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Thermal Characteristics And Kinetics Of Rice Husk For Pyrolysis Process

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Abstract- The trend for material and energy recovery from biomass-waste along with the need to reduce green house gases has led to an increased interest in the thermal processes applied to biomass. The thermal process applied to biomass produces either liquid fuel (bio-oil) or gaseous fuel. One of the biomass wastes that are produced in large quantities in Tanzania is rice husk. The behaviour of this waste is important to any designing of thermal handling equipment when subjected thermal environment such as burning or thermal degradation. Due to this it is imperative to establish thermal characteristics of the rice husk pursued in a laboratory to understand its thermal degradation behaviour. The thermal degradation was conducted in a thermo-gravimetric analyzer from room temperature to 1273 K at different heating rates. The activation energy was 180.075 kJ/mol and suitable heating rate for high degradation of rice husk is 10 K/min, and gives 77.20 wt% of volatile release which is the suitable heating rate for pyrolysis and energy released was -4437 J/kg, although it has been recommended that the rice to be used for gasification since it contains high amount of char.

Keywords Gasification; Kinetics; Pyrolysis; Rice husk; Thermal degradation.

1. Introduction

Since the oil crisis in the mid – 1970s, a considerable effort has been directed toward development of renewable sources of energy. Conversion of biomass based lignocellulosic material that consists of cellulose, hemicelluloses and lignin is a candidate for renewable source of energy [1]. Unlike carbohydrate material type which belongs to food chain that can be digested, lignocellulose in nature cannot be digested. In view of this situation there has been a growing interest looking for alternative way to utilize lignocellulosic biomass material in energy production as it does not compete with the food supply chain [2].

Tanzania economy as is the case for other African countries depends on agriculture, employing over 80% of the population. Experience gained on the agricultural activities show that most agricultural crops produced generate considerable amount of waste providing a large potential source for lignocellulosic material. One among the lignocellulosic biomass species that are obtained in Tanzania in large quantities is derived from the rice husk. An evaluation made on the total amount of rice husk that originates from agricultural activities shows that over 4.1 million tonnes are produced annually and is mostly burned in open heaps as waste [3].

Conversion of lignocellulosic material as feedstock faces problems due to their complex structure and difficulty to separate their components in an efficient way. One of the simplest technologies to convert lignocellulosic materials to most efficient fuel is by means of thermal decomposition process of either pyrolysis or gasification process.

The conversion of biomass material by thermal decomposition process yields a range of useful products dependent on the thermal degradation of material [4]. This study deals with the analysis made to investigate thermal degradation behaviour of the rice husk to enable determination of the energy conversion route.

2. Methodology

The rice husk used in this experiment was collected from Morogoro Region, which is located in southern part of Tanzania. Another material that was mainly used in the experiment was pure nitrogen as inert gas.

The experiments were divided into two steps; the first step was to study the characteristics of rice husk by using proximate, ultimate analysis and higher heating value by using bomb calorimeter. The second step was to study the pyrolysis kinetics of rice husk by using Thermo-gravimetric analyzer.

The proximate analysis of the rice husk sample was carried out according to ASTMD 3172 method and ultimate analysis was done according to ASTMD 3176. The thermal-degradation was carried out by using TGA. The sample of a ground rice husk was obtained by grinding the rice husk to an average particle size of 100 μm. A 20 mg of the rice husk sample was used in the experiment.

Experiments were conducted at heating rate of 5, 10, 20 and 40 K/min in the atmosphere of pure Nitrogen. The residual weight as a percentage of the initial weight of the sample as a function of temperature was recorded.

2.1 Thermal Degradation Kinetics

Understanding the thermal degradation kinetics of the fuel pyrolysis is critical in development of technologies to utilize fuels in the most efficient manner. Kinetic models are useful tool in energy conversion technologies by enabling researchers to predict and understand the depolarization properties of fuels. Most of these kinetic models focus on the chemical reactions simulated by a pyrolysis process and represented by the reaction scheme in Equation (1).

$$Biomass \rightarrow Solid\ residue + Volatile\ and\ gas \quad (1)$$

The pyrolysis rate is expressed by the following nth order as shown in Equation (2), where x is fractional mass of biomass at time t, and k is the reaction rate constant.

$$\frac{dx}{dt} = k(1-x)^n \quad (2)$$

There are different methods for determination of pyrolysis kinetics from Thermo-gravimetric analysis. These are Coats and Redfern [5], Agrawal sivasubramanian [6], Freeman and Carroll [7], Kissinger's method [8] among others. This study will consider Kissinger's method, since the process employed for thermal-gravimetric analysis of rice husk was non-isothermal.

The Kissinger's method does not depend on reaction mechanism for determination of activation energy, although other parameters assume first order reaction mechanism [9]. The peak temperature (Tmax) is used to determine the activation energy (Ea). Thermal decomposition rate are measured at different heating rate, through sequence of experiments. The pyrolysis rate is expressed by using Arrhenius Equation (3) and k is the rate constant, which depends on temperature. Ea is the activation energy, R is the gas constant and Tmax is the absolute temperature.

$$k = A\exp(-E_a / RT_{\max}) \quad (3)$$

2.2 Heat for biomass pyrolysis

Analysis of Heat of biomass degradation can increase understanding of combustion, allowing traditional combustion techniques to be improved and burning methods with high efficiency and environmental effects to be developed. The heat of biomass degradation in the absence of oxidation agent resembles pyrolysis process and is needed for modelling the reactivity of fuel particles in reactors. The release of products decrease the density of the char residue and change its thermal conductivity and specific heat, and the generation of condensable tars and vapors may disturb the measurement. The more accurate measurement of heat of degradation/pyrolysis is obtained by using Differential Scanning Calorimetry (DSC) [10]. The DSC has been used to characterize physical transformations as well as chemical reactions. In most common form, this technique consists of measuring the temperature difference between a sample and a reference, while temperature of the environment in which they both sit is increased linearly with time. This temperature difference is related to the difference in heat flow into the sample compared to the usually inert reference material [11].

3. Methodology

The characterizations of rice husk, which include proximate, ultimate analyses together with higher heating value, are shown in Table1.

Table 1. Characterization of rice husk

Proximate Analysis (%)		**Ultimate analysis (%)**		**Higher Heating Value (MJ/kg)**
Moisture	9.00	C	49.63	
Volatile matter	56.20	H	5.78	
Fixed carbon	12.60	N	0.24	
Ash	22.20	O (by difference)	44.25	13.24
		Cl	0.10	

The carbon and hydrogen contents are the indicative of hydrocarbons that can be released during thermal degradation process also the high oxygen content, it means the fuels has low energy content. This has been shown in van Krevelen diagram in [2].

Figure 1 shows typical weight loss against temperature curve for the degradation/pyrolysis of rice husk in nitrogen atmosphere under non isothermal conditions at heating rate of 10 K/min, this heating rate was chosen, since it gave highest degradation of rice husk. The curve is divided into three regions. The first region is drying zone, the second is devolatilization zone and the third one is char degradation zone.

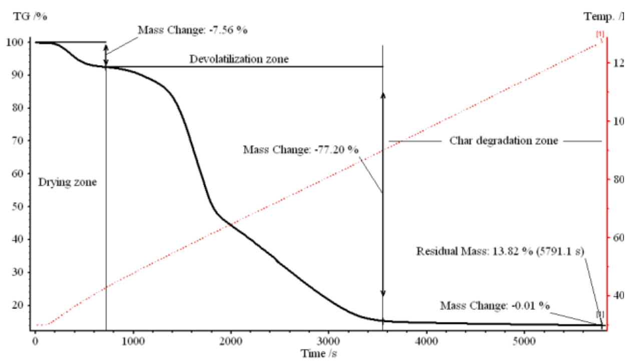

Fig. 1. Thermo-gravimetric curve of rice husk

The curves show moisture released was 7.56%, the volatile was 77.20% and the char yield is 13.82%. The greater mass loss was observed between 400 K and 1000 K, due to volatile release at devolatilization zone.

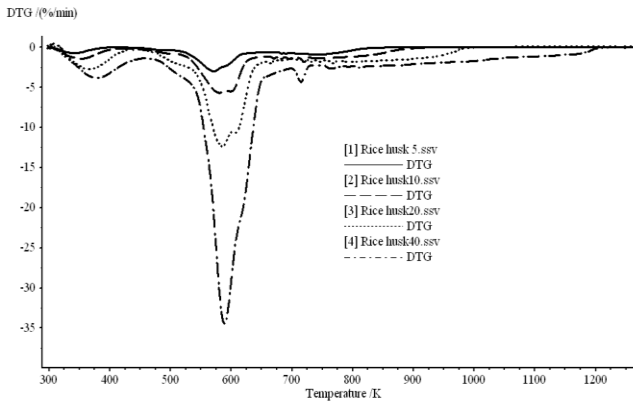

Fig. 2. The DTG of rice husk at different heating rates

Figure 2 shows the derivative thermo-gravimetry (DTG) for rice husk sample at four different heating rates. The peaks of the DTG curve tend to move to the right hand side as the heating rate increases. The peaks were formed at 571.5 , 581.6 , 585.9 and 589.2 K at heating rate of 5, 10, 20 and 40 K/min respectively.

Two distinctive DTG peaks are found at all heating rates. The peak at low temperature corresponds to hemicellulose decomposition, while the peak at high temperature represents decomposition of cellulose [9]. It is believed that lignin decomposition is slow and distributed along a wide range of temperature interval and its peak cannot be distinguishable [ ]. The peaks could be used to determine the kinetic parameters of the cellulose, hemicellulose and lignin, but in this paper the global kinetic parameter will be determined.

3.1 Chemical Kinetics

Determination of kinetics parameters was considered at the peak regions, because it is where, the pyrolysis takes place. The method mentioned earlier was deployed in the analysis. The kinetic parameters calculated for the pyrolysis experiments under non-isothermal conditions were obtained from Figure 2 and the decomposition reaction was assumed to be first order. The results revealed that the activation energy was 180.075 kJ/mol, and pre exponential factor was 2.401E+27 s-1. The reaction constant obtained is expressed as Arrhenius equation (Equation 4).

$$k = 2.401x10^{27} e^{-(180.075/RT)} \quad (4)$$

The mass of biomass decomposed during thermal analysis can be estimated by solving Equation 2, since the reaction was first order, Equation 5 was developed. At every time t and certain temperature T the biomass decomposed is determined using Equation 5. Therefore the rate of decomposition of biomass can be easily estimated.

$$x = 1 - e^{-kt} \quad (5)$$

The heat for rice husk degradation or pyrolysis was obtained by using DSC. The DSC and TG curves are shown in Figure 3. the TG curve is represented by smooth line and DSC curve is represented by dotted line. The DSC curve form a hump at the drying zone, since heat is absorbed for moisture released this process is known as endothermic process and the estimated energy used was 161.5 J/g. The devolatilization zone is exothermic due to the formation due to several chemical reactions such as fragmentation, reforming, cracking, polymerization and dehydration, most of these chemical reactions are exothermic processes and the energy released was -4437 J/g. The char degradation zone is endothermic process, the estimated energy absorbed was 313 J/g.

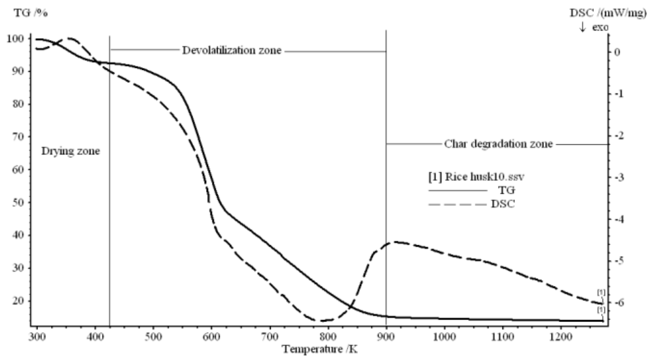

Fig. 3. The DSC and TG of rice husk

4. Conclusion

The high degradation of rice husk was observed at heating rate of 10 K/min and the overall pyrolysis behaviour of rice husk was determined, it was concluded that the rate of rice husk pyrolysis can be estimated by using first order reaction which gives Equation 5.

The energy for devolatilization and char degradation processes were -4437 J/g and 313 J/g, respectively. The devolatilization and char degradation were exothermic and endothermic processes respectively.

The rice husk has high ash and oxygen content, which cause to have low HHV. Although oxygen is not suitable during pyrolysis for bio-oil production, but it makes the rice husk to be suitable for gasification process since it can be used for partial oxidation during the process.

Acknowledgements

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