verses degree of conversion using the FWO and KAS methods.

The pre-exponential factor (A) is crucial for biomass pyrolysis optimization. For the model-free kinetic approach, E_α and A factor have a mathematical relationship such that changing (E_α) according to the pyrolysis extent changes (A) as well [52]. In the current research, the pre-exponential factor was calculated by using Coats-Redfern method as given in equation (12). The values of A (pre-exponential factor) from FWO and KAS ranges for 2.37×10^{13} to 4.35×10^{24} S^{-1}, 2.79×10^{13} to 2.31×10^{25} S^{-1} respectively. The wide variation in pre-exponential

factor with respect to the degree of conversion rate denotes the feedstock natural structure composition complexity and the complex pyrolysis reaction [53]. The pre-exponential factor is the intersection of three different parameters, such as activate energy, gas constant, and heating rate. The value of pre-exponential is greater than 10^9 S^{-1} indicates the reactive system simple complex reaction and the value 10^9 S^{-1} indicates less reactive with a closed complex reaction [54]. The pre-exponential factor values for all KAS and FWO models were summarised in Table 4 using Eq (12).

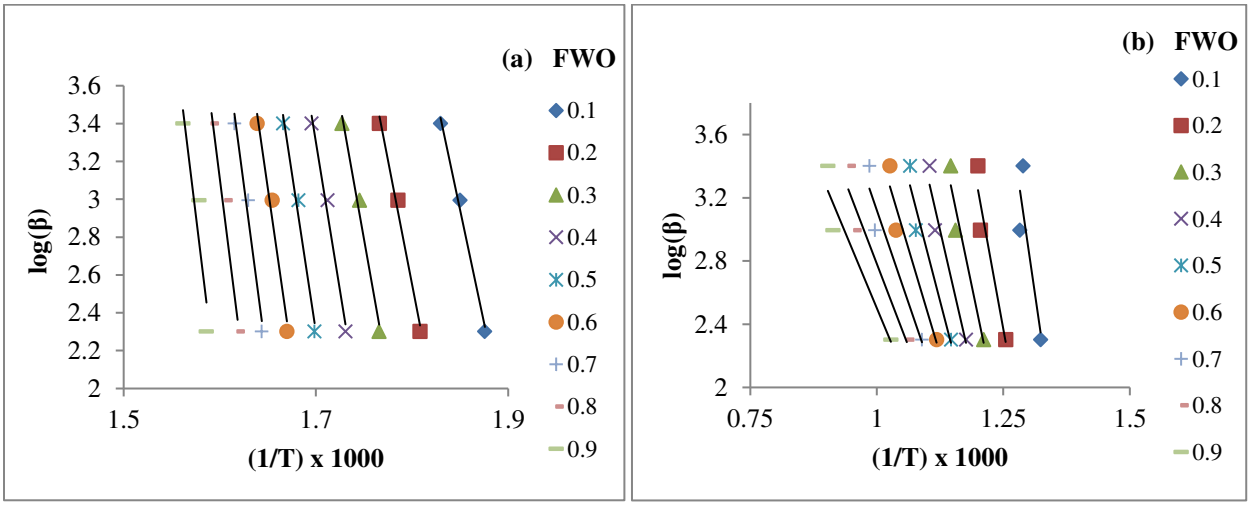

Fig. 3 (a & b) Linear plots of *ln* (β/T₂) versus 1/T for raw bamboo biomass and bamboo biochar respectively using FWO method for calculating the activation energy.

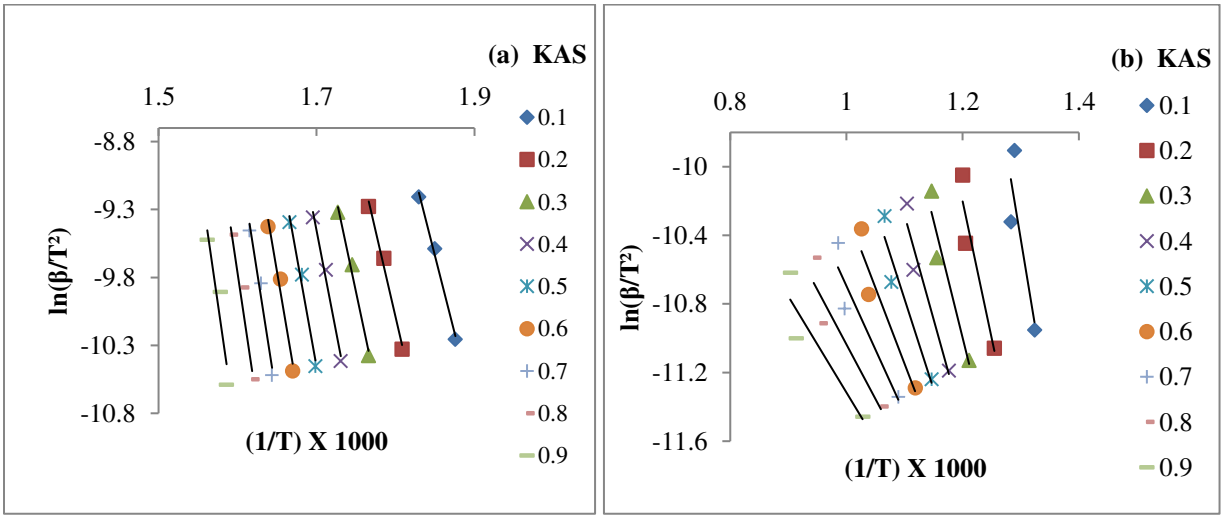

Fig 4 (a & b) Linear plots of *ln*(T) versus 1/T for raw bamboo biomass and bamboo biochar respectively using KAS method for calculating the activation energy.

Table 4 'E_α' (activation energy) and 'A' (pre-exponential factor) for the bamboo biomass significant to degree of conversion (α) at 10 ^{0}C/min.

Conversion factor	FWO			KAS		
α	E_α (KJ/mol)	A(S^{-1})	R^2	E_α (KJ/mol)	A(S^{-1})	R^2
0.10	189.13	2.37×10^{13}	0.9934	189.98	2.79×10^{13}	0.9928
0.20	206.82	6.74×10^{14}	0.9893	208.27	8.87×10^{14}	0.9883
0.30	225.70	2.38×10^{16}	0.9866	227.91	3.61×10^{16}	0.9854
0.40	247.48	1.44×10^{18}	0.9857	250.64	2.61×10^{18}	0.9845
0.50	264.75	3.71×10^{19}	0.9814	268.65	7.72×10^{19}	0.9800
0.60	279.45	5.87×10^{20}	0.9744	283.93	1.36×10^{21}	0.9726
0.70	303.75	5.59×10^{22}	0.9734	309.33	1.59×10^{23}	0.9717
0.80	318.72	9.26×10^{23}	0.9680	324.94	2.96×10^{24}	0.9660
0.90	326.99	4.35×10^{24}	0.8757	335.92	2.31×10^{25}	0.8687
Average	262.53		-	266.62		-

Table 5 'E_α' (activation energy) for the bamboo biochar significant to degree of conversion (α) at 10 ^{0}C/min.

Conversion factor	FWO		KAS	
α	**E_α (KJ/mol)**	**R^2**	**E_α (KJ/mol)**	**R^2**
0.10	173.87	0.7554	174.59	0.7277
0.20	134.35	0.9163	133.02	0.9003
0.30	118.55	0.9427	116.40	0.9289
0.40	102.74	0.9456	99.77	0.9302
0.50	94.84	0.9427	91.45	0.9233
0.60	79.03	0.9370	74.83	0.9108
0.70	71.13	0.9251	66.51	0.8869
0.80	63.22	0.9210	58.20	0.8720
0.90	55.32	0.9123	49.88	0.8483
Average	99.23	-	96.07	-

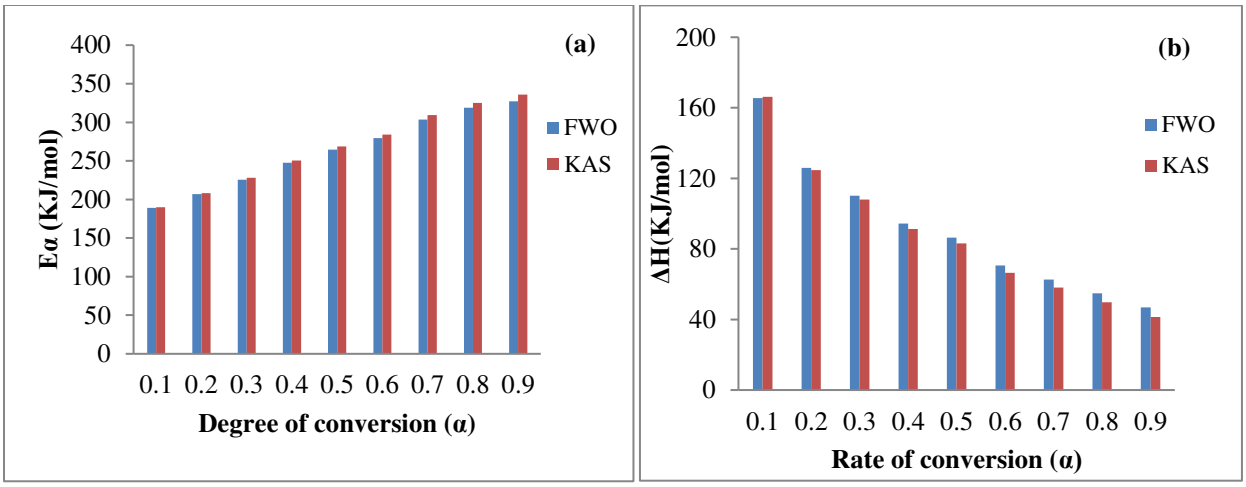

Fig 5 (a & b) Activation energy value changes with respect to degree of conversion (α) for FWO and KAS models for bamboo biomass and bamboo biochar respectively.

3.3 Thermodynamic parameters analysis

Figure 6, 7 and 8 shows changes in enthalpy (ΔH), Gibbs free energy (GΔ), and entropy (ΔS) for both bamboo biomass as a function of conversion rate 'α' using the FWO and KAS methods. The interactions between constituents become more intense during the pyrolysis process as the heating rate increases [55]. A low heating rate, such as 10 °C/min, was proposed to mitigate the effects of such an interaction. The change in enthalpy during the pyrolysis process indicates a difference in energy between biomass and its end products [15]. The ΔH values of bamboo increased with conversion degrees, which fell between 183 to 330 kJ/mol for both FWO and KAS methods, as shown in Table 6. The change in enthalpy value for bamboo biomass rises as the rate of conversion rises, as shown in Fig 6, and for bamboo biochar it first increased for the rate of conversion of 0.1–0.3 and then decreased to 0.4–0.9, respectively which shown Table 6. The average enthalpy values for bamboo biomass FWO and KAS are 257.10 and 261.19, respectively. In Tables 4 and 6, a minimal difference in energy (5 kJ/mol) was detected for activation energy and enthalpy value, which was linked to the production of an activated complex, implying that the lowest amount of energy necessary for effective bamboo pyrolysis [34]. Pawar et al. discovered a minimal energy difference between change in enthalpy (224 kJ/mol) and activation energy (229 kJ/mol) for pyrolysis of coconut shell biomass [47]. The ΔH and E values were in satisfactory correlation, indicating formation of simple product.

The Gibbs free energy (ΔG) states that increases energy in the system as the state of the activated product and the nature of the reactant changes [15]. The ΔG change ranged from 182 to 186 kJ/mol, less than the activation energy. The maximum ΔG value for rate of conversion 0.1, indicating that the system received excessive thermal energy at the start of the pyrolysis process for raw bamboo shown in Fig 7 contrary for bamboo biochar the maximum ΔG value for rate of conversion 0.9 shown in Table 7. The average value of ΔG for bamboo biomass was around 184.41 and 184.33 kJ/mol, respectively, for the FWO and KAS methods. A minimal difference in Gibbs free energy values calculated using FWO and KAS techniques implies the creation of an activated complex, which could be effective in the treatment of flow-related problems. The value of ΔG slightly decreased for the conversion rate of 0.1–0.9, respectively, for both the methods. The change in ΔG (Gibbs energy) value proportional to α (rate of conversion) is shown in Fig 7. The positive ΔG value for bamboo biomass indicates that the reaction was non-spontaneous and would need more energy to complete.

The change in entropy indicates the degree of disorder in a chemical process. For FWO and KAS methods, a minimal entropy value was determined at a conversion rate of 0.1, which rises to 0.9, as illustrated in Table 6. For raw bamboo the value of ΔS for the FWO and KAS method was around -3.68 and - 2.34 kJ/mol for 'α' of 0.1 and then increased to 211.94 and 225.84 kJ/mol for a conversion rate of 0.9 respectively shown in Fig 8. The average value of entropy for FWO and KAS was 111.29 and 117.67 respectively. For bamboo biochar, all the values of ΔS found negatives show that the rate of conversion is lower, as shown Table 7. When compared to the product of thermal degradation, a positive value of entropy (ΔS) indicates that the degree of conversion of product is higher, whereas a negative value of ΔS shows that the conversion rate of the product was lower [56]. The presence of both positive and negative values of entropy suggests the presence of a complex thermal conversion process of biomass into a variety of products [42] [29].

Table 7 summarises the enthalpy ΔH, Gibbs energy (ΔG), and entropy (ΔS) of bamboo biochar derived from bamboo biomass using the FWO and KAS, at 10 ^{0}C/min rate of degree conversion (α) respectively. At 600^{0}C, biochar made from bamboo biomass showed a negative entropy value, indicating biomass feedstock has a lower degree of disorder. Almost comparable results obtained from other biomass, for ΔH, ΔG, and ΔS were determined for wheat straw biochar [45], prosopis juliflora biochar [47], bamboo [34].

Table 6 Thermodynamic parameters of bamboo biomass

Conversion factor	FWO			KAS		
α	ΔH(KJ/mol)	ΔG (KJ/mol)	ΔS (KJ/mol)	ΔH(KJ/mol)	ΔG (KJ/mol)	ΔS (KJ/mol)
0.10	183.70	186.10	-3.68	184.55	186.08	-2.34
0.20	201.38	185.62	24.14	202.84	185.58	26.42
0.30	220.26	185.14	53.77	222.48	185.09	57.25
0.40	242.05	184.64	87.89	245.21	184.57	92.84
0.50	259.32	184.28	114.90	263.22	184.20	120.99
0.60	274.02	183.98	137.85	278.50	183.90	144.84
0.70	298.32	183.53	175.74	303.90	183.43	184.44
0.80	313.29	183.27	199.07	319.51	183.16	208.74
0.90	321.56	183.13	211.94	330.49	182.98	225.84
Average	257.10	184.41	111.29	261.19	184.33	117.67

Table 7 Thermodynamic parameters of bamboo biochar

Conversion factor	FWO			KAS		
α	ΔH(KJ/mol)	ΔG (KJ/mol)	ΔS (KJ/mol)	ΔH(KJ/mol)	ΔG (KJ/mol)	ΔS (KJ/mol)
0.10	165.46	299.84	-132.90	166.19	299.80	-132.14
0.20	125.95	302.01	-174.12	124.62	302.09	-175.51
0.30	110.14	303.06	-190.79	107.99	303.21	-193.07
0.40	94.33	304.26	-207.61	91.36	304.51	-210.80
0.50	86.43	304.93	-216.09	83.05	305.24	-219.74
0.60	70.62	306.47	-233.24	66.42	306.93	-237.85
0.70	62.72	307.35	-241.93	58.11	307.92	-247.06
0.80	54.82	308.34	-250.73	49.79	309.04	-256.39
0.90	46.91	309.46	-259.66	41.48	310.33	-265.89
Average	90.82	305.08	-211.90	87.67	305.45	-215.38

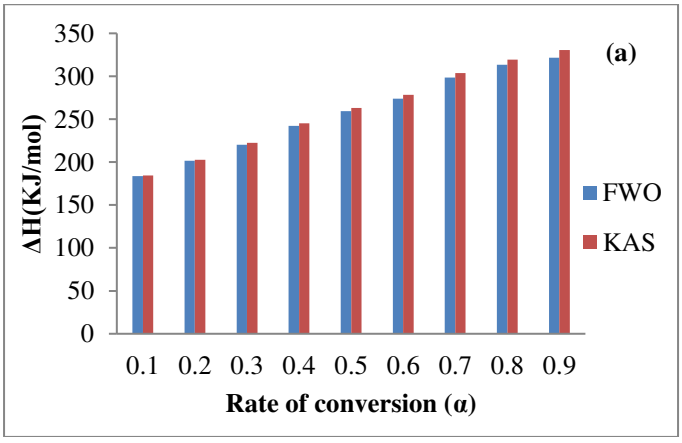

Fig. 6 Enthalpy (ΔH) value changes with respect to rate of conversion (α) for FWO and KAS models for bamboo biomass

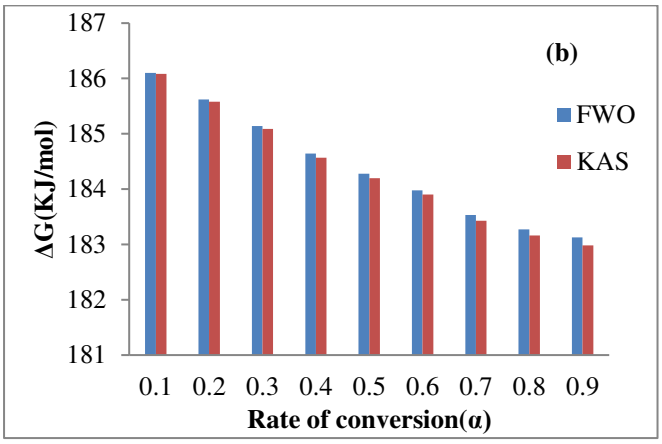

Fig. 7 Gibbs free energy (ΔG) value changes with respect to rate of conversion (α) for FWO and KAS models for bamboo biomass

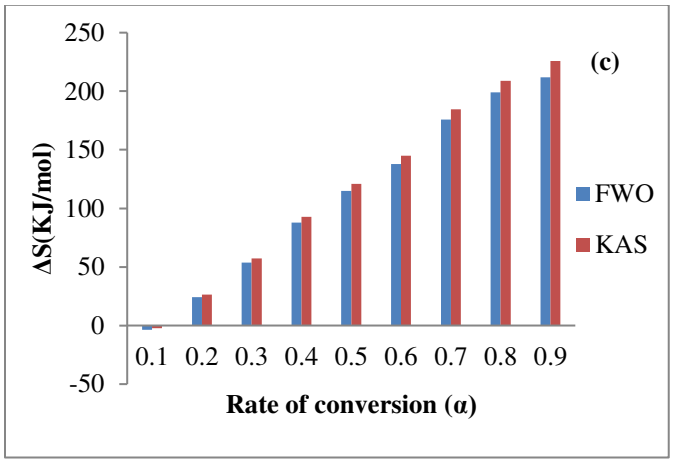

Fig. 8 Entropy (ΔS) value Changes with respect to rate of conversion (α) for FWO and KAS models for bamboo biomass

Table 8 shows how bamboo biomass's thermodynamic and kinetic parameters compare to those obtained for other wood and agricultural residues. Bamboo has lower activation energy than other woody biomass and is very close to, having a value that is very similar to that of other bamboo species. Lower activation energy for bamboo indicates that it can react effectively with a small amount of energy, implying that bamboo biomass can be efficiently utilised for bio-energy production. Furthermore, knowledge of thermodynamic variables would aid in the proper design of thermochemical conversions.

Table 8 Comparison of the thermodynamic and kinetic parameters obtained for bamboo to other wood and agricultural residues

Feedstock	Models	Heating rate ^{0}C/min	Activation energy kJ/mol	Thermodynamic parameters		References
				Enthalpy kJ/mol	Gibbs energy kJ/mol	
Bamboo	FWO, KAS	10,20,30	262.53,266.62	257.10 261.19	184.41 184.33	Present study
Mustard stalk	FWO, KAS, Starink	10, 20, 30, 40	173.83, 173.18, 172.94	168.68, 168.03, 167.78	176.37, 176.39, 176.40	[57]
Prosopis Juliflora	FWO, KAS, Starink Friedman	10,20,30	150.52, 150.47, 149.51, 147	147.88 146.47 146.43 143.89	172.79 172.74 172.71 172.40	[47]
Cedar	FWO, Criado	5, 10, 20, 40	188-205	-	-	[50]
Tectona grandis (teak)	FWO, Starink's	5, 15, 25, 35	300, 222	-	-	[48]
Bamboo waste	KAS FWO,	10, 15, 20 30	183.113 181.973	-	-	[20]
Bamboo subfamily	DAEM (distributed activation energy model)	10, 40, 70	201.59, 220.49, 224.47	170-250	200 - 250	[34]
Cotton stalk	FWO KAS	15, 25, 35, 45 55	142.93 145.39	-	-	[40]

4. Conclusion

Kinetic analysis of bamboo and its biochar using thermogravimetric under non-isothermal conditions was performed at defined rates of heating 10, 20, and 30 ^{0}C/min of temperature 30 to 900 ^{0}C. Bamboo and bamboo biochar are found to have higher heating values of 18.50 and 28.25 MJ/kg, respectively. Thermal decomposition of bamboo mainly occurs in three different temperature stages, viz., drying, devolatilization, and char formation. The major thermal decomposition occurred at a temperature of 180 ^{0}C to 395 ^{0}C, called the active pyrolysis zone. Flynn–wall–Ozawa and Kissinger–Akahira–Sunose methods were used to evaluate the kinetic and thermodynamic parameters. The activation energy was determined using iso-conversational methods such as the FWO and KAS models, which gave the average values for bamboo of 262.53 and 266.62 (KJ/mol) and for bamboo biochar of 99.23 and 96.07 kJ/mol, respectively. The A (pre-exponential factor) was measured within the range of 10^{13} to 10^{25} S $^{-1}$.

The positive values for both ΔH and ΔG for the total degree of conversion suggest that thermal decomposition of bamboo biomass occurs in a non-spontaneous way. The small difference in enthalpy and activation energy indicates that biomass pyrolysis is feasible

Authors' contributions

Priti Jagnade conducted an experimental study, prepared a draft manuscript, and analysed the constructive discussion data. Narayan Lal Panwar and Chitranjan Agarwal contributed to writing the manuscript and interpreting the data. All authors read and approved the final paper.

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Declaration of Competing Interest

The authors declare no competing interests.

References

1. Rehman A, Ma H, Chishti MZ, et al (2021) Asymmetric investigation to track the effect of urbanization, energy utilization, fossil fuel energy and CO2 emission on economic efficiency in China: another outlook. Environ Sci Pollut Res 28:17319–17330. https://doi.org/10.1007/s11356-020-12186-w
2. Hosseini SE, Wahid MA, Aghili N (2013) The scenario of greenhouse gases reduction in Malaysia. Renew Sustain Energy Rev 28:400–409. https://doi.org/10.1016/j.rser.2013.08.045
3. York R, Bell SE (2019) Energy transitions or additions?: Why a transition from fossil fuels requires more than the growth of renewable energy. Energy Res Soc Sci 51:40–43. https://doi.org/10.1016/j.erss.2019.01.008
4. Kumar A, Anushree, Kumar J, Bhaskar T (2020) Utilization of lignin: A sustainable and eco-friendly approach. J Energy Inst 93:235–271. https://doi.org/10.1016/j.joei.2019.03.005

5. Variny M, Varga A, Rimár M, et al (2021) Advances in biomass co-combustion with fossil fuels in the European context: A review. Processes 9:1–34. https://doi.org/10.3390/pr9010100
6. Bilandzija N, Voca N, Jelcic B, et al (2018) Evaluation of Croatian agricultural solid biomass energy potential. Renew Sustain Energy Rev 93:225–230. https://doi.org/10.1016/j.rser.2018.05.040
7. Ghosh U, Das D, Banerjee D, et al (2021) Biomass Energy Potential in India: A Review. Int J Eng Res Technol Nceter 9:42–45
8. IREDA (2022) No Title
9. Adams P, Bridgwater T, Lea-Langton A, et al (2018) Biomass Conversion Technologies. Report to NNFCC. Elsevier Inc.
10. Hoang AT, Ong HC, Fattah IMR, et al (2021) Progress on the lignocellulosic biomass pyrolysis for biofuel production toward environmental sustainability. Fuel Process Technol 223:106997. https://doi.org/10.1016/j.fuproc.2021.106997
11. Cai J, Wu W, Liu R, Huber GW (2013) A distributed activation energy model for the pyrolysis of lignocellulosic biomass. Green Chem 15:1331–1340. https://doi.org/10.1039/c3gc36958g
12. Slopiecka K, Bartocci P, Fantozzi F (2012) Thermogravimetric analysis and kinetic study of poplar wood pyrolysis. Appl Energy 97:491–497. https://doi.org/10.1016/j.apenergy.2011.12.056
13. Burnham A DL (2006) A comparison of isoconversional and model-fitting approaches to kinetic parameter estimation and application predictions. J Therm Anal Calorim 479-490.
14. Mishra RK, Mohanty K (2018) Pyrolysis characteristics and kinetic parameters assessment of three waste biomass. J Renew Sustain Energy 10:. https://doi.org/10.1063/1.5000879
15. Xu Y, Chen B (2013) Investigation of thermodynamic parameters in the pyrolysis conversion of biomass and manure to biochars using thermogravimetric analysis. Bioresour Technol 146:485–493. https://doi.org/10.1016/j.biortech.2013.07.086
16. Jiang Z, Liu Z, Fei B, et al (2012) The pyrolysis characteristics of moso bamboo. J Anal Appl Pyrolysis 94:48–52. https://doi.org/10.1016/j.jaap.2011.10.010
17. Barathi N Theme 3 . ECONOMY : 3 . 1 Industrial uses of Bamboo Bamboo as Energy

Plantation for Renewable Energy Market
18. My T, Le A (2015) Overview of bamboo biomass for energy production To cite this version : Overv bamboo biomass energy Prod 24:0–24
19. Chen D, Zhou J, Zhang Q (2014) Effects of heating rate on slow pyrolysis behavior, kinetic parameters and products properties of moso bamboo. Bioresour Technol 169:313–319. https://doi.org/10.1016/j.biortech.2014.07.009
20. Mallick D, Baruah D, Mahanta P, Moholkar VS (2019) A Comprehensive Kinetic Analysis of Bamboo Waste Using Thermogravimetric Analysis. 2nd Int Conf Energy, Power Environ Towar Smart Technol ICEPE 2018. https://doi.org/10.1109/EPETSG.2018.8658672
21. Poletto M, Zattera AJ, Santana RMC (2012) Thermal decomposition of wood: Kinetics and degradation mechanisms. Bioresour Technol 126:7–12. https://doi.org/10.1016/j.biortech.2012.08.133
22. Wongsiriamnuay T, Tippayawong N (2010) Non-isothermal pyrolysis characteristics of giant sensitive plants using thermogravimetric analysis. Bioresour Technol 101:5638–5644. https://doi.org/10.1016/j.biortech.2010.02.037
23. Brown ME (1988) Reaction kinetics from thermal analysis. Introd to Therm Anal 127–151. https://doi.org/10.1007/978-94-009-1219-9_13
24. Jiang G, Nowakowski DJ, Bridgwater A V. (2010) A systematic study of the kinetics of lignin pyrolysis. Thermochim Acta 498:61–66. https://doi.org/10.1016/j.tca.2009.10.003
25. Apaydin-Varol E, Polat S, Putun AE (2014) Pyrolysis kinetics and thermal decomposition behavior of polycarbonate - a TGA-FTIR study. Therm Sci 18:833–842. https://doi.org/10.2298/TSCI1403833A
26. Vyazovkin S (2006) Model-free kinetics: Staying free of multiplying entities without necessity. J Therm Anal Calorim 83:45–51. https://doi.org/10.1007/s10973-005-7044-6
27. Starink MJ (2003) The determination of activation energy from linear heating rate experiments: A comparison of the accuracy of isoconversion methods. Thermochim Acta 404:163–176. https://doi.org/10.1016/S0040-6031(03)00144-8
28. Ahmad MS, Mehmood MA, Al Ayed OS, et al (2017) Kinetic analyses and pyrolytic behavior of Para grass (Urochloa mutica) for its bioenergy potential. Bioresour Technol 224:708–713. https://doi.org/10.1016/j.biortech.2016.10.090

29. Gupta GK, Mondal MK (2019) Kinetics and thermodynamic analysis of maize cob pyrolysis for its bioenergy potential using thermogravimetric analyzer. J Therm Anal Calorim 137:1431–1441. https://doi.org/10.1007/s10973-019-08053-7
30. Ceylan S, Topçu Y (2014) Pyrolysis kinetics of hazelnut husk using thermogravimetric analysis. Bioresour Technol 156:182–188. https://doi.org/10.1016/j.biortech.2014.01.040
31. Lee XJ, Lee LY, Gan S, et al (2017) Biochar potential evaluation of palm oil wastes through slow pyrolysis: Thermochemical characterization and pyrolytic kinetic studies. Bioresour Technol 236:155–163. https://doi.org/10.1016/j.biortech.2017.03.105
32. Pawar A, Panwar NL (2022) Experimental investigation on biochar from groundnut shell in a continuous production system. Biomass Convers Biorefinery 12:1093–1103. https://doi.org/10.1007/s13399-020-00675-4
33. Chen D, Gao A, Cen K, et al (2018) Investigation of biomass torrefaction based on three major components: Hemicellulose, cellulose, and lignin. Energy Convers Manag 169:228–237. https://doi.org/10.1016/j.enconman.2018.05.063
34. Zhao R, Wang X, Liu L, et al (2019) Slow pyrolysis characteristics of bamboo subfamily evaluated through kinetics and evolved gases analysis. Bioresour Technol 289:121674. https://doi.org/10.1016/j.biortech.2019.121674
35. Ferrara F, Orsini A, Plaisant A, Pettinau A (2014) Pyrolysis of coal, biomass and their blends: Performance assessment by thermogravimetric analysis. Bioresour Technol 171:433–441. https://doi.org/10.1016/j.biortech.2014.08.104
36. Shi L, Liu Q, Guo X, et al (2013) Pyrolysis behavior and bonding information of coal — A TGA study. Fuel Process Technol 108:125–132. https://doi.org/10.1016/j.fuproc.2012.06.023
37. Wiktorsson LP, Wanzl W (2000) Kinetic parameters for coal pyrolysis at low and high heating rates - a comparison of data from different laboratory equipment. Fuel 79:701–716. https://doi.org/10.1016/S0016-2361(99)00138-6
38. Slopiecka K, Bartocci P, Fantozzi F (2012) Thermogravimetric analysis and kinetic study of poplar wood pyrolysis. Appl Energy 97:491–497. https://doi.org/10.1016/j.apenergy.2011.12.056
39. Ma Z, Wang J, Zhou H, et al (2018) Relationship of thermal degradation behavior and chemical structure of lignin isolated from palm kernel shell under different process

severities. Fuel Process Technol 181:142–156. https://doi.org/10.1016/j.fuproc.2018.09.020

40. Chen D, Shuang E, Liu L (2018) Analysis of pyrolysis characteristics and kinetics of sweet sorghum bagasse and cotton stalk. J Therm Anal Calorim 131:1899–1909. https://doi.org/10.1007/s10973-017-6585-9
41. Díez D, Urueña A, Piñero R, et al (2020) and Lignin Content in Di ff erent Types of Biomasses by Thermogravimetric Analysis and Pseudocomponent Kinetic Model. Processes 8:1–21
42. Gajera B, Panwar NL (2019) Pyrolysis and kinetic behaviour of black gram straw using thermogravimetric analysis. Energy Sources, Part A Recover Util Environ Eff 0:1–14. https://doi.org/10.1080/15567036.2019.1662138
43. Kim KH, Kim JY, Cho TS, Choi JW (2012) Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (Pinus rigida). Bioresour Technol 118:158–162. https://doi.org/10.1016/j.biortech.2012.04.094
44. Hamza UD, Nasri NS, Amin NAS, et al (2016) Characteristics of oil palm shell biochar and activated carbon prepared at different carbonization times. Desalin Water Treat 57:7999–8006. https://doi.org/10.1080/19443994.2015.1042068
45. Rathore NS, Pawar A, Panwar NL (2021) Kinetic analysis and thermal degradation study on wheat straw and its biochar from vacuum pyrolysis under non-isothermal condition. Biomass Convers Biorefinery. https://doi.org/10.1007/s13399-021-01360-w
46. Neves RM, Ornaghi HL, Ornaghi FG, et al (2022) Degradation kinetics and lifetime prediction for polystyrene/nanocellulose nanocomposites. J Therm Anal Calorim 147:879–890. https://doi.org/10.1007/s10973-020-10316-7
47. Pawar A, Panwar NL (2022) A comparative study on morphology, composition, kinetics, thermal behaviour and thermodynamic parameters of Prosopis Juliflora and its biochar derived from vacuum pyrolysis. Bioresour Technol Reports 18:101053. https://doi.org/10.1016/j.biteb.2022.101053
48. Balogun AO, Lasode OA, McDonald AG (2014) Devolatilisation kinetics and pyrolytic analyses of Tectona grandis (teak). Bioresour Technol 156:57–62. https://doi.org/10.1016/j.biortech.2014.01.007

49. Lopez-Velazquez MA, Santes V, Balmaseda J, Torres-Garcia E (2013) Pyrolysis of orange waste: A thermo-kinetic study. J Anal Appl Pyrolysis 99:170–177. https://doi.org/10.1016/j.jaap.2012.09.016
50. Cavinato CD, Poletto M (2021) Kinetic Analysis Of Thermal Degradation Of Cedrela odorata, Marmaroxylon Racemosum And Tectona Grandis From timber Industry. Maderas Cienc. y Tecnol. 23:1–10
51. Ornaghi HL, Ornaghi FG, Neves RM, et al (2020) Mechanisms involved in thermal degradation of lignocellulosic fibers: a survey based on chemical composition. Cellulose 27:4949–4961. https://doi.org/10.1007/s10570-020-03132-7
52. Rego F, Soares Dias AP, Casquilho M, et al (2020) Pyrolysis kinetics of short rotation coppice poplar biomass. Energy 207:118191. https://doi.org/10.1016/j.energy.2020.118191
53. Vlaev LT, Georgieva VG, Genieva SD (2007) Products and kinetics of non-isothermal decomposition of vanadium(IV) oxide compounds. J Therm Anal Calorim 88:805–812. https://doi.org/10.1007/s10973-005-7149-y
54. Havilah PR, Sharma PK, Sharma AK (2021) Characterization, thermal and kinetic analysis of Pinusroxburghii. Environ Dev Sustain 23:8872–8894. https://doi.org/10.1007/s10668-020-01001-8
55. Cao H, Xin Y, Wang D, Yuan Q (2014) Pyrolysis characteristics of cattle manures using a discrete distributed activation energy model. Bioresour Technol 172:219–225. https://doi.org/10.1016/j.biortech.2014.09.049
56. Singh RK, Patil T, Sawarkar AN (2020) Pyrolysis of garlic husk biomass: Physico-chemical characterization, thermodynamic and kinetic analyses. Bioresour Technol Reports 12:100558. https://doi.org/10.1016/j.biteb.2020.100558
57. Narnaware SL, Panwar NL (2022) Kinetic study on pyrolysis of mustard stalk using thermogravimetric analysis. Bioresour Technol Reports 17:100942. https://doi.org/10.1016/j.biteb.2021.100942