STUDY ON KINETICS OF PYROLYSIS REACTION (DEGRADATION) OF RICE HUSK, CORN COB AND SUGARCANE BAGASSE AS AGRICULTURAL RESIDUES IN VIETNAM

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ABSTRACT

The thermal degradation of the agricultural residue species such as rice husk (RH), corn cob (CC) and sugarcane bagasse (SGB) in the inert atmosphere has been studied by thermo-gravimetric analysis (TGA). Parameters of the reaction kinetics of biomass pyrolysis were calculated using Flynn-Wall-Ozawa method (FWO) and compared with acacia wood's one. The results show that, the average activation energy of rice husk is lower than activation energy of acacia wood. The average activation energies of corn cob and sugarcane bagasse are higher than that of acacia wood thermal degradation. This result has important role in the reactor design for using agricultural residue to generate power such as pyrolysis or gasification.

Keywords: thermo-gravimetric, rice husk, corn cob, sugarcane bagasse, activated energy.

1. INTRODUCTION

In the last decades, large study was dedicated world-wide to the getting back of energy from renewable fuels. Biomass is an alternative and renewable energy source, abundantly available worldwide. Biomass includes three main components such as hemicellulose, cellulose and lignin with traces of minerals and extractives, which exist in the range of 19 – 25 %, 32 - 45 % and 14 – 26 % (by weight), respectively [1]. The percentage of these constituents varies from biomass to biomass. The difference in thermal response exhibited by biomass is due to the varying proportion of these components. Thermo-gravimetric conversion processes are an important option for integrated energy and chemicals recovery from biomass.

Pyrolysis is the thermal decomposition of biomass occurring in the absence of oxygen and is the first step in any thermochemical conversion process, as gasification or combustion.

Thermal behavior of biomass can be investigated applying thermo-gravimetric analysis (TGA). TGA is the thermal analysis technique which is now being widely used to evaluate the thermal behavior of solid fuels such as biomass, polymers, coal [2, 3]. It gives date on change in weight with respect to temperature corresponding to temperature variation throughout the work. Many studies have focused on TGA of biomass but only few studies have come out in determining the kinetic parameters of all major constituents of biomass such as hemicellulose, cellulose and lignin [4]. Moreover, previous works [5] have taken only one sample as a matter of study. The agricultural residues in Vietnam, such as rice husk, were also studied with the thermal behavior [6] but to the best of our knowledge there is no publication about determination of kinetic parameters. The present study focuses on TGA of different biomass samples such as rice husk (RH), corn cob (CC) and sugarcane bagasse (SGB) at a heating rate of 3, 5 and 10 ^{o}C min^{-1} in inert nitrogen atmosphere. The reasons for lower heating rate is that it facilities effective heat and mass transfer within the particles. Further, small heating rate provide distinct degradation zones in the TGA curves. In the other hand, the current study determines the kinetic parameters (activation energy, pre-exponential factor and order of reaction) for all biomass samples. The focus of this study is to understand the thermal behavior of agricultural residues in Vietnam. Determination of kinetic parameters such as activation energy, pre-exponential factor and order of reaction is essential as all these parameters help in estimating the thermal nature of biomass samples.

2. MATERIALS AND METHODS

Three biomass materials were used in the present study: RH, CC and SGB. The biomass feedstock was provided by the School of Chemical engineering, Hanoi University of Science and Technology (Vietnam) which were farmed and harvested in Thanh Hoa (Vietnam), dried for a period of 2 - 3 weeks and after that dried overnight (15 h at 105 ^{o}C) and the samples were kept in closed polyethylene bags to avoid contamination prior to carrying out the tests. The samples were milled to powder and sieved to a particle size less than 1 mm. The proximate analysis of the dried biomass samples on a dry basis and were shown in the previous publication [6]. The techniques and procedures were also clearly presented in the previous publication [7]. Thermo-gravimetric analysis (TG/DTG) with Parkin Elmer PYRIS Diamond model was used for both pyrolysis analyses. 10 mg sample was loaded into an alumina crucible and heated at programmed temperature by the rates of 3, 5 and 10 ^{o}C min^{-1} in nitrogen environment. The weight loss of biomass samples were recorded during the analysis process. Because of the two step nature of thermal decomposition reactions, it was necessary to determine and use different kinetic parameters to describe the thermal degradation over the entire temperature range of higher than accuracy. Parameters of the reaction kinetics of biomass pyrolysis were applied by Alwani et al. [6] using Flynn-Wall-Ozawa method.

The most commonly used equation to describe the reaction rate in the non-isothermal decomposition kinetics is presented as Eq. 1.

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where α, t, k and f(α) represent the degree of conversion, time, rate constant, and reaction model, respectively. k is the rate constant of reaction whose temperature dependence is expressed by the Arrhenius equation (Eq. 2)

$$k = A. e^{\frac{-E_a}{RT}} \tag{2}$$

where: E_a is the activation energy (kJmol^{-1}), T is the absolute temperature in Kelvin (K), R is the gas constant (8.314 J K^{-1} mol^{-1}) and A is the pre-exponential factor (min^{-1}).

The conversion rate (α) can be calculated according to Eq. 3.

$$\alpha = \frac{m_i - m_a}{m_i - m_f} \tag{3}$$

where: m_i is the initial mass of the sample, m_a is mass at time t, and m_f is the final mass.

Combination of equations 2 and 3 gives the fundamental expression of analytical methods to calculate the kinetic parameters, which is expressed in Eq. 4.

$$\frac{d\alpha}{dt} = A. f(\alpha). e^{\frac{-E}{RT}} \tag{4}$$

For a dynamic TGA process, introducing the heating rate, $\beta = dT/dt$ into Eq. 4, Eq.5 can be derived:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = A. f(\alpha). e^{\frac{-E}{RT}} \tag{5}$$

Eqs. (4) and (5) are the fundamental expressions of analytical methods to calculate kinetic parameters on the basis of TGA data.

The techniques developed for the evaluation of the kinetic parameters for non-isothermal thermo-gravimetric analysis can divided into fitting models and free models. With the free model is not necessary to assume a kinetic reaction while kinetic parameters are obtained as a function of conversion or temperature. Within such model there are the iso-conversional methods which assume a constant degree of conversion and therefore the reaction rate depends only on the temperature. Thus, these methods allow the estimation of the activation energy, E_a, as a function of conversion, α, and independently of the reaction model, $f(\alpha)$.

The Flynn-Wall-Ozawa method (FWO) is an integral iso-conversional technique where regrouping the terms of equation (5), and integrating these with respect to α and T variables and using the approximation of Doyle the following expression is obtained:

$$\ln\beta = \log(\frac{AE}{Rg(x)}) - 5.331 - 1.052 \frac{E_a}{RT} \tag{6}$$

Thus, in the FWO method the plot of $\ln(\beta)$ versus $1/T$ for different heating rates allows to obtain parallel lines for a fixed degree of conversion. The slope (-1.052 E_a/R) of these lines is proportional to the apparent activation energy. If equal E_a values are obtained for different values of α, it can be assumed with certainty that there is a single reaction step. By contrast, a change in E_a with an increase in the conversion degree is indicative of a complex reaction mechanism [3, 8, 9].

3. RESULTS AND DISCUSSION

The thermo-gravimetric analysis (TG) curves for three biomass samples and acacia wood at 10 ^{o}C min^{-1} under nitrogen atmosphere are presented in Figure . Their thermal behavior was similar to each other. Three distinct weight loss stages could be determined and it is in agreement with other research [9]. The first stage is corresponding to removal of moisture content of biomass. In the second stage (first decomposition), it is a rapidly removing volatile in

a narrow temperature range (approximately 200 – 400 °C) of biomass. The degradation of biomass in the second s started at 210, 209 and 230 °C for RH, CC and SGB, respectively. There was 52.7 % weight loss for RH, 56.6 % for CC and 58.7 % for SGB residues. Hemicellulose, cellulose and lignin are the major component of biomass and the decomposition of those ingredients occurred at this temperature range. Hemicellulose decomposition takes place in the range of 200 – 350 °C, cellulose is decomposed in the range of 350 – 500 °C and partial of lignin also decomposed in this temperature range [10].
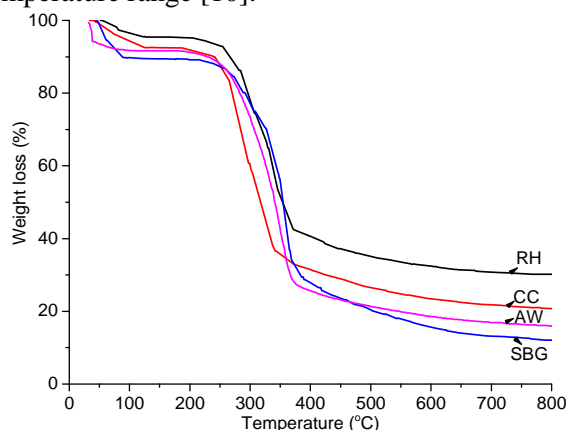

Figure 1. TG curves of biomass samples at heating rate by 10 °C min^{-1} in the nitrogen environment.

For third stages in the range of 400 – 900 °C (second decomposition), all biomass samples had a much lower weight loss in comparison to the second stage. The weight loss for CC and SGB was 14.6 % and 17.8 %, respectively. While for RH, the weight loss was 12.1 %. For this stage, Taro Sonobe et al. [11] reported that the char consists of the residue of lignin and some cross-linking of cellulose with lignin continues to further exothermic polymerization stage of char. The explanation assumes that at the higher temperature, the polymerization of biomass char continuously occurred and the polymerization reaction is dependent on the unique properties of biomass char. The results are the same as the thermal behavior of acacia wood reported in our previous research. Thermo-gravimetric analysis of acacia wood in nitrogen atmospheres at 3, 5 and 10 °C min^{-1} were also three distinct stages of weight loss. The second stage was occurred in a range from 210 to 390 °C and the third stage from 360 - 380 to 850 °C [7].
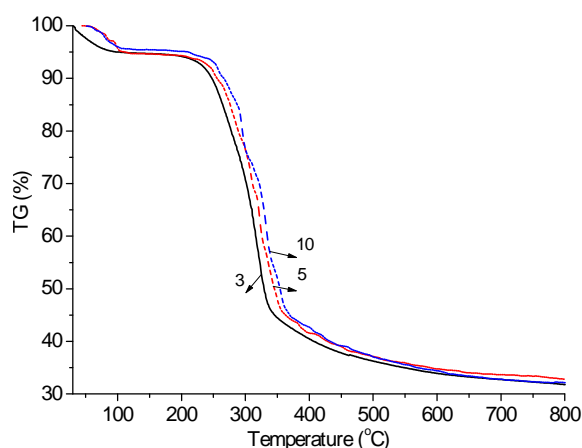

Figure 2. TG curves of RH at heating rate 3, 5 and 10 °Cmin^{-1} in the nitrogen environment.

Heating rate is one of the most important parameters influencing the pyrolysis characteristics. The TG curves for the pyrolysis of rice husk at different heating rates is presented in Figurre 2. It is clear from this TG curve that considerable different trends in the rates of weight losses took place when heating rate changed from 3 to 10 ^{o}C min^{-1}. The weight loss increased with heating rate increasing. The phenomenon related to this important change can be explained by the fact that biomass has a heterogeneous structure and possesses a number of constituents. These constituents gave their characteristic individual decomposition weight loss range in the pyrolysis process. When heating rate was sufficiently low during pyrolysis, most of these temperature ranges and these peaks can be seen as small broken lines or vibrations. However, at high heating rates separate peaks did not occur because some of them were decomposed simultaneously and several sequential temperature ranges were united to form overlapped broader and higher peaks [12 - 14]. This phenomenon can be a result of heat and mass transfer limitations. The temperature in the furnace space can be a little higher as the temperature of the particle and the rate of decomposition are higher than the release of volatiles with heating rate increasing. Because of the heat transfer limitation, temperature gradients may exist in the particle. Temperature in the core of a particle can be a bit lower than temperature on its surface and different decomposition processes or releasing rates can occur. This is the reason why it is necessary to have a small particle, homogeneous sample and the heat transfer surface between the sample and the crucible as large as possible [4].

The kinetic parameters such as pre-exponential factor, activation energy and order of reaction of the biomass samples are determined by FWO method. The details about the method was also shown in our previous report [7]. The plots of the FWO method, which was used for the determination of the E_a values for all species studied, show a general trend. Because the kinetic behavior is similar for the agricultural species studied, only RH was chosen as a representative model for the presentation of the E_a results. Therefore, Figurre 3 shows the results of the application of the FWO method with α value from 15 % to 85 % that occur strong thermal degradation of biomass. The linear fits obtained from the plot of log β vs. 1000/T. The E_a values were calculated from the angular coefficient obtained from the straight line fit. The obtained kinetic parameters for all samples are shown in Table 1.
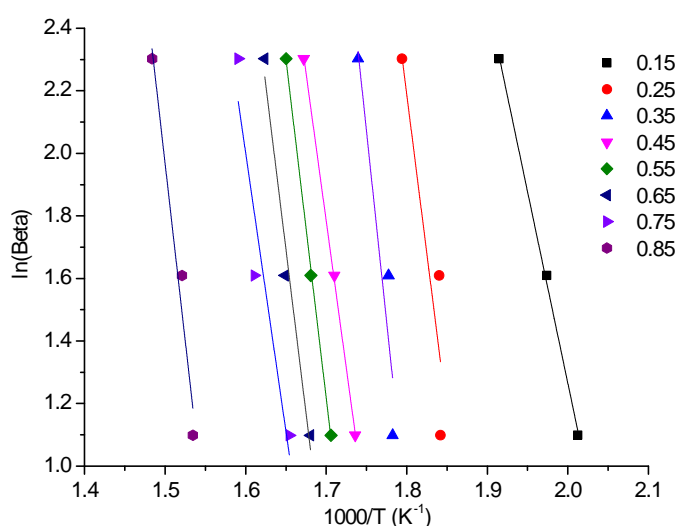

Figure 1. Plot of FWO method for RH showing the linear fits obtained.

Table 1. Activation energies obtained using the FWO method for the wood species studied.

α	RH		CC		SGB	
	E_a (kJmol^{-1})	R^2	E_a (kJmol^{-1})	R^2	E_a (kJmol^{-1})	R^2
0.15	96.8	0.99	110.2	0.92	168.6	0.99
0.25	161.2	0.84	139.4	0.96	180.9	0.99
0.35	192.8	0.89	138.9	0.99	165.4	0.96
0.45	149.1	0.99	252.8	0.97	156.9	0.97
0.55	171.4	0.99	315.5	0.99	173.1	0.99
0.65	166.0	0.98	224.2	0.99	174.2	0.94
0.75	140.8	0.91	212.7	0.98	177.7	0.99
0.85	179.3	0.97	161.8	0.93	171.6	0.99
AV	157.17	0.95	194.43	0.97	171.06	0.98

The activation energy is approximately 157.17 kJmol^{-1} for the RH specie. The average activation energy of CC and SGB is 194.43 and 171.56 kJmol^{-1}. This indicates that RH has a lower thermal stability than corn cob and sugarcane bagasse probably because they contain lower quantities of cellulose. SGB has highest cellulose content [15] leading to a higher activation energy. The activation energy value of CC in this study is the similar with the report of Sittisun et al [16] that the activation energy was from 154 to 255 kJmol^{-1}. The average activation energy of RH is near activation energy of acacia wood (AW) (158.36 kJmol^{-1}). The cellulose and lignin content of AW are from 39 to 25 wt% and 24 to 25 wt%, respectively [17]. According to Mamleev et al. (2006) [18] the polymerization of cellulose by trans-glycosylation during pyrolysis involves an activation energy close to 200 kJmol^{-1}. The E_a of hemicellulose with a value close to 110 kJmol^{-1} [5]. The average activation energy of CC and SGB are higher than the activation energy of acacia wood thermal degradation.

4. CONCLUSION

This study investigated the thermal degradation and determined the kinetic parameters for the reaction of pyrolysis of biomass rice husk, corn cob and sugarcane bagasse in a nitrogen atmosphere for three different heating rates. The activation energy for the RH, CC and SGB with the Flynn–Wall–Ozawa method was also compared with the activation energy of other biomass that was reported. The activation energy of rice husk between 96.8 kJmol^{-1} and 179.3 kJmol^{-1} and the average activation energy is 157.17 kJmol^{-1} lower than activation energy of acacia wood (158.36 kJmol^{-1}). The average activation energy of corn cob and sugarcane bagasse is higher than the activation energy of acacia wood and rice husk thermal degradation which are 194.43 and 171.56 kJmol^{-1}, respectively.

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