



7. DEVOLATILIZATION BEHAVIOR AND PYROLYSIS KINETICS OF RICE HUSK

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ABSTRACT

This study presents the pyrolysis process of rice husk using a thermogravimetric analyzer in nitrogen atmosphere. The samples were heated over a range of temperature from 29 to 906 °C with three different heating rates of 10, 20 and 30 °C min⁻¹. The results of thermal decomposition process show three main stages such as water removal, main devolatilization and continuous slight devolatilization. It also showed that as the heating rates increase from 10-30 °C/min, maximum weight loss shifted to higher peak temperatures. The model free methods of Kissinger-Akahira-Sonose (KAS) and Kissinger were applied to the experimental data, generating kinetic parameters such as activation energy and pre-exponential factor. The average activation energy and pre-exponential factor calculated from KAS method are 73.64 kJ/mol and 9.10×10^6 min⁻¹, respectively while the activation energy and pre-exponential factor obtained for Kissinger method are 67.12 and 2.54×10^5 kJ mol⁻¹, respectively. The kinetic results can be used for better understanding of the composition of the devolatilization process at different temperatures thereby providing data for effective design of a pilot plant which can be effectively scaled up.

Keywords: rice husk, pyrolysis, thermogravimetric analysis, kinetic, KAS, Kissinger.

1.0 Introduction

Many countries around the world are presently placing high priority on agricultural development because it plays a dominant role in the overall wellbeing of human and animal life ensuring adequate food security and employment generation. Agricultural residue such as wood, wood wastes, agricultural crops and wastes, forest residue, mill residue, animal waste, livestock operation residues and aquatic plants. These wastes are by products of agricultural production practice which is reported to have potential to provide about 14% of the world's energy resources and account for about 35% of the primary energy consumption in developing countries (Idris *et al.*, 2010). Presently, the



economic growth of developing nations like Nigeria is focusing on agricultural base. Therefore, utilizing biomass materials which include all residues generated by the agricultural activities, into biofuels is highly attractive (Garba *et al.*, 2006). Biomass in its natural state is characterized with heterogeneous structure, hydrophobicity and low calorific value. Thermochemical conversion is one of the viable techniques for improving the energy potential and conversion of biomass into renewable green fuel.

In the thermochemical conversion of biomass into fuel, pyrolysis represents a first step which requires an in-depth knowledge in order to understand complexity of biomass kinetics (Garba *et al.*, 2012). Pyrolysis is one of the thermochemical processes that take place at temperatures of about 400-500°C in the presence of nitrogen or other inert gas, to retard the occurrence of gasification and combustion reactions. The products of biomass pyrolysis (combustible tar, biochar, and gases) are associated with higher energy content when compared to the original feedstock (Garba, 2013). Presently, pyrolysis of biomass feedstock is the central focus in many research papers about pyrolysis (Anca-Couce *et al.*, 2014; Cardoso *et al.*, 2011) due to its availability and renewability (White *et al.*, 2011).

The goal of every kinetic study is to estimate the kinetic parameters such as activation energy (E_a), pre-exponential factor A , and reaction order n , that will represent the reaction and also to optimize the process and design pyrolytic reactors (Mohan *et al.*, 2006; White *et al.*, 2011). Thermogravimetry analysis (TGA) is traditionally used in modeling the kinetic of pyrolysis using semi-empirical models which assume the decomposition to occur via a single-step reaction. There are many methods for analyzing non-isothermal solid-state kinetic data from TGA (Simon, 2004; Sbirrazzuoli *et al.*, 2009; Khawam, 2007). These methods can be divided into two model-fitting (Differential, Freeman-Carroll and Coats-Redfern methods) and model-free (Kissinger, Flynn-Wall and Ozawa, Vyazovkin and AIC and Kissinger-Akahira-Sonose methods) methods. Model-fitting methods have been used for solid-state reaction to directly estimate the kinetic parameters from a single TGA curve. However, these methods suffer setback because of inability to estimate the reaction model (Khawam, 2007; Opfermann *et al.*, 2002). Model-



free methods require more than one TGA curves (TGA measurement at different heating rate) at different conversion to perform the kinetic analysis. Calculations from many curves at different heating rates are carry out on the same conversion value to allows estimation of activation energy for each conversion point. Model-free method is further divided into isoconversional (Flynn-Wall and Ozawa, Vyazovkin and AIC and Kissinger-Akahira-Sonuse methods) and non-isoconversional method (Kissinger method). Kissinger method is non-isoconversional method because it does not calculate E_a values at conversion point but considered constant activation energy (Sbirrazzuoli *et al.*, 2009).

Therefore, the objective of this study is to present the kinetic modeling of biomass using two model-free methods. This paper compared the applicability of the isoconversional (Kissinger- Akahira- Sunose Method) and nonisoconversional models (Kissinger method) in estimating the kinetic parameters for biomass pyrolysis.

2.0 Material Method

2.1 Proximate and ultimate analysis

The rice husk used in this experiment was collected from Minna, Niger State. The experiments were divided into two steps; the first step was to study the pyrolysis characteristics of rice husk by using proximate, ultimate analysis and thermal decomposition. The second step was to study the pyrolysis kinetics of rice husk. The proximate analysis of the rice husk sample for moisture content, volatile matter and ash was carried out according to ASTM D 3172 method and ultimate analysis was done according to ASTM D 3176. The thermal degradation was carried out by with the aid of TGA. The sample of a ground rice husk was obtained by grinding the rice husk to an average particle size of less than 150 μm because it was considered small enough to avoid the effects of heat and mass transfer between particles (Garba *et al.*, 2016). 20 mg of the rice husk sample was used in the experiment. The weight loss of the sample as a function of temperature was measured.

2.2 Experimental Setup



A thermogravimetric analyser (Perkin Elmer TGA-4000) was used to perform the thermal degradation experiments. The biomass samples were placed in an open platinum pan (6 mm internal diameter and 2.5 mm depth) with initial masses of 10.18 ± 0.09 mg. The temperature was controlled from room temperature (~ 25 °C) up to 900 °C, at the heating rates of 10 °C/min, 20 °C/min, and 30 °C/min. Nitrogen (99.996%) at a flow rate of 20 mL/min was used. The equipment was purged with nitrogen 10 min before starting each run in order to avoid the samples oxidation.

2.3 Analysis and data processing

The weight loss data were processed to thermogravimetry (TG) and derivative thermogravimetry (DTG) curves using the Pyris 1 TGA's design by Perkin Elmer Corporation. The kinetic parameters such as activation energy and pre-exponential factor were calculated using the program MS Excel 2014.

2.2 Determination of Kinetic parameters

The pyrolysis kinetics of reactions in solid-state are described by the following equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

Conversion, α , is normalized form of weight loss data of decomposed sample

$$\alpha = \frac{m_i - m_a}{m_i - m_f} \quad (2)$$

where m_i is the initial mass of the sample, m_a is the actual mass and m_f is the mass after pyrolysis. According to Arrhenius equation, the rate constant k is given by:

$$k = A e^{-E_a/RT} \quad (3)$$



where E_a is the activation energy (kJ mol^{-1}), T is the absolute temperature (K), R is the gas constant ($8,314 \text{ J K}^{-1} \text{ mol}^{-1}$) and A is the pre-exponential factor (min^{-1}). Combination of the two equations (1) and (3) gives the fundamental expression (4) of analytical methods to calculate kinetic parameters, on the basis of TGA results.

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot e^{-E_a/RT} \quad (4)$$

The expression of the function $f(\alpha)$ and its derivative $f'(\alpha) = -1$ are used for describing solid-state first order reaction, hence many authors restrict the mathematical function $f(\alpha)$ to the following expression (Katarzyna *et al.* 2011; Cardoso *et al.*, 2011):

$$f(\alpha) = (1-\alpha)^n \quad (5)$$

where n is the reaction order. Substituting (5) into equation (4) gives:

$$\frac{d\alpha}{dt} = A \cdot (1-\alpha)^n \cdot e^{-E_a/RT} \quad (6)$$

For TGA experiments at linear heating rate $\beta = dT/dt$, equation (6) can be written as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot (1-\alpha)^n \cdot e^{-E_a/RT} \quad (7)$$

This equation expresses the fraction of material consumed in the time. In this work the activation energy was obtained from non-isothermal TGA. The methods used to calculate kinetic parameters are called model-free non-isothermal methods and require a set of experimental tests at different heating rates. Kissinger method allows kinetic parameters of a solid-state reaction to be obtained directly without knowing the reaction mechanism. Here, activation energy is obtained from a plot of $\ln\left(\frac{\beta_i}{T_{mi}^2}\right)$ against $\frac{1000}{T_{mi}}$ for TGA measurement at different heating rates (β), where T_m is the peak temperature of the DTG curve. Kissinger equation is given as follow:



$$\ln\left(\frac{\beta_i}{T_{mi}^2}\right) = \ln\left(\frac{AR}{E\alpha}\right) - \frac{E}{RT_{mi}}$$

(8)

The slope of the plot, which is equal to $-E\alpha/R$ give the activation energy $E\alpha$. Kissinger-Akahira- Sunose Method (Katarzyna *et al.* 2011; Cardoso *et al.*, 2011) can be employed to determine the kinetic parameters based on the following equation

$$\ln\left(\frac{\beta_i}{T_{ai}^2 \alpha_i}\right) = \ln\left(\frac{A\alpha R}{E\alpha g(\alpha)}\right) - \frac{E\alpha}{RT_{ai}} \quad (9)$$

Plot of $\ln\left(\frac{\beta_i}{T_{ai}^2 \alpha_i}\right)$ against $1000/T_{ai} \times 10^{-3}$ given α , with slope equal to $-E\alpha/R$.

3. Results and Discussion

3.1 Characterization of fuel

The proximate and ultimate analysis results are presented in Table 1. The samples presented a significant amount of volatile matter of up to 66% which facilitates the devolatilization process. In addition, the relatively low ash prevents deposit formation such as slagging and fouling, which is cause by the presence of inorganic matter (Garba *et al.*, 2013).

Table 1: Ultimate and proximate analysis of rice husk

Proximate analysis	Moisture	Volatile matter	Fixed carbon	Ash	
	3.81	66.02	22.01	8.18	
Ultimate analysis	C	H	O	N	S
	43.83	6.76	46.07	0.93	0.94

3.2 Thermogravimetric analysis

The weight loss thermogram (TG) and derivative thermogram (DTG) for rice husk at 10 °C/min was first elucidated in Figure 1. Generally, pyrolysis can be divided into three



main stages: moisture removal, primary devolatilization, secondary slight devolatilization. The first stage (<150°C) is usually associated with minor water loss (4-5%). The second stage (between 150 and 400°C) is the main devolatilization stage where the major decomposition take place is associated with removal of large amount of volatile (Katarzyna *et al.*, 2011). Biomass is composed of lignocellulose (hemicellulose, cellulose and lignin) as the major components. Thermal decomposition of lignocellulose components in Rice husk occur second stage as shown in Figure 1. Hemicellulose degrades in the temperature range of 175-240°C while cellulose decomposes between the temperature of 240-386°C. Lignin degrades slowly of temperature range of 175-380°C. The third stage (>380°C) a slight weight loss is observe above 360°C. The weight loss in the TG curve (in Figure 1) shows the weight loss with temperature at different heating rates. As can be observed from the plot, the devolatilization process begins at about 175°C (beginning of stage 2) and proceeds rapidly with increasing temperature until about 580 °C (at the end of stage 2 and beginning of stage 3) and then the weight loss decreases until it reaches a final temperature. The solid residue yields at the final temperature were about 19, 22 and 24 % for heating rate of 10, 20 and 30 °C/min respectively. Figure 1 show the peak temperature at the maximum weight loss (T_p) which was described on the curve of DTG. It was clearly observed in Figure 2a and 2b that as the heating rates increase from 10 to 20 and 30°C/min, maximum weight loss shifted to higher peak temperatures. Katarzyna *et al.* (2011) reported that increase in heating rate tend to delay maximum weight loss to a higher temperature. This is because at higher heating rate, rice husk reaches maximum weight loss within a short time. Also, it was observed from figure 2a and 2b that amount of solid residue remaining after thermal decomposition of rice husk increase from 19, 21, and 22%, as the heating rate increases from 10, 20 and 30 °C/min.

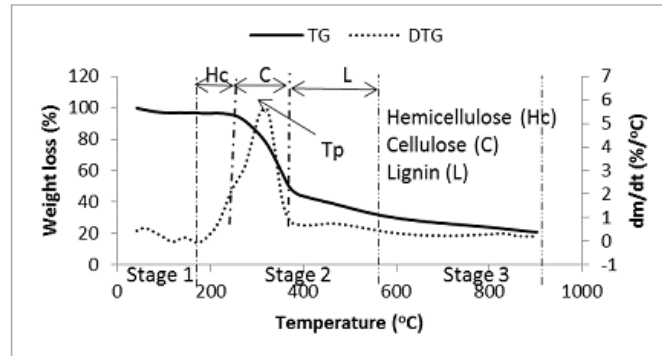


Figure 1: TG and DTG curves of rice husk for heating rate of 10 °C/min.

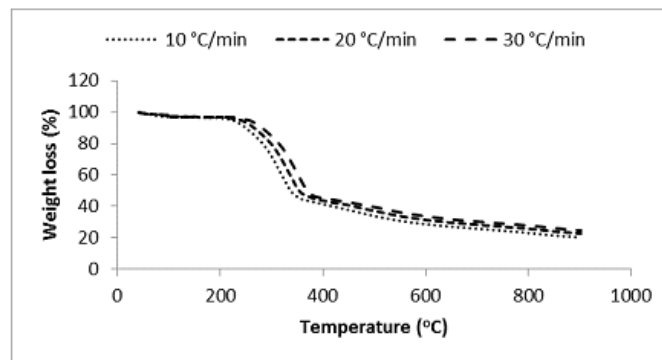


Figure 2a: TG curves of rice husk for heating rate of 10-30 °C/min.

The kinetic parameters are obtained from TGA were elaborated according to model-free methods.

The activation energy (E_a), pre-exponential factor (A) were calculated from K (where there is no need to calculated E_a for each conversion) and KAS (where there is no need to calculate E_a for each conversion). Kissinger plot of $\ln(\beta/T^2m)$ versus $1000/T \text{ K}^{-1}$ of devolatilization process for rice husk is shown in Figure 3. The figure also shows the regression equations and the square of the correlation coefficient (R^2). The activation energies (E_a) and pre-exponential factor (A) were extracted from the slope and intercept of plotting regression line, respectively.

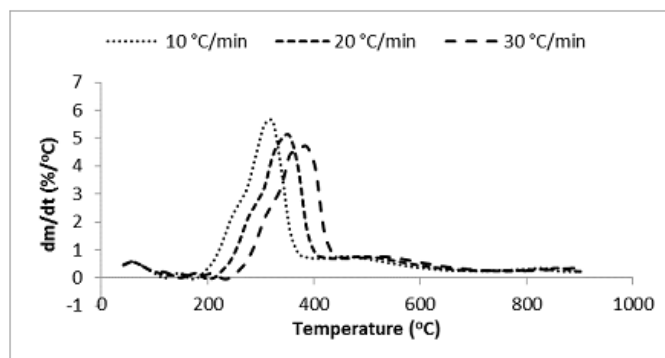


Figure 2b: DTG curves of rice husk for heating rate of 10-30 °C/min.

The results obtained from Kissinger methods are 67.12 kJ/mol and $2.54 \times 10^5 \text{ min}^{-1}$ for activation energy and pre-exponential factor, respectively (see Table 2). The KAS plots of $\ln(\beta_i/T \alpha_i^2)$ versus $1000/T_{ai} \text{ K}^{-1}$ for different conversion values are shown in Figure 4. The value of conversion 0.2 to 0.8 was chosen because at conversion rates less than 0.2 or above than 0.8 have low correlation values, therefore excluded. Figure 4 also shows that most of fitted lines are nearly parallel to each other, indicating similar decomposition mechanisms. The kinetic parameters of Kissinger and KAS methods were shown in Table 2. Comparing the two methods shows that the value of average activation energy calculated using KAS method was (73.14 kJmol^{-1}) higher than the value obtained using K method (67.12 kJmol^{-1}). These could be due to fact that the latter do not account for activation energy at different conversion, but at maximum decomposition temperatures. Also, Table 2 shows that the average frequency factors calculated KAS method was ($9.10 \times 10^6 \text{ min}^{-1}$) higher than the value obtained using K method ($2.54 \times 10^5 \text{ min}^{-1}$). Table 2 also shows that the average activation energy increases as the conversion increases. The activation energy in this study significantly lower than the activation energy of 180 kJ/mol and 100 kJ/mol reported by Williams *et al.*, (1993) and Mahiret *et al.*, (2014) respectively. The discrepancies in activation energy could be attributed to difference in geographical origin, rice varieties and climatic conditions under which the rice paddy. The difference could also be possibly due to different kinetic method applied.

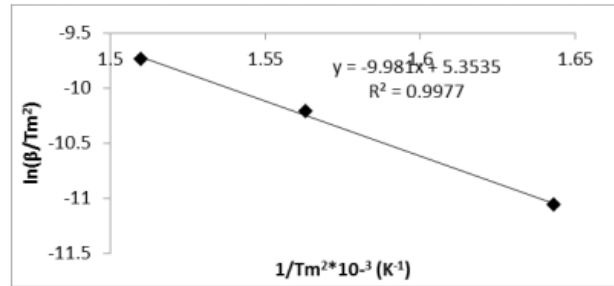


Figure 3: Kissinger plot of rice husk for different values of heating rate.

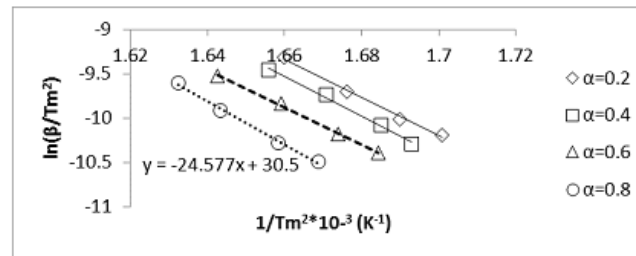


Figure 4: KAS plot of rice husk for different values of conversion

Table 2: Kinetic parameters for KAS and Kissinger

KAS			
A	Ea (kJmol)	A(min)	R ²
0.2	58.35	1.22×10 ⁴	0.9780
0.4	67.27	2.95×10 ⁴	0.9775
0.6	74.65	1.06×10 ⁵	0.9927
0.8	94.32	8.96×10 ⁶	0.9809
Average	73.64	9.10×10 ⁶	0.9823
Kissinger	Ea=67.12 kJmol	A=2.54×10 ⁵	R ² =0.9977

The activation energy as a function of conversion is given in Figure 5. The apparent activation energy for the pyrolysis of rice husk was the same for Kissinger method but



different for KAS method. The values of activation energy extracted from KAS method fall with the range of 58.35- 94.32kJ mol⁻¹.The constant values obtained for Kissinger method was expected because the method does not take conversion into account.

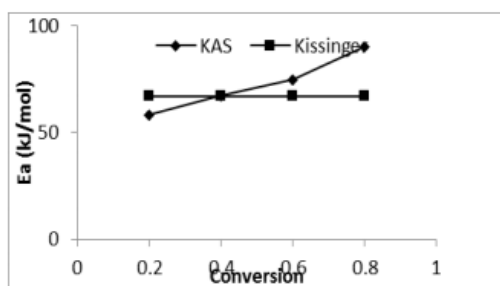


Figure 5: The activation energy as a function of conversion

Conclusion

In this study the pyrolysis process of rice husk using a thermogravimetric analyzer in nitrogen atmosphere at different heating rates of 10, 20 and 30 oC min⁻¹. Thermal decomposition of rice husk proceed via three main stages: water removal, main devolatilization and continuous slight devolatilization. The effect of heating rates at 10-30oC/min shows a shift in the weight loss towards higher peak temperatures as heating rates increases. The model free methods of Kissinger-Akahira-Sonuse (KAS) and Kissinger were applied to experimental data, generating kinetic parameters such as activation energy and pre-exponential factor. The TGA kinetic results can be used for better understanding of the composition of the devolatilization process at different temperature thereby providing data for effective design of a pilot plant which can be effectively scale up.

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