

## Kinetic Modeling of Rice Husk Components Pyrolysis Based on Independent Parallel Reactions

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### Abstract

This study presents the pyrolysis decomposition mechanism of rice husk in nitrogen atmosphere by thermogravimetric analysis (TGA). The thermal decomposition was carried out in three stages: moisture removal (180-200 °C), main devolatilization (200-400 °C) and continuous slight devolatilization (400 °C). The weight loss of rice husk was modeled based on the assumption that lignocellulose components (cellulose, hemicellulose and lignin) undergo pyrolysis independently in parallel first-order reactions. The kinetic parameters of the three lignocellulose components were determined by means of Microsoft Excel Solver tool using least square algorithm. The result of thermal degradation of rice husk samples shows that the model predictions of the cellulose, hemicellulose and lignin components agreed with the experiments. The activation energy and pre-exponential factors of cellulose, hemicellulose and lignin are 187kJ/mol and  $1.2 \times 10^{15} \text{min}^{-1}$ , 29kJ/mol and  $1.6 \times 10^7 \text{min}^{-1}$  and 90 kJ/mol and  $1.8 \times 10^1 \text{min}^{-1}$  respectively. The results suggest that thermal decomposition rate of cellulose was found to be higher, whereas that of lignin decomposition rate was lower. The thermal decomposition of hemicellulose decomposition was intermediate.

**Keywords:** Rice husk, pyrolysis, thermogravimetric analysis, lignocellulose, kinetic model.

### Introduction

The depletion of fossil fuel reserves and its associate environmental problems are the major reasons for the shift and focus on sustainable energy resources. Biomass is extensively used as an alternative renewable energy source which is in abundance and in most cases considered to be a waste. It is the world fourth energy resource after oil, natural gas and coal (Vamvuka *et al.*, 2003). Lignocellulose materials are unlike carbohydrate which belong to food that cannot be digested. The use of lignocellulose biomass as a source of chemical, transportation and energy fuels has been growing at a very rapid rate because lignocellulose biomass does not compete with the food supply chain (Basu, 2006).

Nigeria like many other African countries is blessed with abundant biomass because of its huge agricultural resources and this sector has been reported to provide employment to over 60% of the population. Agricultural activities generate huge waste providing a large potential source of lignocellulosic materials. Among the various lignocellulose species, rice husk has potential for chemical energy. Rice husk is used as a source of energy in rice mill, cooking, furnace and boiler (Garba *et al.*, 2006). In Nigeria, about 664,000tonnes of rice husk is derived from about 3.32 million tons of paddy rice per year (Rainer).

Conversion of lignocellulosic material to efficient fuel remains a burden due to their structural complexity which is responsible for the challenges in separating lignocellulose components.



Thermochemical conversion processes such as pyrolysis, combustion, gasification and liquefaction are considered as the alternative means of converting lignocellulose biomass to efficient fuel. However, pyrolysis remains the focal point in all thermochemical conversion processes as in the case of combustion process in which the first step is pyrolysis followed by the reaction of pyrolysis residue with oxygen. The pyrolysis process is the thermal decomposition of biomass in the presence of inert atmosphere to form liquid (bio oil), char (charcoal) and gas. Lignocellulose biomass is composed of hemicellulose, cellulose and lignin (Garba *et al.*, 2012). Experimental results have shown that pyrolysis of organic matter is a complex process involving parallel and series reactions (Garba *et al.*, 2013). The decomposition of biomass has been described by three-component independent reaction, each corresponding to the decomposition of the hemicellulose, cellulose and lignin. The weight loss kinetic model developed for biomass is of two types. The single component overall model (SOM), which considered the biomass as being composed of a single component and uses its char-volatile reaction to describe the weight loss kinetics (Rogers *et al.*, 1980; Cordero *et al.*, 1989; Cordero *et al.*, 1990). The second one is the multi-component overall model (MOM) considering biomass as being composed of hemicellulose, cellulose and lignin (Orfao *et al.*, 1999; Font *et al.*, 1999). In this case, the components are modeled separately and the biomass decomposition is the summation of all the three components. Generally, the weight loss kinetics change as the temperature increases and the weight loss is controlled

mainly by cellulose, hemicellulose and lignin. Since the weight loss depends on cellulose, hemicellulose and lignin component, SOM cannot account for the possible change in weight loss kinetics. Contrary, MOM can reveal possible change in weight loss kinetics. Koufopoulos *et al.* (1989) developed a modeling approach which described the overall rate of decomposition as a sum of the corresponding rates of the hemicellulose, cellulose and lignin using nonlinear regression method. In a related work, Rao *et al.* (1998) developed a kinetic model in which the pyrolysis of lignocellulose components is described by single reaction first order kinetics. In recent years MOM has been used successfully to describe the weight loss processes of bagasse (Liangfeng *et al.*, 2001; ), jatropha residue (Rajeev *et al.*, 2016), switch grass (Vamvuka *et al.*, 2011) and wood pine and cotton stalk (Wang *et al.*, 2012). The result of almost all the previous studies have shown good agreement between experimental and calculated weight loss pattern. The understanding of biomass pyrolysis is essential for accurate prediction of pyrolysis rates require for optimum design of pyrolyzer. In order to optimize process variable and obtain quality pyrolysis products, there is the need for more profound knowledge of pyrolysis kinetics. In the present work, the pyrolysis of rice husk components is analysed and pyrolysis process is described by independent parallel reactions of first order using nonlinear square methods. The design of equipment for the conversion of biomass through thermochemical processes requires knowledge of pyrolysis kinetic and modeling. Many literatures reported the kinetic investigation however; little



knowledge is available on the modeling aspect. Thermogravimetric curves was used to analysis biomass decomposition, the pyrolysis kinetic model of rice husk based on three-component independent parallel first-order reactions was established by non-linear least squares algorithm. The kinetic parameters obtained for rice components were compared with each other and meaningful results achieved were discussed.

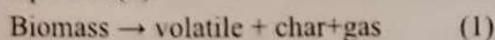
**Methodology**

*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 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 thermogravimetric analysis (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. 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.

*Kinetic modeling of rice husk pyrolysis*

The approach by most of these kinetic models simulate the chemical reactions that take place during pyrolysis and the chemical reaction scheme is presented in equation (1).



The kinetic modeling was performed on the pyrolysis profile provided by TGA. The total mass measured by TGA were assumed to be summation of the pyrolyzable materials such as cellulose, hemicelluloses, lignin, charcoal, and ash (Liangfeng et al., 2011).

$$m = m_p + m_c + m_a$$

where m is the total mass of biomass by TGA, m<sub>p</sub> is the mass of pyrolyzable (cellulose, hemicelluloses, lignin components) organic materials, m<sub>c</sub> is the mass of produced char, and m<sub>a</sub> is the ash mass.

Assuming the ash is ignored, the mass of biomass is a sum of the pyrolyzable organic chemical and the produced charcoal (Liangfeng et al., 2011):

$$m_i = m_{ip} + m_{ic} \text{ for } i=1,2,3 \quad (2)$$

the pyrolyzable organic chemicals are mainly cellulose, hemicelluloses, lignin components.

During the pyrolysis process, the degree of conversion and conversion rate for each component in biomass sample are defined as follows:

$$\alpha_i = \frac{m_{i0} - m_{ip}}{m_{ip}} \text{ for } i=1,2,3 \quad (3)$$

Where m<sub>i0</sub> is the initial weight of biomass and α<sub>i</sub> is the conversion of each lignocellulose components.

For the three lignocellulose components, the overall conversion rate for each reaction can be expressed as

$$\frac{dm}{dt} = \sum_1^3 c_i \frac{d\alpha}{dt} \quad (4)$$

Where c<sub>1</sub>, c<sub>2</sub> and c<sub>3</sub> are the partial contributions of the overall weight loss:

$$c_i \text{ is defined as } c_i = m_{i0} - m_{i\text{char}} \quad (5)$$

The lignicellulose components are presumed to decompose by obeying first-order reaction according to

$$\frac{d\alpha_i}{dt} = k_{i0} \cdot e^{-E_i/RT} (1 - \alpha_i) \quad (6)$$

where  $E_i$ ,  $k_{i0}$ ,  $T$  and  $R$  are the activation energy (kJ/mol), frequency factor ( $\text{min}^{-1}$ ), temperature (K) and respectively.

The nonlinear least square algorithm has been used to identify the kinetic parameters that show the lowest values of the objective function (O.F):

$$O.F = \sum \left[ \left( \frac{dm}{dt} \right)^{\text{exp}} - \left( \frac{dm}{dt} \right)^{\text{sim}} \right]^2 \quad (7)$$

$(dm/dt)^{\text{exp}}$  is the experiment DTG curverate of rice husk and  $(dm/dt)^{\text{sim}}$  is the simulated DTG curve rate of rice husk.

#### Kinetic constants from modeling

Equation 4 shows the thermal decomposition rates of the rice husk components during the heating process was a function of temperature and degree of conversion. Equation (5) is a nonlinear ordinary first-order differential equation. The degree of conversion is the dependent variable and absolute temperature is the independent variable. Two kinetic constants for each component, pre-exponential factor  $k_{i0}$  and activation energy  $E_i$ , are assumed to be independent of the degree of conversion. The numerical solution could be obtained by solving Equation (6) for the known values of  $k_{i0}$  and  $E_i$  respectively. These constants are determined from the least-square method implemented by the Microsoft Excel Solver tool where the difference between experimental and calculated weight loss were minimized.

## Results and Discussion

### Characterization of fuel

The proximate and ultimate analysis results are presented in Table 1. The result show that the rice husk was characterized by high volatiles content of about 66% which makes them desirable for a good regulation of gasification processes. The high percentage of ash in rice husk indicates potential slag or foul formation during combustion. However, the content of sulfur is very low, which means that there will be fewer emissions or corrosion when utilization for power generation (Koufopoulos *et al.*, 1989; Rao *et al.*, 1998).

**Table 1.** Ultimate and proximate analysis of rice husk

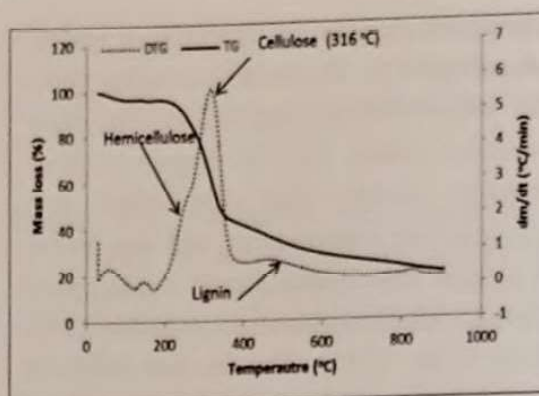
Proximate analysis (wt.%)	Ultimate analysis	Ultimate analysis				
		C	H	O	N	S
Moisture	3.81					
Volatile matter (VM)	66	43.83	6.76	46.07	0.93	0.94
Fixed carbon (FC*)	22.01					
Ash	8.18					

### Thermal decomposition characteristic

The thermogram and derivative thermogram (TG/DTG) curves in Fig. 1 were obtained for the pyrolysis of the rice husk at a heating rate of 10 °C/min. The TG/DTG curves represent the weight loss of the tested biomass with respect to temperature. The curves are generally divided into three different stages regardless of what biomass sample is tested. The first stage is drying and release of some light volatiles resulting into slight weight loss at temperature below 200 °C as shown in the TG curve. The second stage is the thermal decomposition of hemicellulose, cellulose and lignin where a significant weight loss was observed at a temperature between 200 and 400 °C. In the third stage, the weight loss occurs



slowly over wide range of temperature higher than 500 °C mainly due to thermal decomposition of heavy components. In the previous studies (Liangfeng *et al.*, 2011; Vamvuka *et al.*, 20011; Wang *et al.*, 2012), DTG has been reported to qualitatively identifies the components of lignocellulose structures. Generally, hemicellulose decomposition occurs at temperatures between 150 and 350 °C; cellulose decomposition occurs at the temperatures range of 275-350 °C, and lignin is decomposed slowly over a wider temperature range of 250-500 °C (Vamvuka *et al.*, 20011; Wang *et al.*, 2012). The distribution of lignocellulose components in the DTG curve of rice husk is presented in Fig. 1. The DTG curve of rice husk exhibited only one peak. The main peak at temperature of 316 °C stems from cellulose decomposition and its shoulder peak in the DTG curve (which is almost merged to cellulose) is due to hemicellulose decomposition. The curve after the main peak (cellulose) is the decomposition of lignin whose intensity is smaller than that of the hemicellulose and cellulose peaks. It is important to note that one small peaks induced between the temperatures of 800°C and 850°C are due to the fact that rice husk includes another important component which is reactive at a higher temperature. In addition, from DTG curve in Fig. 1 it can be observed that two bumps developed at the temperature between 70 °C and 150°C as a results of moisture removed from the rice husk.



**Fig. 1:** TG/DTG curves of rice husk at heating rate of 10 °C /min showing the three lignocellulose components.

#### *Kinetics analysis*

Figure 2 and 3 shows TG and DTG curve of the modeling for the rice husk. Figure 2 shows that the model simulation gives good prediction compared to the experimental data for the TG curve of rice husk sample. The model simulation of the DTG curve (Fig. 3) also shows good prediction compared to the experimental data. Fig. 4 shows the individual contribution of each lignocellulose to the total decomposition rate. With regard to each lignocellulose biomass component, hemicellulose proved to be least stable lignocellulose component and it decomposes first and fast at low temperature. Lignin is more stable lignocellulose component and decomposition takes place over wider temperature range. Finally, the cellulose decomposition started last and that is the reason why kinetic value has high values (Table 2). Among the lignocellulose component, cellulose shows the maximum total decomposition. Generally, the differences between the thermal behaviours of the lignocellulose components are attributed to their different in the intrinsic chemical structures. Hemicellulose is least thermally stable

component due to its amorphous nature and cellulose is the next thermally stable than hemicellulose due its strong intra-molecular bonds. Finally, Lignin is more thermally stable than the other two lignocellulose components and the reason for this is that it has strong cross-linked polymer (Pasangulapati *et al.*, 2012; Xiong *et al.*, 2015). The thermal behavior of each lignocellulose components agreed with other works in the literature (Jeguirim *et al.*, 2001; Vamvuka *et al.*, 2003).

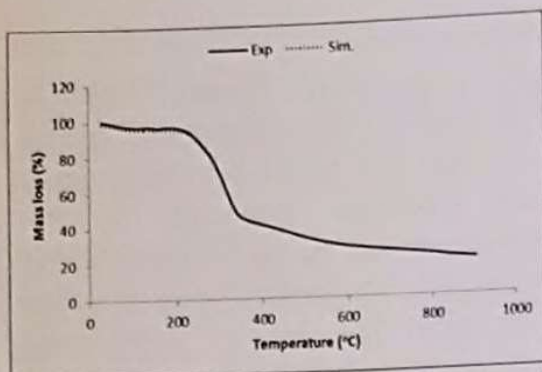


Fig. 2. Comparison of experimental and simulated TG pyrolysis profile of rice husk.

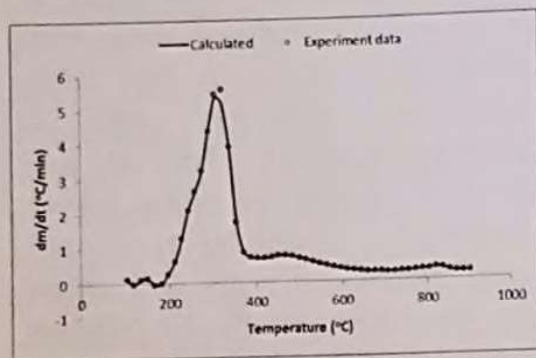


Fig. 3. Comparison of experimental and simulated DTG pyrolysis profile of rice husk.

Kinetic parameters are illustrated in Table 2. In the cellulose decomposition, kinetic constants appeared to have higher values than hemicellulose and lignin. Activation energy is the minimum energy required for each decomposition starts. Subsequently,

the higher its value is, the higher is the temperature for the initiation of each decomposition. Cellulose requires more energy compared to the other lignocellulose components because of its strong intra-molecular bonds, which prevent its decomposition in lower temperatures (Xiong *et al.*, 2015). Pre-exponential factor is another important kinetic constant indicates indicate molecular collisions that lead to chemical reaction. A higher value of the pre-exponential factor, the more the molecular collisions that can lead to decomposition.

Lignin shows lowest values of activation energy and pre-exponential factor in Table 2. This fact could be observed from the DTG curves (Fig. 4), where the decomposition is seen to have started at lower temperatures and its decomposition rate was lower, compared to that of the other decomposition reactions. In term of thermal stability, lignin is the most stable component, therefore it is not easily decomposed. The observation made herein have been confirmed by previous studies (Xiong *et al.*, 2015; Jeguirim *et al.*, 2009).

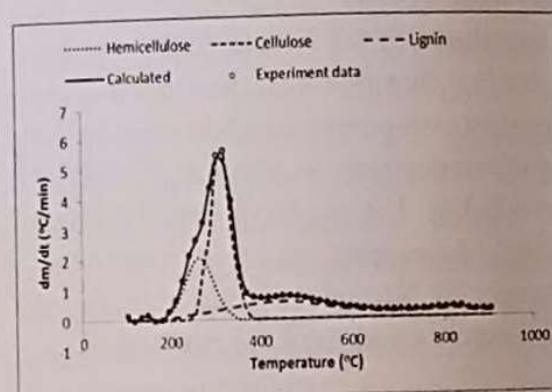


Fig. 4. Comparison of experimental and simulated pyrolysis profile of rice husk and rice husk components.



The calculated pyrolysis kinetic parameters of rice husk are presented in Tables 2. The activation energy of cellulose decomposition is higher (187kJ/mol), whereas that of lignin decomposition is lower (29kJ/mol). The activation energy of hemicellulose decomposition is intermediate (90 kJ/mol). The pre-exponential factors of cellulose, hemicellulose and lignin are in the ranges of  $1.2 \times 10^{15}$ ,  $1.6 \times 10^7$ ,  $1.8 \times 10^1 \text{ min}^{-1}$ , respectively.

Table 2. Content of lignocellulose and the kinetic parameters of the pyrolysis process.

Component	Kinetic parameters		
	C(%)	A(min)	E (kJ/mol)
Hemicellulose	26.9	$1.6 \times 10^7$	90
Cellulose	48.9	$1.2 \times 10^{15}$	187
Lignin	24.2	$1.8 \times 10^1$	29

### Conclusions

In this study, the thermal decomposition and pyrolysis kinetics were studied. The thermal decomposition shows that rice husk was divided into moisture removal, main devolatilization and continuous slight devolatilization stages. The mass loss process of rice husk was modeled by assuming cellulose, hemicellulose and lignin undergo pyrolysis independently and in parallel first-order reactions. The kinetic parameters of the three components were determined by means of Microsoft Excel Solver tool using least square algorithm. The simulation rate of thermal decomposition is very close to the experimental data.

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