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Global Kinetics of Rice Husks in an Inert Atmosphere: A Case Study of Kyela, Tanzania

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Abstract

A thermogravimetric analyzer was used to conduct a kinetic investigation of rice husk pyrolysis. The major goal is to investigate the reaction kinetics of rice husk at various heating rates in an inert 99.5 percent nitrogen atmosphere. Kinetics' importance can be explained by the fact that it provides evidence for chemical process mechanisms. Understanding reaction mechanisms can help you figure out the best way to get a reaction to happen. Furthermore, it is of fundamental scientific interest. The samples were heated at different heating rates of 5, 10, 20, and 40 K min^{-1} from ambient temperature to 973 K. The thermal degradation characteristics and the kinetic parameter were determined. The values show that the activation energy (E_a) and pre-exponential factor (A) vary with heating rates and temperature.

Keywords

Global Kinetics, Rice Husks, Biomass Energy

1. Introduction

Biomass is any hydrocarbon consisting of carbon, hydrogen, oxygen and nitrogen, and other components in a small amount [1]. Biomass waste is now a known agenda for energy recovery to mitigate the greenhouse gas effect. The biomass waste includes wood wastes, different organic wastes, biodegradable municipal solid waste, agricultural and crop wastes, animal wastes, and energy plantations, among others [2]. The greenhouse gases are such as CO, CO_2, CH_3, and SO_4.

Biomass energy is common and available almost all over the world, being a renewable and carbon-neutral source of energy [3] [4]. Currently, biomass accounts for around 10% of the worldwide energy supply, with two-thirds of that used for cooking and heating in undeveloped countries. Biomass contributes about 85%

of total energy consumption in Tanzania [5]. Rice production is one of the key agricultural food crops produced in Kyela district Mbeya the southern highland Zone in Tanzania [6]. Rice is grown almost all over Tanzania's regions and is a staple food for a huge number of Tanzanians [7] [8]. The rice husk shown in **Figure 1** is the remaining waste from rice milling. The rice husks pose a big challenge for disposal [9]. The rice husk can be utilized to make activated carbon [10] and as a source of energy [11]. The disposal of rice husks for energy recovery can be done by thermal chemical conversion processes such as pyrolysis, combustion, gasification [12], and plasma arch. The kinetic study of rice husks can contribute to the accurate modeling and design of an appropriate reactor for chemical conversion technology. Chemical kinetics is a study of chemical reaction that occurs and the study of the factors that affect the speed of the reaction and how the reaction takes place [13].

The speed of reaction is the rate at which the concentration of reactants and products changes [11]. Such reaction rates range from an explosion, instantaneous reaction to the slow unnoticeable reaction of the mixture as a function of time. The chemical kinetics of rice husk is an important parameter in determining the speed and reaction that take place during the loss or gain of a material due to decomposition, oxidation, or loss of volatile [14]. The common applications of their gravimetric analysis include the study of decomposition, degradation mechanism, and reaction kinetics [15]. Kinetics is the study of chemical reaction rates; the combustion system is the combination of chemical Kinetics, fluid dynamics, and heat transfer [16].

The process of combustion causes the emission [17] [18]. By knowing fluid flow, chemical kinetics, and heat transfer it is possible to design the combustion system with minimum emission [16].

The curves obtained are represented by mass against temperature (Thermo-gravimetric curves) or the rate of mass loss against temperature (differential thermo-gravimetric curves) [19]. The Thermo-gravimetric curves are having 3 parts a plateau portion which shows that there is no mass loss, the curved portion,

Figure 1. Rice husks collected.

which indicates there is mass loss with time and the inflection part which shows the rate of change at a minimum but not zero. The curves' shape may vary due to different factors such as heating rate, recording speed, TGA atmosphere, the geometry of the sample holder, the sensitivity of the recording mechanism, and the material used to make a sample container [20]. This work aims to study the kinetics of rice husk. The processes were performed using the thermo-gravimetric analyzer. The chemical reactions study involves thermo-gravimetric analysis which shows the curves or the number of mass changes.

2. Materials and Methods

2.1. Materials

The samples of rice husk were collected from Kyela Tanzania. These rice husks were used as raw materials for this experiment. Thermogravimetric analyzer type NETZSCH STA 409 PC_{Luxx} is used to study the pyrolysis experiments.

2.2. Methods

2.2.1. Thermal Degradation Analysis

The rice husks samples collected were grounded to an average particle size of less than 1 mm and oven-dried for a constant weight at 378 K. Then a sample of 30 ± 0.1 mg of rice husk was put on the crucible and subjected to a thermogravimetric analyzer for pyrolysis. These samples' mass is minor and therefore it is assumed that the thermal degradation within the sample is negligible [21].

Thermogravimetric analyzer connected to PC installed with proteus software for data acquisition, storage, and analysis. The experiments were conducted at heating rates of 5, 10, 20, and 40 K min^{-1} in the inert atmosphere using 99.5% Nitrogen. A thermogravimetric analyzer measures the physical and chemical processes related to the thermal effect. Thermal decomposition profile curves were drawn using proteus software [22].

2.2.2. Kinetic Parameters of Rice Husk

The method deployed to determine Kinetic parameters were Coats and Redfen [23]. The method is suitable for analyzing the thermal degradation of rice husks under non-isothermal condition [24].

The kinetics of the reaction in a solid-state is described by the following equation.

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

The rate constant for the process is expressed by Arrhenius Equation (2) [25].

$$k = A\exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

where

k is the rate constant which depends on temperature;

A is the pre-exponential factor (s^{-1});

E_a is the activation energy (kJ mol^{-1});

R is the universal gas constant (8.314 JK^{-1} mol^{-1}) and;

T is the temperature (K).

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (3)$$

where

$f(\alpha)$ Algebraic function depending on the reaction mechanism.

$$\alpha = (w_0 - w_t)/(w_0 - w_\infty) \quad (4)$$

where

w_0 —Initial mass;

w_t —The mass remaining at the time t;

w_∞ —The final mass remaining.

The temperature rise at a constant heating rate β is expressed as shown in Equation (5).

$$\beta = \frac{dT}{dt} \quad (5)$$

Differentiate Equation (2) yield Coasts and Redfen method [23] [26] which is used to calculate the kinetics parameters of a first-order reaction.

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \quad (6)$$

Using known heating rates, the line graph versus $1/T$ understudied material will be a straight line graph. The slope and intercept of the line graphs were used to calculate the kinetic parameters.

The line slope is E_a/R and the interception on the vertical axis is $\ln\left(\frac{AR}{\beta E_a}\right)$ which were used to determine the values of E_a and A [25] [26].

3. Results and Discussion

Thermo Degradation Analysis of Rice Husk

Thermal gravimetric analysis using a Thermal gravimetric analyzer was done and the results of Thermal gravimetric curves of rice husks at a heating rate of 5, 10, 20, and 40 K/min is shown in **Figure 2**.

The thermogravimetric curves show that the lower heating rates have a more accurate shape than the higher heating rate curves. This is because the temperature changes faster at high heating rates; this increases the rate of mass change per unit time. The heating rate affects the location of thermogravimetric analysis curves and the maximum decomposition rate [27]. At higher heating rates the maximum decomposition rate is shifted toward higher temperature [28].

Since the temperature in the middle of the particle can be lower than the temperature on the surface, a different devolatilization process will occur [29]. The heating rates of small particles and the homogeneous surface are faster than the heating rate in large particles [29]. The TG curves show that the mass of the rice

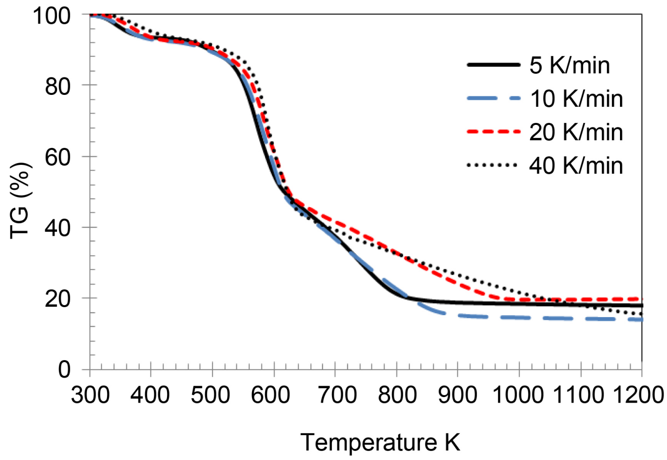

Figure 2. TG curves of rice husks at a different heating rate of 5, 10, 20, and 40 K/min.

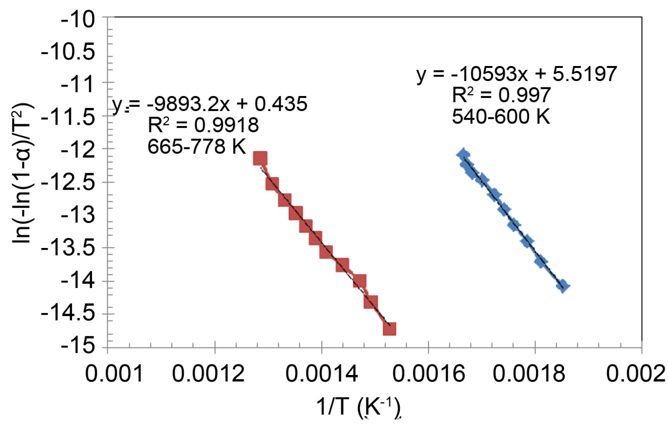

Figure 3. Kinetic parameters of rice husks at a heating rate of 5 K min^{-1}.

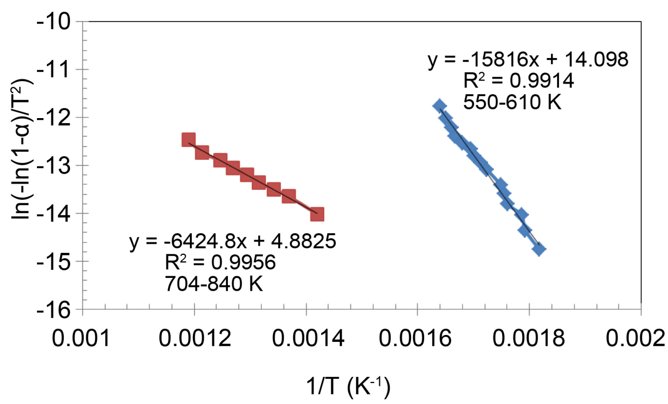

Figure 4. Kinetic parameters of Rice husk at a heating rate of 10 K min^{-1}.

husk is greatly degraded at the temperature between 500 and 800 K, this is the result of the contribution of the lignocelluloses materials in rice husk (hemicelluloses, cellulose, and lignin), and these materials normally decompose at a temperature range between 473 and 673 K. Lignin has a wide range of decomposition profiles which increases up to 1173 K [30].

The rice husk kinetic parameter at different heating rates is shown in Figures 3-6. Figure 3 shows kinetic energy at a heating rate of 5 K min^{-1}, Figure 4 at a heating rate of 10 K min^{-1}, Figure 5 at a heating rate of 20 K min^{-1}, and Figure 6 at 40 K min^{-1}. Using Equation (6) yield value of activation energy is decrease

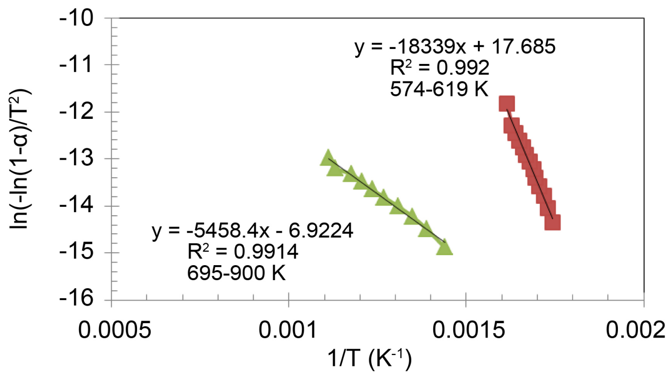

Figure 5. Kinetic parameters of rice husk at a heating rate of 20 K min^{-1}.

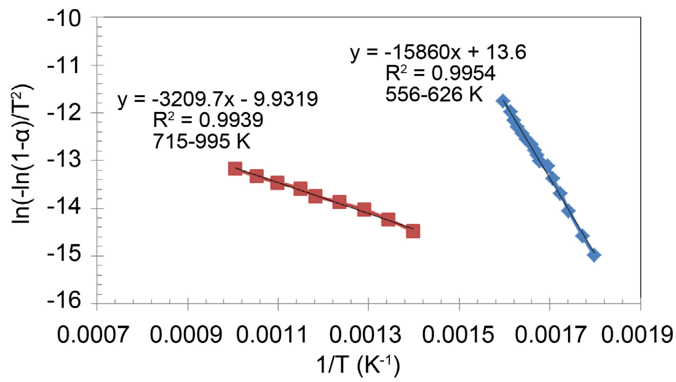

Figure 6. Kinetic parameters of Rice husk at a heating rate of 40 K min^{-1}.

Table 1. Kinetic parameter of rice husk with different heating rates and temperature.

Heating rate β (K min^{-1})	Temperature range (T) (K)	Pre exponential factor (A) (s^{-1})	Activation energy (E_a) (kJ mol^{-1})
5	540 - 600	2.2×10^5	88.07
	655 - 778	1.27×10^3	82.25
10	550 - 610	3.50×10^9	131.50
	704 - 840	8.11	53.42
20	574 - 619	2.93×10^{11}	152.47
	695 - 900	1.79	45.38
40	556 - 626	8.52×10^9	131.86
	715 - 995	1.04	26.69

as the heating rate increases and also within the same heating rate activation energy decreases as the temperature increases. The pre-exponential factor decreases as you increase the temperature within the same heating rate increases.

Table 1 shows the summary of Figures 3-6. The pre-exponential factor decreases as you increase the temperature within the same heating rate and increases as you increase the heating rate. The same behavior is repeated as you increase the temperature. This can be seen clearly in heating rates of 5, 10, 20 and 40 K min^{-1}. The pre-exponential factor also decreases as the heating rates increases. The activation energy is increasing as the heating rate rises, while the activation energy falls as the temperature rises at the same heating rate [31].

4. Conclusion

A thermogravimetric analyzer was used to study the kinetics of rice husk. Activation energy value and pre-exponential factor were determined the activation energy is greatly dependent on temperature. The higher heating rate shifts the degradation temperature ahead. The activation energy decreases as the heating rates increases, and also it decreases as the temperature increases.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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