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Keywords: fixed-bed, pyrolysis, kinetics, TGA, heating rate, jute stick

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Article

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Abstract: Thermochemical process of biomass is being considered as a latest technique for the restoration of energy source and biochemical products. In this study, the influence of the different heating rates on pyrolysis behaviors and kinetic of jute stick were investigated to justify the waste jute stick biomass as a potential source of bioenergy. Pyrolysis experiments were carried out at four several heating rates of 10, 20, 30 and 40 °C/min, by utilizing the thermogravimetric analyzer (TG-DTA) and a fixed-bed pyrolysis reactor. Two different kinetic methods, Kissinger–Akahira–Sunose (KAS) and Ozawa–Flynn–Wall (OFW) were used to determine the distinct kinetic parameters. The experimental results showed that, the heating rates influenced significantly on the position of TG curve and maximum T_m peaks and highest decomposition rate of the jute stick biomass. Both the highest point of TG and the lowest point of Derivative thermogravimetry (DTG) curves were shifted towards the maximum temperature. However, the heating rates also influenced the products of pyrolysis yield, including bio-char, bio-oil and the non-condensable gases. The average values of activation energy were found to be 139.21 and 135.99 kJ/mol based on FWO and KAS models, respectively.

Keywords: jute stick; heating rate; TGA; kinetics; pyrolysis; fixed-bed

1. Introduction

Rapid growth of demography and urbanization causes an enormous use of energy, which consequently results a rapid reduction of natural resources. However, this universal requirement of enormous energy was fulfilled mainly by the consumptions of the fossil fuels and other general resources such as natural gas, coal dominant energy and petroleum etc. [1]. As the results, a significant reduction of fossil fuels was anticipated by the mid of this century [2]. Excessive use of fossil fuel results an increment of greenhouse gases, particulate matters and the other pollutants, which ultimately causes different environmental problems, i.e., global warming and atmospheric pollutions [1,3].

As an alternative measure, biomass provides a suitable option, as it is considered as renewable and pure. Recently biomass is one of the most significant sources of energy by occupying about 14% of the world's primary energy trade [4,5]. It can promote for the production of energy in diverse ways from traditional ignition to the pyrolysis and gasification process. An economically feasible and a technically durable process is highly recommended for the successful reproduction of considerable amount of energy from biomass. In the direct burning process, only 10% to 15% of biomass was converted to the heat, whereas the rest are wasted in the form of gas [6]. Thus, at present, this method is not economically feasible for the commercial purpose. On the other hand, thermochemical process (pyrolysis, combustion, gasification etc.) can play a significant role for the successful conversion of the different biomasses (i.e., city waste, agricultural residues and forestry product) into the bioenergy.

Among the various thermochemical methods, pyrolysis process is the major step of thermochemical conversion, which occurred at oxygen-free atmosphere [7,8]. Based on a sequence of compound

reactions, it's a thermal decomposition process which was influenced by the several factors, i.e., temperature, pressure, heating rate, residence time, moisture, different configurations of biomass, the catalyst and sizes of particles, etc. [9–11]. Suitable models to predict the pyrolysis products are essential for the power plant optimization and to offer an improved understanding about the behavior of combustion engines fueled by pyrolysis products [12]. Thus, for a better understanding of the pyrolysis process, many researchers studied and recommended, the thermal decomposition of biomass by thermogravimetric analysis (TGA) [5,9,13–18]. Therefore, TGA is being considered as one of the most general technique which was applied for the different kinetic analysis of devolatilization method. In addition, the knowledge about biomass pyrolysis kinetics is essential to assess the biomass as a feedstock for fuel or/and for an efficient design and control of thermochemical processes.

Waste jute stick can be considered as a good and alternative sources of renewable biomasses due to the reason that of a concise growth cycle along with the massive yield. For a long period, jute stick is being mainly used as a fuel for cooking purpose in the rural areas. However, the jute stick can be utilized for production of bioenergy by employing pyrolysis technology. Many researchers have investigated the pyrolysis of other biomasses, for example, tobacco waste and sorghum bagasse [5], poplar wood [9], pinewood [13], soybean straw [15] and hazelnut husk [17], coconut shell [19], Sorghum straw [20]. Asadullah et al. [6] studied the jute stick pyrolysis by using the fluidized bed reactor to produce bio-oil, at a temperature ranging from 300 to 600 °C Islam et al. [21] investigated the pyrolysis behaviors of ten biomass samples, in which jute stick was one. However, they only focused on the product yield of jute stick by varying temperature from 400 to 600 °C. Unfortunately, the investigation related to the allocation of the pyrolysis yield and behaviors of jute stick, particularly the characteristics of the fixed-bed pyrolysis product by varying condition of different heating rates, is not carried out.

Therefore, the main objectives of this study are to clarify the impact of different heating rates on the pyrolysis behaviors along with the kinetics study of the jute stick biomass, and to justify the potentiality of the jute stick as a renewable biomass. Furthermore, to provide a better understanding of the kinetics study, two different kinetic method Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS), was considered for the comparison purpose under non-isothermal solid state condition.

2. Materials and Methods

2.1. Materials

In this study, jute stick was selected for the pyrolysis process and were collected from Jessore division in Bangladesh. After collecting jute stick, the samples were sun dried for a period of several days to keep the moisture lower than 10 wt%. After that, the feedstock was powdered and strained to a size, smaller than the 250 µm by the crusher and sieved by using the shaker. Ultimate or elemental analysis was executed by using a CHN Corder (Model MT-5 Yanaco, Co., Ltd., Yanaco, Japan). To determine the moisture content, ash content and the volatile matter, Japanese Industrial Standard was followed. The estimation of fixed carbon (FC) can be expressed as [19]:

$$\text{FC (wt\%)} = 100 - (\text{moisture (wt\%)} + \text{ash (wt\%)} + \text{volatile matter (wt\%)}) \quad (1)$$

Dulong's formula was used to estimate the higher heating value (HHV) of the raw material and expressed by:

$$\text{Higher Heating value (HHV) (MJ/kg)} = 0.338 C + 1.428 (H - O/8) + 0.095S \quad (2)$$

where, C = carbon, H = hydrogen, O = oxygen and S = sulfur were weight percentages of primary contents in each material.

2.2. Thermogravimetric Analysis

Thermogravimetric analysis were performed by using TG-DTA (Model DTG-60, Shimadzu Co. Ltd., Kyoto, Japan). Simultaneous TGA and DTG curves were acquired and the weight loss of the samples was recorded constantly. All of these processes were carried under different dynamic conditions. The schematic features of the experimental apparatus is shown in Figure 1a. The instrument provides a constant recording of TGA and DTG curves in terms of weight loss percent per second. In each case, 10 mg of jute stick biomass sample was weighted within a platinum crucible of the TG-DTA. In the trial experiment, we have witnessed that, before reaching the targeted temperature the experiment got finished due to pyrolysis when working with 1–2 mg sample. Moreover, standard error was found to be very high. However, many researcher [10,18,20–22] investigated the pyrolysis process with a mass of 10 to 25 mg sample in their experiment. Due to this reason, a mass of 10 mg sample is used in this present study. Argon was used in order to maintain the inert condition, which acts as a carrier gas and was supplied with a constant flow rate of 200 mL/min. Non-isothermal experiments were carried out by varying condition of various heating rates, i.e., 10, 20, 30 and 40 °C/min. In all the cases the temperatures were varied from 25 °C to 900 °C. The volumetric weights of each sample and furnace temperatures were recorded during heating process and every cases was repeated for the three times.

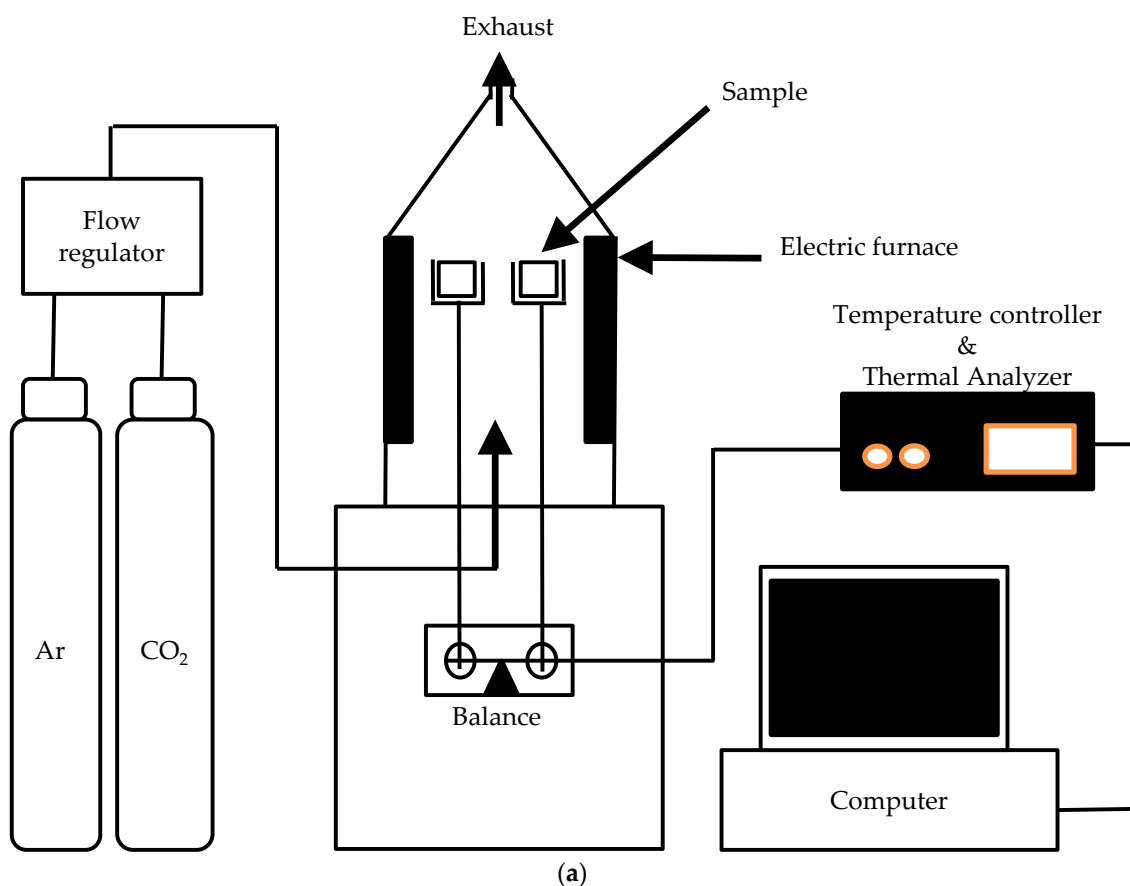


Figure 1. Cont.

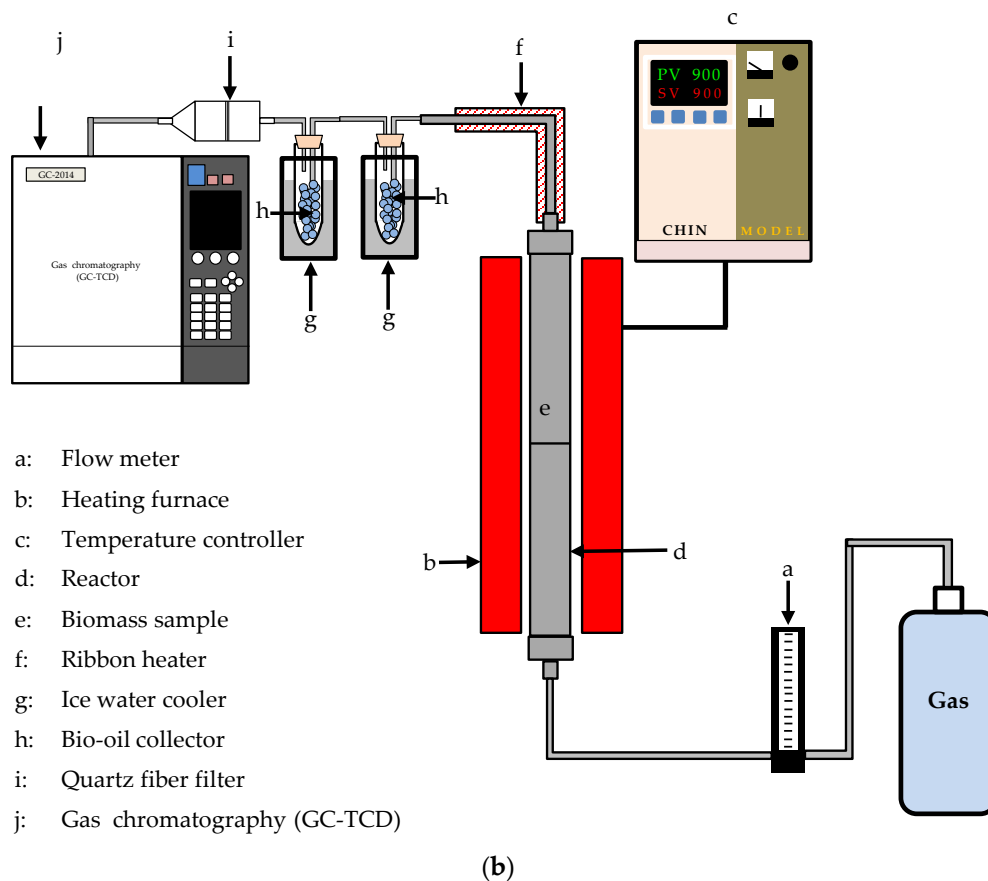


Figure 1. Schematic diagram of (a) thermogravimetric analyzer (TG-DTA) and (b) fixed-bed reactor.

2.3. Experimental Apparatus for Jute Stick Fixed-Bed Pyrolysis

Jute stick pyrolysis were performed on a laboratory scale fixed-bed reactor and was shown in Figure 1b. Two stainless coupling reactors having internal diameter of 21.4 mm with length of 500 mm was involved in both the liquid decomposition system and the pyrolysis system. Biomass was kept within the reactors having a mesh size of 40 μm . The independent heating process of the apparatus was basically governed by the two distinct electric furnaces. Between the liquid tapping system, the stainless pipe was paired, and the reactors was heated to 300–400 $^{\circ}\text{C}$ in order to avoid further contraction of liquids. However, to collect the glass beads and the condensable products, several test tubes were inserted. Both the ice and water were supplied to preserve the temperature of cooling bath at -3°C . In addition, to calibrate the gaseous products a Gas chromatography was adopted.

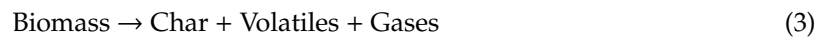
2.4. Pyrolysis Procedure

In this study, approximately 4 g of the dried jute stick sample was used in each case. Jute stick biomass sample was heated under argon atmosphere by varying condition of various heating rates of 10, 20, 30 and 40 $^{\circ}\text{C}/\text{min}$, with a temperature extending from 25 $^{\circ}\text{C}$ to 900 $^{\circ}\text{C}$. The sample was kept at temperature 900 $^{\circ}\text{C}$ for a duration of approximately 10 min. The heater was opened and cooled for 1 h by using fan after the completion of the analysis. The generated gaseous products in the fixed-bed pyrolysis of jute-stick biomass sample was measured in every 6 min using gas chromatography (Model GC-2014, Shimadzu Co., Ltd., Kyoto, Japan). The gas chromatography requires 6 min to analyze the gas due to this reason the pyrolysis gasses were analyzed in every 6 min. The liquid products were calculated by the weight difference method. To dissolve the condensable products within the test tube, about 20 mL of 2-propanol was inserted. However, for the estimation of the moisture content within the sample, Karl Fischer moisture measurement method was adopted. After finishing the experiment,

the remaining char was removed from the reaction tube. The elemental analysis of solid bio-char and bio-oil were performed by employing a CHN Corder HHV of the bio-char was estimated by employing Dulong's formula.

2.5. Kinetic Study

The ordinary process of biomass pyrolysis can be described as [22,23]:



In our study, we investigated the pyrolysis reaction kinetics from the collected data of the thermogravimetric analysis. Many researchers used various methods for the estimation of kinetic parameters [24–27]. However, in this study, two different kinetic models, OFW and KAS method was applied on TGA data of jute stick.

The significant rate equation utilized in all kinetic studies can be expressed as [22,23]:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (4)$$

where, α = the degree of conversion, t = conversion time, k = rate constant and $f(\alpha)$ = reaction model, respectively. The conversion factor (α) is the weight loss data of the normalized form of the decomposed sample and can be described as:

$$\alpha = \frac{m_i - m_a}{m_i - m_f} \quad (5)$$

where, m_i = initial mass of the sample, m_a = actual mass and m_f = mass after pyrolysis. The rate constant k was expressed by Arrhenius equation:

$$k = Ae^{\frac{-E}{RT}} \quad (6)$$

where, E = activation energy (kJ/mol), R = gas constant (8.314 J/K mol), A = pre-exponential factor (s^{-1}) and T = absolute temperature (K).

By combining the Equation (4) and Equation (6) results:

$$\frac{d\alpha}{dt} = Ae^{\frac{-E}{RT}} f(\alpha) \quad (7)$$

The expression of the function $f(\alpha)$ and its derivative $f'(\alpha) = -1$ are used to describe solid-state first-order reaction, hence Slopiecka et al. [15] and Chandrasekaran et al. [21] the mathematical function $f(\alpha)$ as:

$$f(\alpha) = (1 - \alpha)^n \quad (8)$$

where, n = reaction order.

The combination of Equations (7) and (8) gives:

$$\frac{d\alpha}{dt} = A(1 - \alpha)^n e^{\frac{-E}{RT}} \quad (9)$$

For a dynamic TGA process and with the introduction of the heating rate, $\beta = dT/dt$, Equation (9) can be rearranged as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} (1 - \alpha)^n e^{\frac{-E}{RT}} \quad (10)$$

Thus, Equations (9) and (10) expresses as a fundamental analytical method to determine kinetic parameters based on TGA data.

2.6. Model-Free Methods

Kinetic parameters were determined from various curves at different heating rates having an equal substance of feed stock conversion. These processes are solely recommended by the ICTAC Kinetics (Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry Committee) [28]. The four different methods such as, Vyazovkin (V), Kissinger–Friedman (FR), Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) were being considered as a better practice for the isoconversional methods. In the present study, two different model-free methods, i.e., KAS and FWO; were used. These two methods were also used to measure the apparent activation energy.

2.6.1. Flynn–Wall–Ozawa (FWO) Method

The FWO method [29,30] permits to achieve, apparent activation energy (E_α) from a scheme of natural logarithm of heating rates, $\ln \beta_i$, versus $1/T_{\alpha i}$ and can be expressed as following:

$$\ln \beta_i = \ln \frac{A_\alpha E_\alpha}{R g(\alpha)} + 5.331 + 1.052 \frac{E_\alpha}{RT_{\alpha i}} \quad (11)$$

where, $g(\alpha)$ = constant at a known value of conversion, i = given value of heating rate, $1/T_{\alpha i}$ = the linear relation with a given value of conversion at various heating rates and α = given value of conversion, respectively. The activation energy E_α was estimated from the slope $-1.052E_\alpha/R$.

2.6.2. Kissinger–Akahira–Sunose (KAS) Method

KAS method [31,32] is a standard isoconversional method which was commonly used to determine pyrolysis kinetics and can be expressed as:

$$\ln \frac{\beta_i}{T_{\alpha i}^2} = \ln \frac{A_\alpha R}{E_\alpha g(\alpha)} - \frac{E_\alpha}{RT_{\alpha i}} \quad (12)$$

The apparent activation energy can be retrieved from a plot of $\ln(\beta_i/T_{\alpha i}^2)$ vs. $1/T_{\alpha i}$ for a given value of conversion, α , where slope = $-E_\alpha/R$.

3. Results and Discussion

3.1. Proximate and Ultimate Analysis of Jute Stick

Proximate and ultimate analysis of the different major chemical components of the raw jute stick is presented in Table 1. The HHV of jute stick was found to be 15.26 MJ/kg, where HHV is likely to be affected by the higher amount of oxygen present in the biomass. However, due to the lack of the experimental facilities the amount of sulfur (S) was not detected. From the proximate analysis of jute stick, the volatile matter was found to be high approximately 86.64 wt%, whereas the amount of ash content was witnessed to be very low approximately 1.18 wt%. Volatile matter of biomass has played a significant role in the bio-oil production. Moreover, the higher volatile matter implies an increased amount of production of bio-oil in the pyrolysis process. However, at the end of the experiment the remained powdery residue was found to be ash. A higher amount of volatile content was observed in the jute stick which is in favor to this study and this phenomenon was also beneficial for the pyrolysis process. The lowest amount of ash is significant because, the higher ash amount can cause aggregation in the thermochemical process and can result an unproductive heat transfer rate. In addition, the presence of inorganic minerals in ash can also influence the mechanism of biomass pyrolysis [33].

Table 1. Proximate and ultimate analysis of jute stick biomass.

Ultimate Analysis (wt%)		Proximate Analysis (wt%)	
Carbon	43.41	moisture content	8.59
Hydrogen	5.78	Volatile matter	86.64
Nitrogen	7.81	fixed carbon	3.59
Oxygen	43.00	ash	1.18
Sulfur	ND		
HHV (MJ/kg)	15.26		

Note: ND: not detected.

3.2. Thermogravimetric Analysis of Jute Stick

Thermogravimetric analysis were accomplished at four several heating rates and the effect of the heating rates on the thermogravimetric analysis was presented in Figure 2. The weight-loss curve in Figure 2 represents a decrease of weight with the increase of pyrolysis temperature at several heating rates for jute stick. The devolatilization process initiates at about 220 °C and advances swiftly with the further raise in temperature up to 400 °C for the lowest heating rate and 450 °C for the high heating rate. However, afterwards a gradually decreasing trend in the weight loss was observed to the concluding temperature. For the jute stick, the yield of solid residue was found to be approximately 14%. In addition, similar results were observed during the pyrolysis process of the other different biomass products [21,34–37].

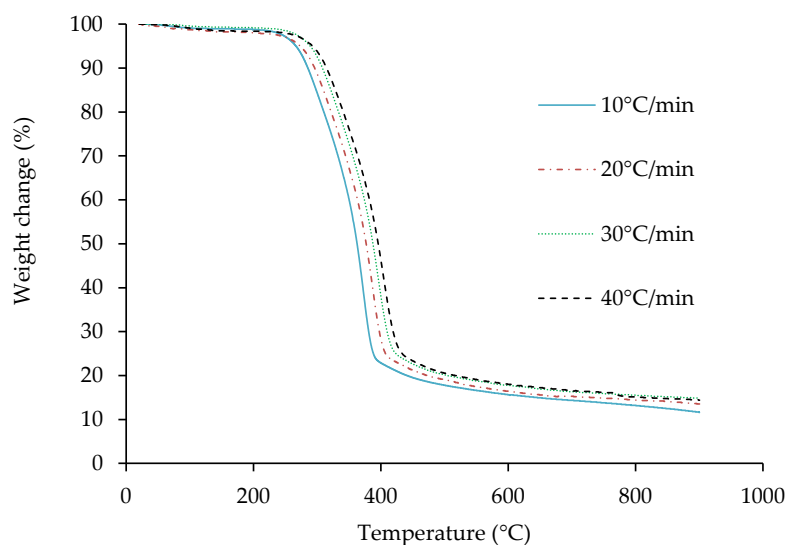


Figure 2. TGA of weight-loss curves of jute stick recorded in argon at different heating rates.

The thermal decomposition of DTG of jute-stick pyrolysis was shown in Figure 3. Two sections are apparent which agrees to the active and passive pyrolysis. The principal pyrolysis step continues to an extent from 220 °C to 400 °C for the low heating rate and 450 °C for the high heating rate. However, due to the diverse thermal stabilities, the hemicellulose, cellulose and lignin, influences significantly to the pyrolysis process. Lv and Wu [38] studied on the behaviors of corn stalk pyrolysis and revealed that, the pyrolysis of the corn stalk has an extensive contemplation of its major constituents (decomposition of hemicellulose was obtained at around 300 °C, cellulose at a provincial temperature length of 320 to 410 °C, lignin at a wide range of temperature, ranges from of 240 to 550 °C). However, at 300 °C and 390 °C, two clearly noticeable peaks, were observed (Figure 3). Compared with the previous research [38], it was clear that, the main DTG peak (at 390 °C) of jute stick was associated due to the decomposition of cellulose, and the peak at subordinate temperature (at 300 °C)

was solely due to the decomposition of hemicellulose. According to the previous studies [15,37,39–41] the two peaks in this region (active pyrolysis) shows to be associated with the cellulose and the hemicellulose decomposition, while in all regions of active and passive pyrolysis, the lignin got decomposed without a representative peak.

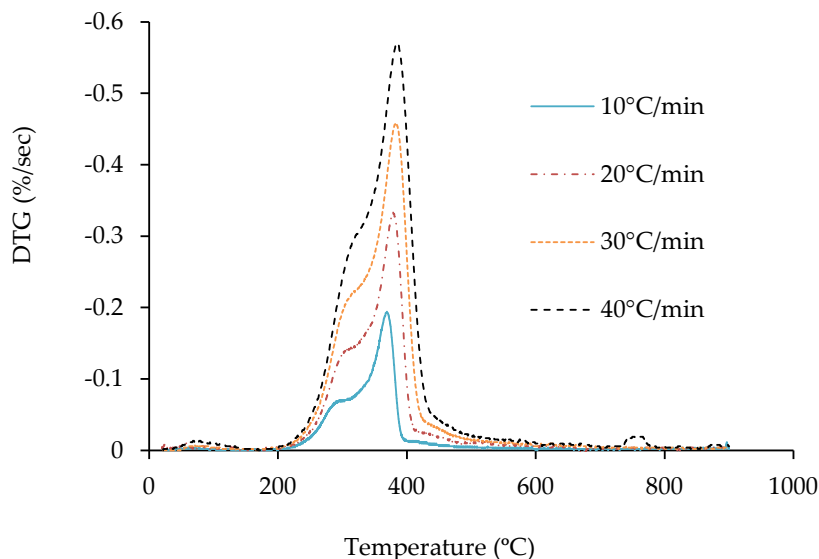


Figure 3. DTG of a jute stick recorded in argon at different heating rates.

The information related to the heating rate is crucial because of its effect on product allocation and the conversion process [42]. The heating rate influenced the locations of the TGA curve, maximum decomposition rate and location of T_m peaks. When heating rate raises, both the initial and critical temperature of operative and inactive pyrolysis section increased (Figure 3). The maximum points of TGA and minimum points of DTG curves were shifted to the higher temperature due to the reason that, the interpretation is based on the limitations of heat transfer. Throughout the analysis, a higher amount of instantaneous thermal energy was supplied into the process, at lowest heating rate. However, at this stage, a longer time may be needed for the purge gas to reach equilibrium state. A higher heating rate has a short reaction period at the similar time and the similar temperature region. Therefore, the required temperature was found to be higher for the sample to decompose and resulted the maximum rate curve to move towards the higher temperature.

3.3. The Yield of Pyrolysis Products

The influence of pyrolysis reaction at the distinct heating rates on the product yields was illustrated in Figure 4. It was observed that, pyrolysis heating rates was one of the significant parameters that can influence on the further modification of biomass into several products. Due to the increasing of the heating rate, bio-char production apparently reduces from 19.8% to 16.7%, and the bio-oil reduces from 52.89% to 47.21%, respectively. Moreover, at the same considered range of temperature, the production of non-condensable gas increased from 18.65% to 23.68%. The obtained results from the fixed-bed pyrolysis reactor were found to be different from TGA: (i) the production of bio-char remarkably moves to the fixed-bed pyrolysis reactor, on the other hand, a minor change was observed in TGA; (ii) the production of biochar within the fixed-bed pyrolysis reactor reduced with the increase of the heating rates, however in case of TGA the manifest shift tendency was not clearly observed. Due to the thermal effect of 4 g jute stick element on the fixed-bed pyrolysis reactor, makes the outcomes predominant, but more accurate results was found when the element was more than 10 mg in TGA. However, for a long period in the equivalent temperature stage, the remaining jute stick yields the higher carbonization degree and became dominant to higher bio-char yield at the end of the analysis.

Nonetheless, many researchers were also witnessed that, the lower heating rate was significant for the production of bio-char [43–46].

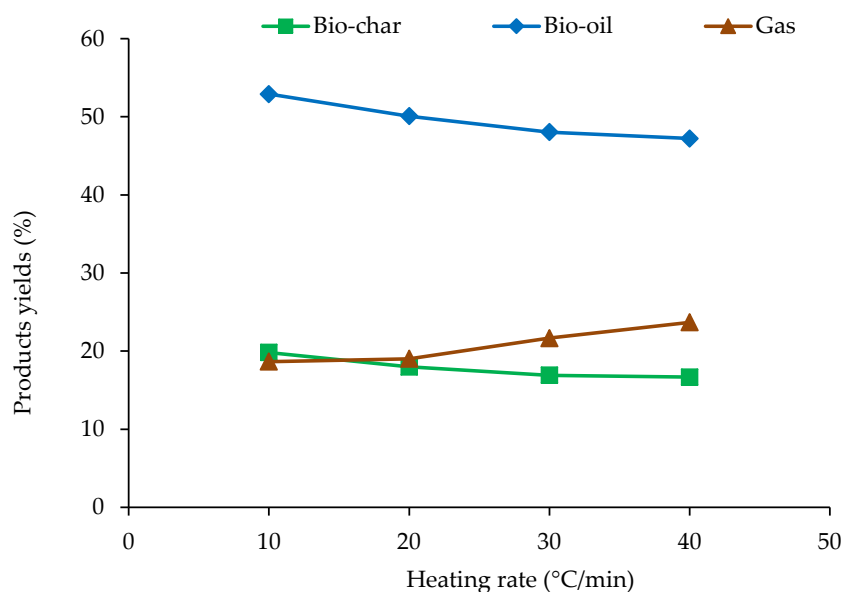


Figure 4. Influence of heating rate on products yields of jute stick pyrolysis.

3.3.1. Influence of Heating Rate on Bio-Oil Properties

Table 2 represents the effect of heating rates on the elementary ingredients of bio-oil. The amount of carbon in bio-oil reduces and the amount of oxygen increased with the further rising of heating rate, whereas hydrogen and nitrogen contents on bio-oil varies slightly. Moreover, the quantity of water within the bio-oil was reduced about 33.59%–30.71% with the increase of the heating rate. The results are consistent with the experimental analysis by H.F. Gercel [47], Salehi et al. [48] and C. Acikgoz & O. M. Kockar [49]. However, the water originates from the confined water of the jute stick and the thermochemical reactions of hemicellulose, cellulose and lignin are still unknown and need further research. Nevertheless, this quantity of water of bio-oil could be achieved at the lowest heating rate, but the amount of water is larger than that of the bio-oil achieved from higher heating rate due to reason that, in the slow pyrolysis process, the volatiles in the secondary cracking is very important. Furthermore, to dive the sample shell, the core volatile shifts by means of transport diffusion process. In the diffusion process of the consequent cracking, the volatile reaction results water and insignificant amount of non-condensable gases.

Table 2. Influence of heating rate on the elementary properties of bio-oil.

Heating Rate (°C/min)	Ultimate Analysis (%)				Water Content (%)
	H	C	O	N	
10	5.65	56.32	37.73	0.30	33.59
20	5.70	54.39	39.61	0.31	32.95
30	5.66	54.16	39.86	0.31	31.12
40	5.72	52.97	41.01	0.30	30.71

3.3.2. Effect of Heating Rate on Non-Condensable Gas

Figure 5 illustrates the effect of heating rates on the yield of the different non-condensable gases, i.e., H₂, CH₄, CO₂, CO. Overall, an increasing trend was observed for the concentration of CO₂, CO and CH₄, whereas the H₂ concentration followed a lightly decreasing trend under varying condition of the heating rates. A similar increasing trend was observed by Yang et al. [50,51] for concentration

of CO and CO₂, because CO and CO₂ remained dominant throughout the initial period of pyrolysis, and in the decomposition of hemicellulose and cellulose.

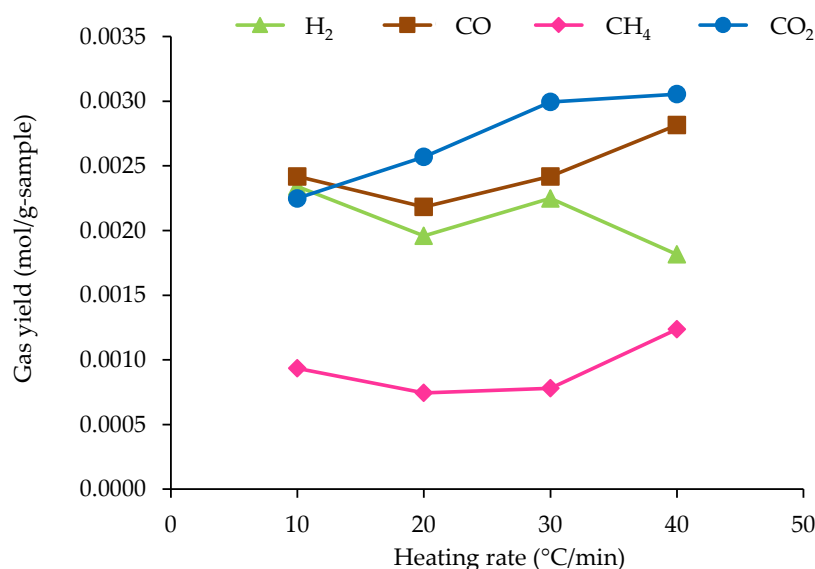


Figure 5. Influence of heating rate on non-condensable gas properties.

3.3.3. Influence of Heating Rate on Bio-Char

The ultimate, proximate and HHV of the jute-stick bio-char were presented in Table 3. At the certain heating rates, the amount of C, H, N and O of bio-char were highly related when the temperature was same. It was suggested that the heating rate of pyrolysis had an insignificant impact on the fundamental composition of bio-char. The amount of volatile in bio-char was found to be lower than 12%, whereas jute stick contains high as 86% of volatile material. The amount of fixed carbon of the biochar limits from 84.32% to 85.32%. The amount of volatile in the biochar degenerates with the rising of the heating rate, on the other hand the fixed carbon and the amount of ash apparently increased. The HHV of bio-char was found to be larger than that of the raw biomass. Apparently, the heating rates was found to have a small impact on the HHV of bio-char.

Table 3. Proximate, ultimate and higher heating value (HHV) of jute-stick bio-char at several heating rate.

Heating Rate	Ultimate Analysis (%)				Proximate Analysis (%)			HHV (MJ/kg)
	C	H	O	N	Fixed Carbon	Volatiles	Ash	
10	85.46	0.81	13.29	0.44	84.32	11.63	4.06	27.66
20	84.94	1.09	13.48	0.49	85.03	10.33	4.64	27.86
30	84.26	1.11	14.16	0.47	84.87	9.61	5.52	27.54
40	84.08	1.45	13.89	0.58	85.32	8.84	5.84	28.01

3.4. Kinetic Study of Jute Stick

For the conversion of biomass to the bioenergy, the kinetic analysis is a significant criterion for the ideal design procedure of the thermochemical processes [52]. The results of the thermogravimetric analysis were elaborated according to the FWO and KAS methods for the calculation of the kinetic parameters under varying condition of different heating rates, i.e., 10 to 40 °C/min. The fractional conversions were varied from 0.10 to 0.80 to resolve the dissimilarity of the apparent activation energy throughout the process of the thermal decomposition. When, the conversion value was over 0.8, a very low value of the correlation factor was witnessed. The activation energy can be explained as the lowest quantity of energy which is mandatory to begin the reaction process. However, it is very challenging to initiate a reaction that needs an advanced activation energy. An upsurge in the discernible activation

energy was witnessed throughout the primary phases of the pyrolysis. A decrease in the apparent activation energy was witnessed when the conversion rises. The corresponding variations in the activation energy was presented in Figures 6 and 7. An increment in the activation energy (E_a), ranging from 0.1 to 0.6 represents the existence of the endothermic reactions, whereas, the existence of the exothermic reactions was observed with the further increase in the activation energy from 0.6 to 0.8. Due to a rapid increasing trend of the E_a from 119.90 to 148.12 kJ/mol in FOW method and from 116.70 to 144.95 kJ/mol in KAS method (Table 4), the process is defined as endothermic process, whereas due to a slight decreasing trend of E_a from 148.12 to 140.71 kJ/mol in FOW method and from 144.95 to 136.86 kJ/mol, the process is defined as exothermic process. This phenomenon was occurred because the chief constituents of the jute stick have dissimilar pyrolysis contents and activation energies. The values of R^2 (correlation coefficients) were higher than 0.9600 for all lines (Table 4). From Figures 6 and 7 and Table 4 we can summarize that; the model free methods are dependent regarding in deciding the activation energy. For the several pyrolysis heating rates a straight line could be obtained from the various conversions. In addition, from the gradient of regression lines, the activation energy could be anticipated (Figure 7).

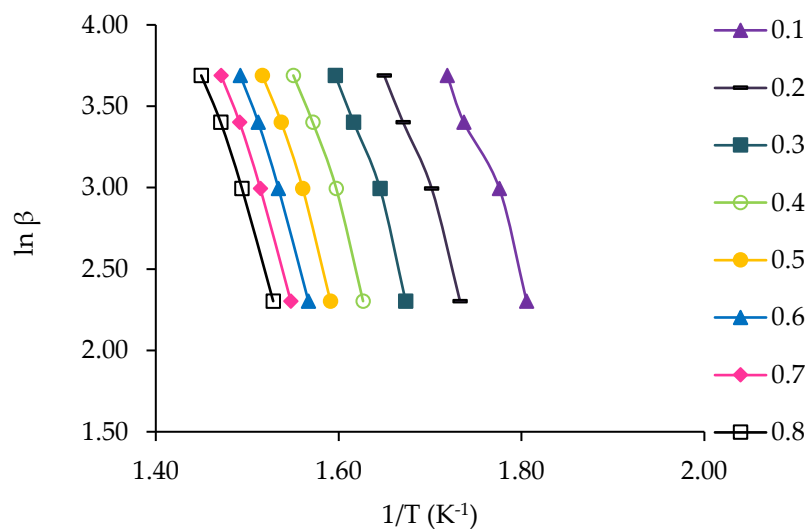


Figure 6. FWO plot of jute stick for different values of conversion.

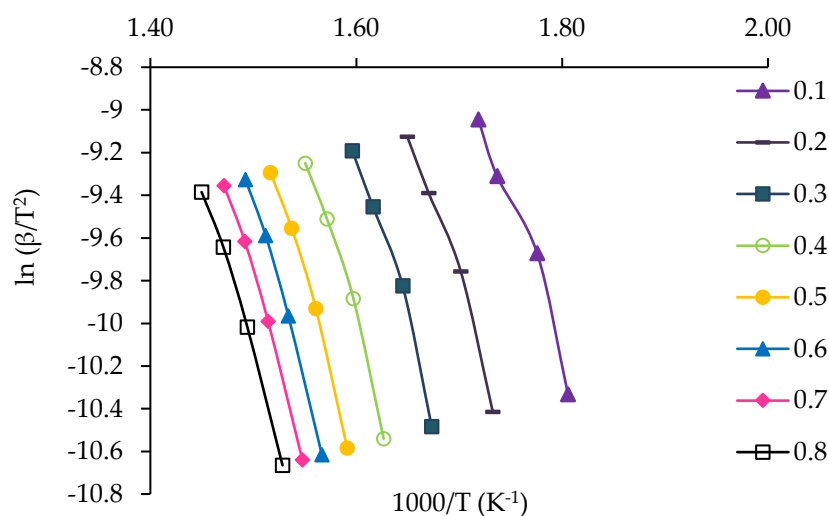


Figure 7. KAS plot of Jute stick for different values of conversion.

Table 4. The fitted equations, correlation coefficients (R^2) and activation energies (E , kJ/mol) obtained by the FWO method and KAS method.

α	FWO Method			KAS Method		
	Fitted Equation	R^2	$E\alpha$	Fitted Equation	R^2	$E\alpha$
0.1	$y = -15.17x + 29.78$	0.97	119.90	$y = -14.04x + 15.10$	0.97	116.70
0.2	$y = -16.41x + 30.80$	0.98	129.67	$y = -15.22x + 16.03$	0.98	126.57
0.3	$y = -17.68x + 31.96$	0.98	139.73	$y = -16.46x + 17.13$	0.98	136.82
0.4	$y = -18.15x + 31.88$	0.98	143.42	$y = -16.90x + 16.99$	0.98	140.41
0.5	$y = -18.63x + 32.00$	0.99	147.25	$y = -17.35x + 17.07$	0.99	144.21
0.6	$y = -18.74x + 31.70$	0.99	148.12	$y = -17.44x + 16.73$	0.99	144.95
0.7	$y = -18.33x + 30.71$	0.99	144.88	$y = -17.01x + 15.72$	0.99	141.40
0.8	$y = -17.80x + 29.55$	0.99	140.71	$y = -16.46x + 14.53$	0.99	136.86

The activation energies were achieved from the FWO and KAS methods are quite few. The activation energy was expanded from 119.90 to 148.12 kJ/mol, and after this, it was reduced to 140.71 kJ/mol in the FWO method. On the other hand, for the KAS method, it increased from 116.70 to 144.95 kJ/mol and then decreased to 136.86 kJ/mol, respectively. The achieved outputs from the FWO and KAS methods were in a good consent when deviation is lower than 3% and thus, validates the calculations and projecting ability of KAS and FWO methods [17,18].

Results of kinetic analysis revealed that the activation energy is extremely reliant on the conversion of biomass. When the conversion process proceeds, the variations in the reaction mechanism was clearly noticed which caused a significantly variations in the $E\alpha$ values (Table 4). The higher $E\alpha$ values represents a comparatively reluctant reaction since the activation energy was the lowest required energy to initiate a reaction process. Moreover, to calculate the reactivity of a fuel, the knowledge of $E\alpha$ will also be helpful [22]. For the pyrolysis kinetics of cardoon, Damartzis et al. [25] reported that the $E\alpha$ is 224.1 kJ/mol for the cardoon stems and 350.07 kJ/mol for cardoon leaves. In addition, for the pyrolysis of orange waste, Lopez-Velazquez et al. [18] estimated that, the $E\alpha$ values varied from 120 to 250 kJ/mol. Moreover, Gai et al. [22] focused on the kinetic mechanism of the rice husk and corn cob and the estimated the $E\alpha$ values approximately 79 and 129 kJ/mol, respectively. In addition, Huang et al. [15] examined soybean straw pyrolysis kinetics and stated that the $E\alpha$ ranges from 154.42 to 179.31 kJ/mol for KAS method and 155.20 to 179.71 kJ/mol for FWO method. In this paper, the calculated $E\alpha$ values for jute stick was found to be consistent with the previous research.

4. Conclusions

In the present study, the pyrolysis of a specific biomass (jute stick) was performed to obtain pyrolysis products under different heating rate conditions by varying the temperature from room to temperature 900 °C. For the clarification of the kinetic studies, the FWO and KAS method was used. The reduced amount of ash and moisture and enormous volatile matter states the significance of the jute stick as a probable source for the production of bio-chemicals. With the increase of the heating rate, the temperature extent of devolatilization period increased and the yields of the non-condensable gas were also increased. Moreover, the heating rate reduced the bio-char production and water content of bio-oil. The simulated results of the kinetics of the jute stick pyrolysis from the TGA analysis validates the experimental results. The activation energy increased from 119.90 to 148.12 kJ/mol, and then it was reduced to 140.71 kJ/mol in the FWO method. Moreover, for the KAS method, it increased from 116.70 to 144.95 kJ/mol and then reduced to 136.86 kJ/mol, respectively. Therefore, the kinetic results kinetic result would be helpful to model, design and to progress in the thermochemical processes for the utilization of waste jute stick. Combining with the different physicochemical characteristics, the outcomes of the present study conclude that, jute stick biomass can be used as an alternative source of energy or chemicals.

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