Kinetic Modelling of the Pyrolysis of Biomass for the Development of Charcoal Briquette

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Abstract. Waste of biomass can be utilized as an energy alternative such as a charcoal briquette. In the waste of biomass, there is carbon element bonded in the cellulose which can be utilized as an energy source of solid fuel. Charcoal briquette from waste of biomass can be developed via pyrolysis process. *Terminalia Catappa L.* and *Myristica fragran*s (nutmeg seeds shells) shells were used as raw material for the manufacture of charcoal briquettes. Pyrolysis process took place under isothermal conditions at a temperature of 350ºC, 400ºC, 450ºC, 500ºC, and 550ºC with variation of times were 30 minutes, 60 minutes and 90 minutes. During the pyrolysis process, there were three main components observed, namely liquid (bio oil), gases and solids (char). Data obtained for measuring the kinetics of liquids and gases were taken in interval of 5 minutes. The results showed that the rise in temperature will increase the rate of pyrolysis process and increase the yield of gases and liquids as well as lowering the yield for solid. The best fitted kinetic model is the representation of biomass pyrolysis process involving secondary decomposition of the liquid. The results of briquette development showed that these two biomasses can be used as raw material of energy alternative.

1. Introduction

1.1. Background

Biomass can be converted into a material that can be used as other forms of energy such as carbon for briquettes production. Charcoal briquette is charcoal (one type of fuel) of various kinds of biological material or biomass, such as wood, twigs, grass, straw and other agricultural waste. As raw material of briquettes production, it should be chosen a material that has carbon element.

The benefit of this research is to increase the economic value of biomass waste by converting it into a more useful product. The purpose of this study is to obtain data the effect of temperature and time toward pirolysis products yield and to obtain the value of the pyrolysis kinetic parameters of biomass and to determine the effect of temperature and pirolysis time on the quality of the briquettes. *Terminalia Catappa L.* and *Myristica fragran*s shells (nutmeg seeds shells) were used as raw material for the manufacture of charcoal briquettes.

1.2. Theoretical basis

Pyrolysis is the chemical decomposition of organic materials through a process of heating without oxygen or under conditions of little air, causing the release of volatiles and char formation [1]. Thurner and Mann [2] proposed a parallel reaction mechanism, in which each of these reactions occurs separately. The reaction mechanism is as follows:

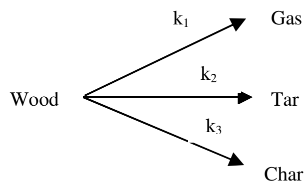

Figure 1. The mechanism of pyrolysis reaction fromTurner and Mann [2].

Mass balance equation for the decomposition of biomass and formation of product are as follows:

$$\frac{dm_w(t)}{dt} = -(k_1 + k_2 + k_3)m_w(t) \quad (1)$$

$$\frac{dm_G(t)}{dt} = k_1 m_w(t) \quad (2)$$

$$\frac{dm_T(t)}{dt} = k_2 m_w(t) \quad (3)$$

$$\frac{dm_C(t)}{dt} = k_3 m_w(t) \quad (4)$$

In this experiment, three reaction models were proposed to obtain the kinetic parameters.

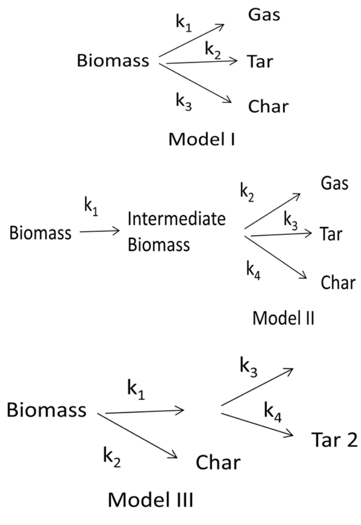

Figure 2. Models of Pyrolysis Reaction Mechanism

Arrhenius equation is used to calculate reaction rate constants in those equations above.

$$(k) = A_0\left(\exp\left[-\frac{E_a}{RT}\right]\right) \quad (5)$$

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2. Research Methodology

2.1. Materials

Terminalia Catappa L. biomasses used was taken from several places in the city of Yogyakarta, which is at the Gadjah Mada University and Tempel region. Nutmeg seeds shells were from Gurabati village in Tidore islands. As the adhesive it was used 'Rose Brand' Tapioca flour and water.

2.2. Experimental set-up

Pyrolysis apparatus consists of a reactor made of metal pipe, the upper part of the reactor was covered by insulation. The outside of the reactor is insulated with a furnace insulator. The temperature inside the reactor was measured with thermocouples. The liquid product from the reactor is cooled through a condenser pipe and collected into different flask.

2.3. Procedure of operation

Biomass was crushed in crusher to form granules, and then it was weighed and loaded into the reactor and sealed. Then, it was heated up to the desired temperature of 350-550°C. During pyrolysis process, the volumes of liquids and gases were measured every 15 minutes. After 60 minutes of the process, gas samples were taken and stored in a vacuum tube to be analyzed its content of CO, CO_2 and CH_4. The gas pressure was measured using a manometer. After reaction time was completed, weigh the solid as charcoal. Then the charcoal was mixed with adhesive (2.5-5% by weight), stirred evenly and was pressed using hydraulic press equipment.

2.4. Research analysis

The analysis includes proximate analysis, lignocelluloses, gases and solids. The purpose of proximate analysis is to determine the amount of fixed carbon (FC), volatile matters (VM), moisture content (MC) and ash in the sample of briquettes in units of weight percent (wt). Lignocelluloses analysis was intended to determine levels of hemicelluloses, cellulose and lignin. Gas content data was used to calculate the mass of the gas using the following equation 6.

$$Gas\ Mass\ (G) = \frac{PV_G}{RT}\ x\ Average\ MW \tag{6}$$

3. Result and discussion

3.1. Material characteristic

From proximate analysis test results it was found that the content of volatiles in the biomass was very high. With 62.66 % of the total composition of materials, volatile content is higher than the fixed carbon which was only 18.81 %. The calorific value of the raw material itself was quite high, up to 4471.26 cal / g.

The analysis results showed that the biomass was dominated by lignocelluloses. The content of lignin in the material used was 43.4 5%, which is higher compared with cellulose and hemicelluloses. The amounts of those components were 16.60% and 24.69 % respectively.

3.2. The effect of temperature and time toward pyrolisis product

The example of the effect of temperature to yield product of gases, liquids and solids can be seen in Figures 3 to 5.

In the pyrolysis process, there were three products, gas, liquid and solid. The solid product was then presurized to be charcoal briquette. From the preliminary research, it was found that the increasing temperature and pyrolysis time will decrease the solid product. The thermal decomposition of hydrocarbons involves a series of primary and secondary reactions leading to a complex mixture of products. Studies show that the distribution of pyrolysis products varies considerably with the pyrolysis conditions and the type of reactor used. A study by Tsai and Albright [3] reported that at least seven surface reactions occur during most industrial pyrolysis processes.

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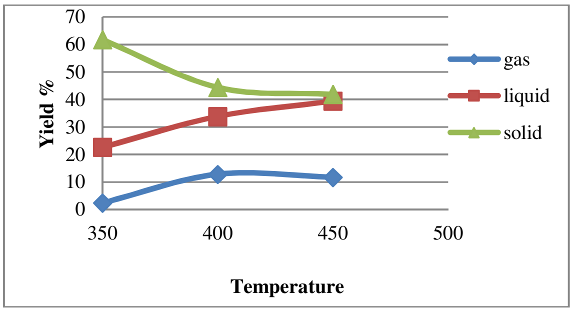

Figure 3. Yield products

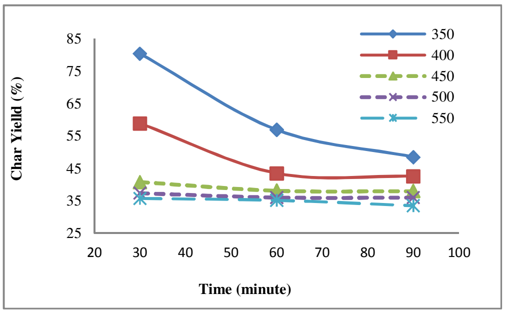

Figure 4. Char yield

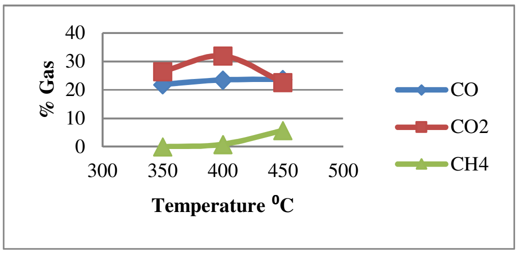

Figure 5. Percentage of gas product

In the pyrolysis experiments, the condensate formed is in the range of 25 to 45 percent of the original weight of biomass while the gas formed is in the range of 10 to 20 percent, and the rest is the solid product. This study demonstrated that more than 36 components; mainly alcohol like methanol, ethanol and propanol; were produced during the pyrolysis process. The experimental results also show that the condensate and gas formed are affected by the temperature in the reactor and the heating rate. Further studies show that the reaction rate of the decomposition process depends on temperature. Therefore, the gas and liquid pyrolysis products increase when the pyrolysis temperature increases.

3.3. Determining reaction rate constant

The primary data were obtained from the laboratory in the form of liquid and gas mass for 5 minutes interval. This data was then processed using computer program to get some of other data needed to determine the reaction rate constant of biomass pyrolysis. Example data from experimental and calculation can be seen in Figure 6 below.

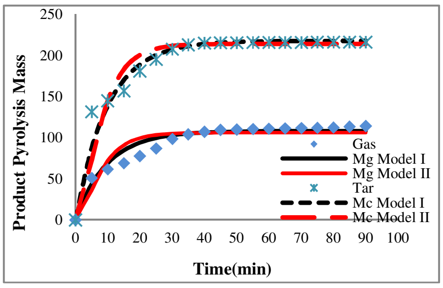

Figure 6. Example of pyrolysis product

Compared to the second model, the first model is closer to the experimental data. To assure that first model is the appropriate model, it was then developed a third model as a comparison against the first model. The third model is a compilation model, by modifying the first and second models. In this third model, biomass is not experiencing biomass intermediate stage. There is a secondary reaction in the next stage, where the secondary reaction will produce both gas and liquid. Comparison of the experiments results with the model I and III can be seen in Figure 7 below.

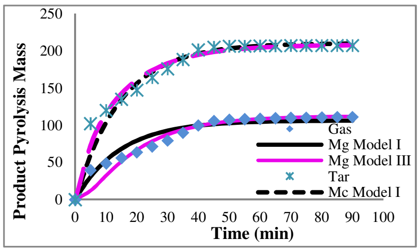

Figure 7. Correlation Chart of Time and Pyrolysis Product mass on Simulation of Model I and III for 500 °C

As discussed previously, model I is much closer to the experimental data than model II. Therefore, model I is then compared with a modified model. From R^2 value obtained, the average R^2 for model III is better than model I.

The effect of temperature on reaction rate constant follows the Arrhenius equation below

$$\ln k = \ln A_0 - \frac{E_a}{RT} \tag{7}$$

By plotting ln k and 1/T the value of Ea and A_0 can be obtained. The correlation of ln k and 1/T can be seen in Figure 8 below.

Reaction rate constant k_1, k_2 and k_3 are determined in five different reaction temperatures within the range of 350-550°C. In Figure 8, ln k is reported as a function of 1/T, and graphically they form a straight line correlation. It proves that the reaction occurred was still in line with Arrhenius equation in experimental temperature range. Ea values for various models are presented in Table 1 below.

The activation energies obtained are within the range of Ea values given in the literature. The activation energy of Ketapang seed shell is lower than the activation energy of Casew, Pistachio and Walnut which has a value of E above 100 kJ/mol. But still between the activation energy of almonds (42.4 to 99.7 kJ/mol), Brazil nut (47.2 to 82.0 kJ/mol), coconut (58.9 to 114.8 kJ/mol), and Peanut (44.3 to 71.5 kJ/mol) [4, 5 and 6].

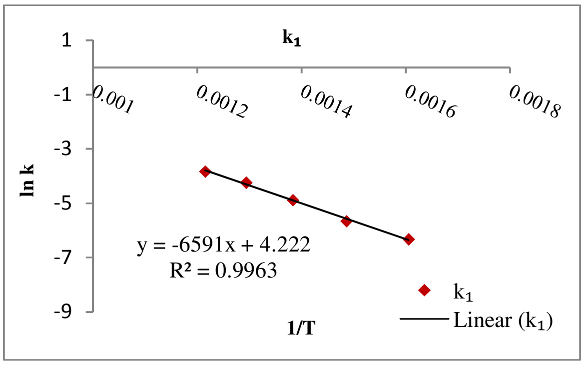

Figure 8. Correlation of ln k and 1/T

Table 1. Value of Ea for Various Model

Reaction Rate Constant (min^{-1})	Model I	Model II	Model III
Ea(kJ/mol)	71.3292	26.5562	65.0602

3.4. Quality of briquette

The quality of briquettes is better when moisture content, ash content and volatile matter is lower. Standard SNI No. 1/6235/2000 stated that the moisture content and ash content should be less than 8%, while the volatile matter should be less than 15%.

Figures 9 show the calorific value for the briquette developed. This result is good enough if compare to the calorific value of wood (4491.2 cal/g) or young age coal (1887.3 cal/g). However this value is still lower than the value of charcoal from wood which has calorific value of 7047.3 cal/g). Table 2 shows the calorific value of some solid fuels [7].

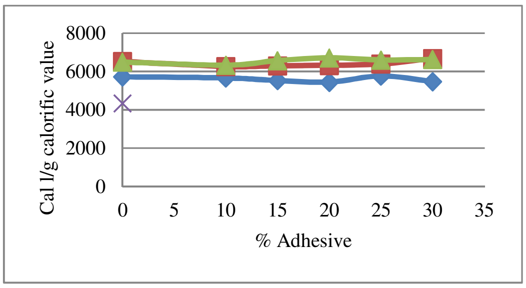

Figure 9. Calorific value for different pyrolysis temperature

3.5. Gas emission testing

The testing of gas emission resulting from the burning of charcoal briquette can be seen in Table 3. From the table, it can be seen that the pyrolysis process will affect the production of emission gases.

Table 2. Calorific value of several types of fuel

Type of fuel	Calorific value (cal/g)
Dry wood	4491.2
Young coal (lignite)	1887.3
Coal	6999.5
Charcoal	7047.3
Crude oil	10008.,2
Fuel oil	10224.6
Natural gas	9722.9

Table 3. Results of gas emission test from burning the charcoal briquette, % volume.

Time (min)	Gas CO		Gas CO_2	
	Temperature of pyrolysis		Temperature of pyrolysis	
	250°C	300°C	250°C	300°C
0	0.09	0.09	2.0	2.0
30	0.08	0.08	2.1	2.2
60	0.06	0.04	2.2	2.5
90	0.04	0.03	2.4	2.7

4. Conclusions

It can be concluded that the *Terminalia Catappa L.* and *Myristica fragran*s (nutmeg seeds shells) shells can be used as raw material for the manufacture of charcoal briquettes. The most suitable model is a model III with the reaction rate constant equation and the activation energy for solids as adalah $k_2 = 487{,}8461 \exp\frac{-7825}{T}$ and Ea = 65.0602 (kJ/mol). The calorific value obtained was better than some of solid fuels.

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