RESEARCH ARTICLE

Kinetic analysis of Malaysia type biomasses via thermogravimetric analyser (TGA)

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Abstract

The kinetic behaviour of biomass pyrolysis samples was successfully studied via thermogravimetric analysis. The biomass samples were empty fruit bunch, oil palm trunk, rice husk, coconut copra, sawdust, coconut shell, sugarcane bagasse, and wood bark. The analysis was performed in a nitrogen atmosphere from 30 to 700°C. The effect of heating rate on kinetic behaviour of biomass at two different high heating rates was evaluated at 40°C/min (HR1) and 80°C/min (HR2). The kinetic parameters of biomass samples such as pre-exponential factor (s^{-1}), activation energy (kJ/mol), and reaction order (n) were determined using one-step global kinetic model. The wood bark sample has the lowest activation energy (38.14 kJ/mol), while coconut copra was reported for the highest activation energy (145.42 kJ/mol). High positive activation energy was achieved at a higher heating rate (HR2) than at lower heating rate (HR1) for biomass samples.

Keywords: Biomass, thermogravimetric analysis, kinetic parameters

INTRODUCTION

Biomass is a biological material that frequently referring to plant-derived materials [1]. Moreover, biomass is categorized as renewable energy resources and sustainable [2]. Biomass is solid waste produced in large quantities which have no economic values [3]. Thus, the utilization of biomass can preserve the environment from the disposal wastes. Currently, the Malaysian government has established targets for conversion of biomass wastes into fuels as an alternative source of fuel energy [4]. It is because, Malaysia is rich in biomass sources such as agricultural wastes, forest residues, and municipal solid wastes [5]. For example, it has estimated that approximately 168 million tons of biomass annually produced in Malaysia, according to the report published by National Biomass Strategy 2020 in the year 2011 [6]. Hence, the renewable energy resource of biomass with sustainability has motivated many researchers to investigate the conversion of biomass wastes into valuable products [7–10]. Henceforth, many researchers have agreed that thermochemical conversion known as pyrolysis is the promising route to convert biomass wastes into valuable energy such as pyrolysis oil (bio-oil), biochar, and pyrolysis gas (H2 and CH4) [10–13]. Pyrolysis of biomass can be defined as thermal degradation of biomass in an inert environment (nitrogen) at the moderate reaction temperature (350 – 700°C) [11]. In addition, pyrolysis of biomass is highly generated pyrolysis oil yield in the range of 60 – 75 wt.% than pyrolysis gas (20 – 30 wt.%) and biochar products (15–25 wt.%) [12]. Interestingly, this pyrolysis oil has wide applications, for example, as gasoline enhancers in the petrochemical industry and as high-value-added chemical feedstock to manufacture detergents, synthetic fibres, and plastics [13]. Since pyrolysis is about

the thermal degradation of biomass in the absence of oxygen, thus it is important to understand the kinetic behaviour of biomass pyrolysis.

Thermogravimetric analysis (TGA) is the most commonly applied analysis for solid-phase thermal degradation studies and it has gained wide attention in thermal studies of biomass pyrolysis due to easy handling and low-cost system [14]. It has been shown extensively in the literature, particularly in recent times [3,7,8,14–17]. Other than that, the kinetic characteristics of biomass such as activation energy, pre-exponential factor, and reaction order are important in forecasting the thermal response of biomass sample [15]. Hence, TGA can also be applied to study the kinetic behaviour of biomass pyrolysis [16]. TGA-pyrolysis applied the non-isothermal condition to evaluate all the kinetic parameters, in which described by an Arrhenius equation [17]. On the other hand, kinetic studies of thermal degradation of biomass are known to be very complex. In a similar manner, biomass is degraded with increasing reaction temperature in parallel and series reactions. Ahmed and Gupta [18] indicated that the pyrolysis of biomass undergone parallel reaction at a high heating rate, while it undergone series reaction at the low heating rate. Therefore, it is important to determine the kinetic parameters of pyrolysis of biomass such as pre-exponential factor (A), activation energy (Ea), and reaction order (n). Interestingly, pyrolysis of biomass via TGA provides general information on the overall reaction kinetics [19]. In addition, various iso-conversional kinetic models are available in literature such as Flynn-Wall-Ozawa (FWO), Coats-Redfern (CR), and Kissinger-Akahira-Sunose (KAS) in order to understand the kinetic mechanism of biomass pyrolysis [20]. However, these models are proficient at lower heating rates (5 – 20°C/min). Since in this study, higher heating rates were employed which closer to

conventional pyrolysis condition (40–80 °C/min) and a straightforward kinetic model which known as a one-step global kinetic model was chosen in order for understanding the kinetic behaviour of biomass under higher heating rates.

On the other hand, limited studies on kinetic analysis have been conducted on Malaysia's biomasses. For example, Lim and co-workers [21] studied TGA-pyrolysis on rice husk from a local rice mill in Malaysia at various heating rates of 10, 20, 30, and 50 K/min. Shaaban *et al.* [22] investigated the thermal behaviour of rubberwood sawdust via TGA at a very low heating rate of 5°C/min, in which obtained from a sawmill in Malaysia. Thus, it can be concluded that currently most of the literatures are available on the effect of lower heating rates (5-20°C/min) on kinetic analysis of biomass pyrolysis [21-28]. Hence, the comprehensive study on the kinetic analysis biomass pyrolysis at a higher heating rate which closer to conventional pyrolysis condition on thermal degradation of Malaysian biomasses via thermogravimetric analysis (TGA) is still lacking in the literature. For this reason, the present study aimed to determine pyrolysis kinetic characteristics such as pre-exponential (A), activation energy (E), and reaction order (n) of eight types of Malaysia's biomass samples at two different heating rates (HR); HR1 (40 °C/min) and HR2 (80°C/min). The aim of selecting higher heating rates was due to its similiarity to the conventional pyrolysis conditions. The selected biomass samples were empty fruit bunch (EFB), oil palm trunk (OPT), rice husk (RH), coconut copra (CC), coconut shell (CS), wood bark (WB), sawdust (SD), and sugarcane bagasse (SB). These selected biomasses were chosen according to their availability in Malaysia.

EXPERIMENTAL

Materials

Biomass samples investigated in this study were abundantly available in Malaysia, which were empty fruit bunch (EFB), oil palm trunk (OPT), rice husk (RH), coconut copra (CC), sawdust (SD), coconut shell (CS), sugarcane bagasse (SB), and wood bark (WB). The EFB and OPT samples were collected from the nearest palm oil plantation in Johor, Malaysia. The WB samples were collected from Universiti Teknologi Malaysia (UTM) compound and SD samples were sampled from wood processing factory in Johor, Malaysia. Meanwhile, the CC, CS, and SB samples were collected from the local market. Lastly, RH samples were supplied by Padiberas Nasional Berhad (BERNAS). These samples were ground and sieved to obtain a particle size of less than 0.5 mm. Then, the samples were allowed for pre-treatment of drying at $105 \pm 2°C$ for about 24 hours until the weight remained constant. The samples were kept in a desiccator to prevent moisture absorption from the surrounding humidity.

Kinetic analysis of biomass pyrolysis

For TGA-pyrolysis of biomass, samples were carried out using TGA/SDTA851 (METTLER TOLEDO, USA) under nitrogen (N2) atmosphere at a fixed flow rate of 150 mL/min. For each experimental run, about 5 mg of biomass samples was pyrolyzed from 25°C to 700°C at a constant heating rates of 40 °C/min (HR1) and 80°C/min (HR2). Each sample was first heated to 110 °C and kept for about 30 minutes to remove any remaining moisture. Samples were then retained at the final temperature (700°C) for about 10 minutes. In general, TG graph of volatile mass loss over temperature and DTG graph of rate of mass loss over temperature are obtained from TGA-pyrolysis. Thus, for kinetic analysis, the kinetic parameters were determined from TG-DTG data using the modified form of Arrhenius equation suggested by Duvvuri *et al.* [29] and successfully used by Goenka *et al.* [30]. Hence, in light of literature, a simple kinetic model which is a one-step global kinetic model was selected for the simplification on understanding the kinetic behaviour of biomass under higher heating rates. Thus, the one-step global kinetic model of the volatilization reaction could be summarized as shown in Eq. (1).

$$Biomass \xrightarrow{k} Volatiles + Char \qquad (1)$$

The kinetic model in Eq. (1) could be expressed as a rate of conversion respect with time ($-\frac{dX}{dt}$), the rate constant (*k*), conversion of biomass sample (*X*), time (*t*) and reaction order (*n*) as shown in Eq. (2):

$$-\frac{dX}{dt} = (kX)^n \qquad (2)$$

Applying the Arrhenius equation with pre-exponential factor (*A*), absolute temperature (*T*), activation energy (*E*), universal gas constant ($R = 8.314 \ J. \ K^{-1}. \ mol^{-1}$).

$$k = Aexp^{-\frac{E}{RT}} \qquad (3)$$

Substituting Eq. (3) into Eq. (2):

$$-\frac{dX}{dt} = [Aexp^{-\frac{E}{RT}}X]^n \qquad (4)$$

Taking *ln* on both sides,

$$-ln\frac{dX}{dt} = ln A - \left(\frac{E}{RT}\right) + n(ln X) \qquad (5)$$

X could be written as:

$$X = \frac{w-w_f}{w_o-w_f} \qquad (6)$$

The initial weight of samples (w_o) at T = 30°C, final weight of samples (w_f) at T=700°C, weight of samples undergoing the reaction (*w*), the time taken for the degradation (*t*), temperature of degradation (*T*) for every step of temperature change were made into Microsoft-Excel sheet. Substituting Eq. (6) in Eq. (5):

$$-ln \left(\frac{\frac{dw}{dt}}{w_o-w_f}\right) = ln A - \frac{E}{RT} + n(ln \left(\frac{w-w_f}{w_o-w_f}\right)) \qquad (7)$$

Finally, Eq. (7) was of the form

$$y = B + Cx + Dz \qquad (8)$$

The parameters *y*, *x*, *z*, *B*, *C* and *D* in Eq. (8) were defined as follows:

$$y = -ln \left(\frac{\frac{dw}{dt}}{w_o-w_f}\right) \qquad (9)$$

$$x = \frac{1}{RT} \qquad (10)$$

$$z = ln \left(\frac{w-w_f}{w_o-w_f}\right) \qquad (11)$$

$$B = ln A \qquad (12)$$

$$C = -E \qquad (13)$$

$$D = n \qquad (14)$$

The aforementioned parameters were extracted from TG-DTG data attained from TGA experiments of each biomass samples. The multiple-linear regression method was applied in Microsoft-Excel using Linest Function to establish the constants *B*, *C* and *D* which corresponding to pre-exponential factor (*A*), activation energy (*E*), and reaction order (*n*). The kinetic parameters of biomass samples at HR1 and HR2 were obtained from TG – DTG data.

RESULTS AND DISCUSSION

Kinetic analysis of biomass samples

The multiple-linear regression method was employed in Microsoft-Excel using Linest Function to determine all the kinetic parameters. Hence, it was assumed that all biomass samples followed the one-step global kinetic model. The methodology used in the determination of kinetic parameters was adapted from Duvvuri *et al.* [29]. This methodology was successfully applied by Parthasarathy *et al.* [17] for a kinetic study on rice husk, sawdust and wheat husk as well by Goenka *et al.* [30] for sugarcane bagasse, rice husk, and sawdust samples. The calculated kinetic parameters for each biomass at HR1 (40°C/min) and HR2 (80°C/min) are given in Table 1. The coefficient of determination (R^2) values at HR1 and HR2 for all biomass samples were high (> 0.98). The high coefficient of determination (R^2) indicated that the kinetic parameters of all biomass samples were well correlated. As shown in Table 1, it can be observed that high positive activation energies were observed for all biomass samples at HR1 and HR2. This suggested that the pyrolysis reaction was strongly depended on heating rate. Higher heating rate increases the collision of molecules, influencing in a rapid degradation of biomass [14]. It could be further proved with a higher pre-exponential factor in HR2 than HR1 as shown in Table 1.

Table 1 Kinetic parameters of biomass samples at HR1 (40 °C/min) and HR2 (80 °C/min).

Biomass	Heating rate (°C/min)	Pre-exponential factor, A (s^{-1})	Activation energy, Ea (kJ/mol)	Reaction order, n
CC	40	0.95	64.70	0.62
	80	1.11	145.42	0.48
CS	40	0.85	68.46	0.46
	80	0.91	98.82	0.41
EFB	40	0.78	79.86	0.37
	80	0.89	101.52	0.38
OPT	40	0.89	65.71	0.50
	80	0.90	83.99	0.44
RH	40	0.73	47.37	0.40
	80	0.73	61.73	0.36
SD	40	0.81	49.99	0.45
	80	0.81	66.00	0.40
SB	40	0.99	97.15	0.48
	80	1.07	116.96	0.49
WB	40	0.62	38.14	0.37
	80	0.64	51.19	0.34

Table 1 illustrate that the activation energy of coconut copra (CC) drastically increased from HR1 (64.70 kJ/mol) to HR2 (145.44 kJ/mol). The corresponding pre-exponential factor was found to be 0.95 s^{-1} at HR1 and 1.11 s^{-1} at HR2. The augmentation in activation energy from HR1 to HR2 could be expected to, at higher heating rate more mass loss was accomplished, hence higher activation energy was expected to constantly crack the solid cellulose-hemicellulose structure. However, the biomass of lower activation energy is highly preferable when being applied in industrial scale. Alternatively, the reaction order for CC sample at HR1 and HR2 was found at 0.62 and 0.48, respectively (refer Table 1). Similarly, in a coconut shell (CS), the activation energy at HR1 was found to be lower (68.46 kJ/mol) than HR2 (98.82 kJ/mol) (see Table 1). As shown in Table 1, it is noticed that the corresponding pre-exponential factor of CS sample was reported to be 0.85 s^{-1} for HR1 and 0.92 s^{-1} for HR2. In addition, the reaction order for CS at HR1 and HR2 was found to be 0.46 and 0.41, respectively. Empty fruit bunch (EFB) showed high positive activation energy at HR2 (101.52 kJ/mol), while low at HR1 (79.86 kJ/mol). The pre-exponential factor for EFB at HR1 and HR2 was reported at 0.78 and 0.89 s^{-1}, respectively (refer Table 1). The reaction order of EFB showed that HR1 and HR2 were not influenced by

biomass concentration. Chew *et al.* [31] did a similar study on the kinetic parameters of EFB at 20°C/min using TGA. They recounted the activation energy was 35.18 kJ/mol and the pre-exponential factor was 0.45 s^{-1} at the second stage of EFB degradation (200 – 300°C). Hence, it could be concluded that the activation energy of pyrolysis of EFB was increased with increasing heating rate.

TGA pyrolysis of OPT at a higher heating rate (HR2) has an activation energy of 83.99 kJ/mol. In meantime, HR1 has lower activation energy (65.71 kJ/mol). Further, reported the pre-exponential factor for HR1 and HR2 were 0.89 and 0.90 s^{-1}, respectively. Rice husk (RH) was indicated to exhibit higher activation energy (61.72 kJ/mol) for HR2 than HR1 at 47.37 kJ/mol. The reaction order was found to be 0.40 for HR1 and 0.36 for HR2. Recently, Goenka *et al.* [30] in their work on TGA of rice husk at a heating rate of 5°C/min reported that the activation energy for the second zone (170.32 - 402.01°C) was 31.51 kJ/mol. At the same time, they reported that the order of reaction was 0.55. Thus, the increment in heating rate concurrently decreased the reaction order of rice husk sample. The activation energy for sawdust (SD) at HR1 and HR2 was found to be 49.99 kJ/mol and 66.00 kJ/mol, respectively. The corresponding pre-exponential factors were 0.71 and 0.81 s^{-1} respectively. Similarly, Parthasarathy *et al.* [17] investigated the kinetic parameters of sawdust at the heating rate of 10 °C/min. They found that the activation energy was 62.29 kJ/mol for a second zone (182.69 - 372.14°C). Further, they reported the order of reaction and the pre-exponential factor was 0.67 and 2.14 × 10¹⁰ s^{-1}, respectively. Pyrolysis of SB via TGA showed the promising result of obtaining positive activation energy at both HR1 and HR2. The activation energies were found to be 97.15 kJ/mol (HR1) and 116.97 kJ/mol (HR2). El-Sayed and Mostafa [32] did a similar study on kinetic parameters of SB at a heating rate of 15 °C/min using direct Arrhenius method. They reported that the activation energy of SB was 57.0 kJ/mol for second zone degradation (200 – 500°C) Hence, increasing heating rate would increase the activation energy. In their study, they found the order of reaction (n) was 0.50, in which almost similar to the results obtained from this study for HR1 (n = 0.48) and HR2 (n = 0.49) (see Table 1).

Lastly, kinetic parameters of wood bark (WB) have lower activation energies at both HR1 (38.14 kJ/mol) and HR2 (51.19 kJ/mol) compared to other types of biomass (see Table 1). This might be due to the structure of WB that was too rigid and difficult in cracking the cell wall. Other than that, low compositions of hemicellulose and cellulose in woody type biomass might influence the kinetic parameters. The pre-exponential factors were obtained at 0.62 s^{-1} (HR1) and 0.64 s^{-1} (HR2). Anastasakis *et al.* [12] did a similar study on wood at a heating rate of 10°C/min and reported that the activation energy was 38.40 kJ/mol. It could be concluded from our calculations that all types of biomass pyrolysis have higher activation energy at HR2. The variance in reaction order with previous work could be due to the diverse set of heating rates for the similar type of biomass [30]. In general, pyrolysis of biomass at higher heating rate has a short residence time that avoids secondary reactions [14]. Moreover, the kinetics were well described by the high activation energy (Ea) and pre-exponential factor (A) values at HR2. In contrast, a lower heating rate would slow down the pyrolysis reaction and produce a lower value of reaction rate constant [33]. In summary, the variance in kinetic parameter values of the present and past works was due to the difference in physical and chemical composition of the biomass samples. In one hand, the difference in heating rate has a profound influence on the values of the kinetic parameters. On the other hand, the results of kinetic parameters were dependent on varying factors such as instrument used, the methodology adopted, heating rate and type of biomass. These results suggested that this one-step global model method could be an effective tool for revealing the kinetics of biomass pyrolysis.

CONCLUSION

Kinetic analysis via TGA-pyrolysis on biomass samples (EFB, OPT, RH, CC, SD, CS, SB, and WB) was successfully conducted at two different heating rates of 40°C/min (HR1) and 80°C/min (HR2) in

a nitrogen atmosphere. The results of kinetic analysis would provide a crucial insight into the thermal degradation behaviour of Malaysia's biomasses that could be used as feedstock for industrial thermal conversion specifically pyrolysis. In future, it is suggested that the pyrolysis of biomass should be conducted in a lab-scale reactor at heating rates of 40°C/min and 80°C/min, in order to study the product distribution of pyrolysis products (pyrolysis oil, pyrolysis gas, and biochar). Other than that, it is also suggested that the study on the effect of catalyst on biomass pyrolysis towards the kinetic behaviour of catalytic pyrolysis of biomass should be conducted, due to an efficient conversion of biomass and lower activation energy that will require the application of inexpensive catalyst in biomass pyrolysis to meet the industry perspective.

ACKNOWLEDGEMENT

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