Slow pyrolysis of coconut wood (*Cocos nucifera* L.) and bio-char compositions

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**Abstract.** Biomass in the form of coconut wood (*Cocos nucifera* L.) was pyrolysed in an externally heated batch reactor. In order to determine the lignin, cellulose and hemicellulose content was used a Van Soest method as reference method. The effects of final temperature and heating rate on the yields and compositions of the bio-char were investigated. Pyrolysis runs were performed using reactor temperatures were 375 °C, 475 °C and 575 °C with heating rates of 5 min⁻¹, 10 min⁻¹ and 20 min⁻¹. The bio-char yields were significantly influenced by the process conditions. The result showed that the bio-char mass decreased with increasing the final temperature, but increased with the increase of heating rate. The activation energy increases with increasing final temperature and heating rate. While the highest activation energy was 38.89 kJ mol⁻¹ and the obtained on bio-char product amounted to 6858.84 cal/g at the final temperature 575 °C and heating rate 5 min⁻¹. It was characterized by Fourier transform infrared spectroscopy. This study showed that FTIR spectra have the potential to be an important source of information for a quick evaluation of the chemical composition of coconut wood (*Cocos nucifera* L.).

1. **Introduction**  
As a result of the increase of energy demand and the decrease of fossil energy, there is a high interest in development of alternative energy[6]. Biomass is one of the great potentials to be used as alternative energy[6]. Biomass includes all organic materials such as agricultural waste. One of agricultural waste is coconut wood (glugu). Coconut wood contain mixed components such as cellulose (45%), hemicellulose (35%) and lignin (15%), where the each component will be decomposed in the different rates[2]. Conversion of energy from biomass can be used a pyrolysis process. Pyrolysis is a decomposition process of material in a high temperature without oxygen presence or with limited oxygen and produces bio-oil, bio-char and gas[1]. The aim of the study was to investigate the effect of heating rates and final temperatures of pyrolysis process on coconut wood to determine their influence on bio-char physical and chemical properties. The bio-char physical properties of activation energy were determined by Arrhenius equation and calorific value were determined by ASTM D2015-00. Bio-char chemical characterization was determined by Fourier Transform Infrared (FTIR) and characterization of raw materials was determined by Van Soest Method.
2. Experimental
2.1 Materials
The materials used in this research were coconut wood waste which were collected from Kartasura, Sukoharjo regency. Samples were crushed by crusher equipment until passing 20 mesh and then dried until the water content is not more than 10%. The calorific value of the sample was tested by ASTM D2015 standard method.

2.2 Methods
The pyrolysis process was conducted by taking 50 grams sample and put it in to sample holder. Sample holder was placed in the pyrolysis reactor then all the apparatus were arranged as shown at figure 1. The heating rate variations of pyrolysis were 5 min\(^{-1}\), 10 min\(^{-1}\) and 20 min\(^{-1}\) with final temperature variations were 375 °C, 475 °C and 575 °C and holding time of 20 min. The heating temperature was increased every minute using thermocontroller. Char yielded from pyrolysis process were tested for its calorific value using ASTM D2015 standard method.

2.3 Characterization
The raw material was tested for calorific value, cellulose, hemicellulose and lignin. The calorific value was determined using a bomb calorimeter with ASTM D2015-00 as standard method. Bio-char characterization was determined by calorific value and Fourier Transform Infrared Spectroscopy (FTIR).

2.4 Activation energy determination
Activation energy of pyrolysis process can be calculated by Arrhenius equation using first order reaction as the following equation.

\[
k = A \exp\left(- \frac{E}{RT}\right)
\]

(1)

Where A is pre-exponential factor, E is activation energy, T is temperature then can be calculated with this following equation.

\[
k_t = \frac{1}{(m-m_{\text{oo}})\Delta t} dm
\]

(2)

where \(m_{\text{oo}}\) is final mass, with this following equation:

\[
\ln k = \ln A - \frac{E}{RT}
\]

(3)

by make a plot the relation between \(\ln k\) and 1/T, gives a straight line with \(-E/R\) slope thus the activation energy can be defined.
3 Results and discussions

3.1 Characterization of raw materials

The Van Soest analysis showed that raw materials had a hemicellulose content, so the pyrolysis process was predicted to be occur in between 200-500 ℃.

| Compositions  | Content (%) |
|---------------|-------------|
| Cellulose     | 34.41       |
| Hemicellulose | 37.47       |
| Lignin        | 17.83       |

3.2 Bio-char yields

Figure 2 shows the effect of heating rate and final temperature toward char yield in pyrolysis process. Higher heating rates caused the increasing of char yield which mean the weight-loss of the material was lower, while higher final temperatures caused the decreasing of char yield. This was because the higher final temperature will causes the operating time lasts longer, so carbon will be converted to liquid and gas.

| Heating Rate (°C/minute) | Final Temperature (°C) | Calorific Value (cal/g) |
|--------------------------|------------------------|-------------------------|
|                          | 375                    | 4678.64                 |
|                          | 475                    | 4582.85                 |
|                          | 575                    | 4651.74                 |

Figure 2. (a) Effect of heating rates on char yield; (b) Effect of final temperatures on char yield

3.3 Calorific value

Calorific value is the maximum amount of heat energy released by a fuel through a combustion reaction\(^5\). Calorific value of raw coconut wood is 4784.09 cal/g, while the calorific value of pyrolysis biochar were shown in table 2.

| Calorific Value (cal/g) |
|-------------------------|
| Heating Rate (°C/minute) | Final Temperature (°C) |
|--------------------------|------------------------|
| 5                        | 375                    | 5646.61 |
|                          | 475                    | 6516.47 |
|                          | 575                    | 6858.84 |
| 10                       | 375                    | 5582.88 |
|                          | 475                    | 6451.74 |
|                          | 575                    | 6786.77 |
| 20                       | 375                    | 5482.85 |
|                          | 475                    | 6338.85 |
|                          | 575                    | 6694.49 |

The result of calorific value from pyrolysis of coconut wood with heating rate and final temperature variations are presented in table 2. The final temperature got higher thus the calorific value got bigger, because the increase of temperature caused the termination of lignocellulose bond which got...
much more so that pure carbon atom that was obtained got bigger\cite{3} with the amount of carbon atom which was much therefore the calorific value got higher, but the pyrolysis process will reduce the caloric value of char with increasing heating rate. The heating rate of 5 °C/minute with a final temperature of 575 °C gives the highest calorific value of 6858.84 cal/g.

3.4 Activation energy

Activation energy was determined using Arrhenius equation with the first order of kinetics reaction which was often called global kinetics. The results of activation energy values in all samples are shown in the following table 3.

Table 3. The relation of activation energy and various heating rate

| Final Temperature (°C) | Heating Rate (°C/minute) |
|------------------------|--------------------------|
|                        | 5                        | 10                       | 20                       |
| 375                    | 33.88                    | 26.88                    | 29.07                    |
| 475                    | 34.19                    | 29.54                    | 35.44                    |
| 575                    | 21.88                    | 25.40                    | 38.89                    |

Table 3 shows that the heating rates and final temperatures affects the activation energy of pyrolysis. Based on the results, pyrolysis process produces fluctuating activation energy values. The lowest activation energy was obtained at the final pyrolysis temperature of 575 °C with heating rate of 5 °C/minute. It shows that pyrolysis proces will be easier to occur because it only requires a small amount of energy to decompose.

3.5 FTIR characterization of bio-char

Figure 3 shows FTIR spectra of bio-char. The results of this study using FTIR showed that the bio char from pyrolysis process of heating rate variations didn’t show any changes in the functional groups. Based on FTIR spectra of 375 °C showed that the stretching vibrations of –O-H groups with a strong and wide absorbance at 3314-3414 cm\(^{-1}\) represents dehydration of the cellulose and lignin components. The stretching vibrations of C-H\(_2\) groups absorbance at 2925-2934 cm\(^{-1}\). The carboxyl C=O stretching vibrations with an absorbance at 1707 to 1711 cm\(^{-1}\) indicates the presence of ketons and the vibration of C=C at 1455 cm\(^{-1}\) to 1459 cm\(^{-1}\) indicates the presence of an aromatic ring, while the vibrations at 812 to 874 cm\(^{-1}\) indicates the presence of aromatic C-H. FTIR spectra of 475 °C also showed that the stretching vibrations of –O-H groups at 3418-3443 cm\(^{-1}\), the stretching vibrations of C-H\(_2\) groups absorbance at 2923 cm\(^{-1}\), the vibration of C=C at 1434 cm\(^{-1}\) to 1587 cm\(^{-1}\), and the vibrations at 1229, 1222 and 1227 cm\(^{-1}\) represents of C-O stretching from alcohol. But, FTIR spectra of 575 °C only gives one vibration at 1500 cm\(^{-1}\) that indicates of C=C stretching.
4 Conclusions

In this study, slow pyrolysis experiments of coconut wood (*Cocos nucifera* L.) were performed in a batch reactor and the produced bio-chars were physically and chemically characterized. Heating rate and final temperature affects the activation energy and calorific value of bio-chars. The effect of heating rate and final temperature produces fluctuating activation energy values. The lowest activation energy was obtained at the final pyrolysis temperature of 575 °C with heating rate of 5 °C/minute. It shows that pyrolysis process will be easier to occur because it only requires a small amount of energy to decompose. Calorific value of the bio-chars was higher than its raw material. The increasing of final pyrolysis temperature will raised the calorific value of bio-chars. The highest calorific value of bio-chars was 6694.49 cal/g and was found at 575 °C with heating rate of 20 °C/min. FTIR spectra indicated that heating rate doesn’t affect chemical compositions of bio-chars, but the final temperature does. Chemical compositions of bio-chars decreased as the final temperature increased.

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