Pyrolysis study of coconut leaf's biomass using thermogravimetric analysis

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Abstract. Coconut leaf is one of the most potential biomass to be converted into bio-oil through pyrolysis process and the availability in Indonesia is abundance. The mechanism of decomposition of coconut leaf into bio-oil productions requires further research because of the complexity of pyrolysis and differences in biomass composition. Therefore, the design, optimization and modeling of pyrolysis processes is strongly influenced by biomass characteristics. The purpose of this study was to find the characteristic differences in pyrolysis behavior of the three main parts of coconut leaf based on its constituent parts; leaflets, midrib and whole leaf. Moisture is removed by drying the sample in an electric oven at 110°C for 24 hours. Characteristics were tested using Cellulose Analysis, Ultimate Analysis, and Heat Value, whereas pyrolysis behavior used Thermogravimetric Analyzer (TGA). The results show that leaflets, midrib and whole leaf exhibit different pyrolysis behavior. In terms of considering flow process of separation, the whole leaf becomes an option as a fuel for further pyrolysis processes. The maximum temperature that as a reference in the pyrolysis process of coconut leaves is 500°C with temperature rate of 20°C/min and the process lasts as long for 130 minutes.

1. Introduction
The future of energy is recently an emerging issue. Anxiety arises as fossil fuel reserves keep running low, urging the human to find other new energy resources (Mohan et al., 2006). One of potential renewable energy resources is biomass since the availability in Indonesia is abundance. Some biomass are commonly used such as the sugarcane and corn grain, lignocellulosic biomass, algae and oil seeds (Zaimes et al., 2015). The main materials of lignocellulosic biomass include rice husks, wood waste such as pine wood sawdust, potential energy corps such as Mahua seeds, castor seeds, and industrial and municipal solid waste (Abu Bakar dan Titiloye, 2013), (Miandad et al., 2016), (Dhanavath et al., 2017), (Aguiar et al., 2008). Biomass fulfills 9% of market demand upon energy in the world and this percentage is expected to increase as concerns on global warming and sustainable energy keep emerging (Gadonneix et al., 2010). The attempt has been implemented the last decades, in which the spotlight is on the importance of converting biomass to biofuel through thermochemical conversion processes such as pyrolysis, gasification, and combustion (Patel et al., 2016). Pyrolysis conversion process appears to be a promising technology as it is able to convert biomass to syngas, bio-oil and bio-char. Syngas and bio-oil have ideal heating value to be used as a potential alternative energy. Bio-oil can also be upgraded to become renewable diesel fuel (Quan et al., 2016).

Pyrolysis is a thermochemical decomposition that produces several products which process absence of oxygen. During the pyrolysis process, the large and complex hydrocarbon bonds break down into smaller molecules in the forms of gases, liquids, and charcoal. Pyrolysis shares similarities with cracking, devolatilization, carbonization, torrefaction, dry distillation, destructive distillation, and thermolysis processes. However, pyrolysis is not similar to gasification process that involves external agents in its chemical reaction which is known as medium gasification. Pyrolysis is usually administered at a
temperature that ranges from 300-650 °C, while gasification occurs at between 800-1000 °C, and between 200-300 °C for torrefaction (Basu, 2013).

The characteristics of pyrolysis products are strongly influenced by the type of biomass, pre-treatment of the materials, type of reactor and its parameters including temperature, heating rate, pressure, residence time, catalyst, and air in the environment. Among those factors, temperature is the key factor in pyrolysis process (Auta et al., 2014). Biomass pyrolysis is a complex process that involves a number of chemical reactions. Biomass mainly contains cellulose, hemicellulose, and lignin, as well as other organic extracts and inorganic minerals (Mohan et al., 2006). The main contents of biomass vary depending on the type of the biomass. Commonly, cellulose, hemicellulose, and lignin share 40-60%, 20-40% and 10-25% respectively in the total weight of dry biomass (Burhenne et al., 2013). Cellulose, hemicellulose, and lignin are also known to have different thermal behaviors. As the complexity of biomass conversion determines the variety of products, it is necessary to exclusively investigate the conversion of each composer. Adequate knowledge about the pyrolysis characteristics of those three main components is the key to better understanding of chemical conversion of thermal biomass conversion, which eventually makes the selection of the most appropriate biomass sources and pyrolysis technique to produce certain intended products easier.

Figure 1. The three main parts of coconut leaves; leaflets, midrib and whole leaf

Biomass from coconut leaves is a potential biomass that can be used as an alternative energy source. Coconut palm (Cocos Nucifera L.) is a commodity that is widely available in tropical areas. Coconut palm can be found in more than 80 tropical countries. Indonesia is an agricultural country that ranks third in after the Philippines and India in coconut production. According to the statistical data on Indonesian agriculture released by the Directorate General of Farming, the Ministry of Agriculture in 2015 - 2017, the coconut plantation area in Indonesia in 2017 reached 3,544,393 Ha. It implies that Indonesia has a massive coconut biomass potential. Coconut leaf consists of two parts; leaflets and midrib that contain different amount of cellulose, hemicellulose and lignin. Biomass from materials that have high amount of cellulose and hemicellulose can be decomposed faster, resulting in more fractions of liquid and gas compared to biomass that contain greater amount of lignin (Quan et al., 2016).

This study was conducted to investigate the different characteristics of pyrolysis behaviors of the three main parts of coconut leaves; leaflets, midrib and whole leaf as illustrated in Figure 1. Due to the abundant presence and complex nature of coconut leaves make it very interesting to study and as a recommendation of the next energy conversion process where this is still little found in the open literature.
2. Materials and methods

2.1 Materials
In this study, the materials used were 3 samples in form of powder made by parts of coconut leaves. The leaves were obtained from coconut tree (Cocos nucifera) ecologically in Bali-Indonesia. Coconut leaves were separated between the leaflets and midrib in order to obtained three variations. They are the samples of midrib, leaflets, and whole leaf. Each sample was chopped and blended, and then they were sifted with 80 Mesh. The sample powder then was dried in an electric oven in 110°C holding temperature for 24 hours to get rid the humidity.

2.2. Experimental methods
Cellulose composition was determined through extraction method in accordance to ASTM D1107-96, in which cellulose, lignin and ash in accordance to ASTM D 1103-60, ASTM D1106-56, and ASTM D1102-84 respectively. To get a good validity value, the extraction containing cellulose, hemicellulose, lignin, and ash was tested three times in a kind of sample, and then the result was averaged. The data from the testing result are presented in Table 1.

The chemical elements of C, H, N, and O were tested with LECO elementer CHN add-on O type 628. The testing results are presented in Table 2 as an ultimate analysis. A testing on moisture, volatiles, fixed carbon and ash contents was measured using TGA 701. The analysis method used was in accordance to ASTM D7582 MVA biomass. The data of the testing result are presented in Table 3 as a proximate analysis.

The implementation of thermogravimetric analysis (TGA) to investigate the nature of thermal was very useful in determining thermal behavior experienced by biomass in various temperatures. The understanding of the thermal behavior of biomass was important because the process parameter had a direct impact on chemical composition (quality and quantity) of the product produced. A fast, simple, and reliable analysis method used to investigate thermal decomposition was TGA. It has been widely used by researchers to investigate generally and specifically thermal characteristic of organic materials (Burhenne et al., 2013)(Quan et al., 2016), (Gunasee et al., 2016), (Lazdovica et al., 2017). A test using Thermogravimetric Analysis (TGA) was conducted differentially using TGA 701. The accuracy for temperature measurement was ± 2°C. In each sample, 5 mg dry biomass was heated from 50°C to 900°C in dynamic condition with 20°C/min heating rate. TGA Test was administered to atmosphere pressure and 20 ml/min nitrogen flow (N2).
Table 1. Composition of dry biomass by wt.% compared to Ref.

|          | Cellulose | Hemicellulose | Lignin | Ref.        |
|----------|-----------|---------------|--------|-------------|
| leaflets | 45.58     | 10.35         | 39.64  |             |
| midrib   | 60.75     | 11.42         | 22.10  |             |
| whole leaf | 56.71   | 10.66         | 28.44  |             |
| Coconut leaf | 59.39 | 8.45          | 27.97  | (Poddar et al., 2016) |

Table 2. Ultimate analysis of the biomass by wt.% compared to Ref.

|          | C     | H     | N     | O     | Ref.        |
|----------|-------|-------|-------|-------|-------------|
| leaflets | 47.78 | 6.13  | 1.16  | 28.21 |             |
| midrib   | 47.49 | 5.95  | 0.29  | 39.94 |             |
| whole leaf | 47.63 | 6.10  | 1.07  | 38.87 |             |
| Coconut leaf | 47.89 | 6.19  | 1.66  | 37.93 | (Phichai et al., 2013) |

Table 3. Proximate analysis by wt.% and HHV-LHV of the biomass samples compared to Ref.

|          | Moisture | Volatiles | Fixed carbon | Ash  | HHV (MJ/kg) | LHV (MJ/kg) | Ref.          |
|----------|----------|-----------|--------------|------|-------------|-------------|---------------|
| leaflets | 2.74     | 82.10     | 7.69         | 7.48 | 18.631      | 18.029      |               |
| midrib   | 2.24     | 93.69     | 2.06         | 2.02 | 17.848      | 17.181      |               |
| whole leaf | 2.55   | 83.32     | 7.16         | 6.97 | 18.369      | 17.696      |               |
| Coconut leaf | 4.77  | 87.75     | 12.92        | 6.33 | 20.828      | -           | (Phichai et al., 2013) |
3. Result and Discussion

3.1 Characterization of Biomass

The result of biomass biochemical analysis presented in Table 1 explained that the content of cellulose, hemicelluloses, and lignin were around 93-96%. The other contents such as extractive substance and ash which was dissolved in water or the organic solvent which usually got up to 10% of the total biomass, can be ignored its role in characterization. This extractive substance was phenolic, alkaloid, non-proteinogenic amino acids, acid, terpene, and fatty acid compounds (Ranzi et al., 2008).

Leaflets and midrib had cellulose content as much as 24.58% and 60.75%, respectively. Each of them also had lignin content as much as 39.64% and 22.10% respectively. From its cellulose, midrib had higher cellulose content compared to leaflets. This had made cellulose to form stronger and more rigid tissue. Meanwhile, leaflets had higher lignin content which made the decomposition process became longer. Hemicellulose evaporates easily which cause on the number of volatile products produced. In this study, midrib had higher hemicelluloses than leaflets.

The composition of cellulose, hemicellulose, and lignin in biomass was formed the atom balance of its component. Cellulose and hemicellulose substances formula for all biomass were assumed as C₆H₁₀O₅ and C₅H₁₀O₅, respectively. Lignin was polymerase product of three kinds of monolignols such as paracoumaryl, coniferyl, and synapyl alcohols, which were put on each lignin in form of p-hydroxyphenyl (H lignin), guaiacyl (G lignin), and syringyl (S lignin). Each formula of H, G, and S lignin was C₉H₁₀O₂, C₁₀H₁₂O₃, and C₁₁H₁₄O₄ (Burhenne et al., 2013).

Referring to the test results of C, H, N, O and S components presented in Table 2, it can be inferred that the percentage of C and H were not comparable with cellulose or hemicellulose percentages in wither leaflets or midrib. C and H in leaflets refer to the lignin formation while in midrib, they refer to cellulose formation.

3.2 Pyrolysis kinetics in TGA

In the experiment of thermogravimetric analysis (TGA), the average mass changes in all samples were declared as temperature function between 50°C and 750°C. The target temperature in TGA was set up to 900°C. However, because there were no mass changes any longer start from 650°C temperature, automatically, the analysis process was stopped on 750°C. The results were presented in Figure 2. During 50°C until 110°C temperature, there was evaporation process. Leaflets had lost its mass bigger than midrib due to its moisture substance which was higher in leaflets compared to in midrib and whole leave.

Pyrolysis decomposition of all biomass of coconut leaves ideally occurred during 230°C until 650°C temperature. Referring to DTGA Curve in Figure 3, decomposition process dominantly occurred during 230°C until 500°C temperature. Above those, the process tended to be constant. This data could be a future consideration in pyrolysis coconut leaves into bio-oil. The maximum temperature which could be referenced was 500°C. It can be a reference in the planning of pyrolysis reactor design which saves energy during the process.
Midrib experience decomposition at a lower temperature compared to leaflets. It explained that biomass with high cellulose content could be easily elaborate. Meanwhile, biomass with dominant lignin substance was elaborated longer as visualized in Figure 4. The process time needed to reach 500°C temperature with 20°C/minute temperature rate was 130 minutes.

Thermogravimetry for leaflets curve shifted for around 30°C compared to midrib curve. This shows that the bigger energy is needed to disentangle leaflets since it has bigger and stable lignin substance compared to its cellulose and hemicellulose.

The behavior in this situation was not systematically. Especially in whole leave, there was a significant deviation. Seen from the contents of cellulose, hemicellulose, and lignin, whole leave was in the position between leaflets and midrib. However, its decomposition curve in TGA shifted for around 110°C compared to midrib.

The composition of the product produced by coconut leaves pyrolysis was moisture, volatile, fixed carbon and ash, visualized in Figure 5. Those three kinds of biomass produced a high volatile matter content. This product was in form of steam which could be condensed into a liquid form known as bio-oil. This bio-oil was future energy potential. Midrib produced higher volatile than leaflets. It can be seen in DGA curve where mass changes were bigger in a narrow temperature range, 230°C until 250°C. The three kinds of the biomass were suitable to proceed into bio-oil. However, from their separation process between leaflets and midrib, whole leave was more likely to be considered.

One of the products of pyrolysis which needed to get more attention was ash. Ash which experienced further heating would form hard lumps attached to the bottom of the reactor. Ash factor would be a hindrance of the pyrolysis process in the reactor.

Each ash produced by leaflets and midrib was 7.48% and 2.02% respectively. This difference is significant, almost 5%. If midrib was chosen as pyrolysis material, there would be fewer problems caused by ash. However, if leaflets or whole leave was chosen instead, a special mechanism needs to be applied in the pyrolysis reactor in order to run well.

### 3.3 HHV of Biomass

The heat value in bio-oil was one of the important characteristics. The standard measurement of energy from heat could be reported as higher heat value (HHV) and lower heat value (LHV). The difference between HHV and LHV was the same as the heat of water evaporation formed by burning fuel.

The results of HHV testing showed high heat value of leaflets, midrib, and the whole leaf were 18.631 MJ/kg, 17.848 MJ/kg and 18.369 MJ/kg, respectively. Those three values were considered almost
the same. However, there was significantly different compared to the HHV reported by (Phichai et al., 2013) as much as 20.828 MJ/kg. This difference possibly influenced by the type of biomass which was from different varieties of coconut leaves.

Fig.4. TGA curves of three coconut leaves of time heating

Fig.5. Pyrolysis product composition by wt.% in TGA

In determining the appropriate kind of biomass based on HHV value, whole leave was worth to be considered. Besides HHV value which was similar to leaflets, the shorter process in separating leaflet and midrib also became the consideration as previously discussed.

4. Conclusion
A study on pyrolysis of coconut leaves using Thermogravimetric Analysis (TGA) had been conducted with a conclusion that leaflets, midrib, and whole leave showed the different testing result as well as different pyrolysis behavior. Considering the separation process, thus, leaflets were chosen as the fuel for the next pyrolysis process. The maximum value which can be used as a reference in the pyrolysis process of coconut leaves was 500°C and 20°C/minute temperature rate. Thus, the process will be 130 minutes. Further research which is needed to support this study is ash characterization produced by the above parameter.

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