



THE CALORIFIC VALUES OF SOLID AND LIQUID YIELDS CONSEQUENCED BY TEMPERATURES OF MAHOGANY PYROLYSIS

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ABSTRACT

Due to the potential pyrolysis products to be bio-fuels, the pyrolysis yield products were measured its calorific indicating important-physical properties of fuel. The study aims to analyze the influence of different temperatures on the calorific value of pyrolysis by means of calorimetric measurement. The biomass feedstock used was mahogany wood, and then it would be pyrolyzed in the slow pyrolysis experimental run. The pyrolysis temperatures were conducted from 250 °C to 800 °C and the heating rate at each process was 0.44 °C/sec. It was accompanied to proceed for 3 hours. The influence of temperature toward the solid (char) and liquid (tar) yields were examined by means of a bomb calorimeter. The result was presented by the potential products of mahogany wood pyrolysis in the mass and volume changes of char and tar. Then, the char and tar were measured its calorific values. The calorific value of untreated mahogany wood (before pyrolyzed) were around 3700 kal/g, but the pyrolysis treatment significantly increased its calorific values in various pyrolysis temperatures. It referred that the calorific values of solid yields were pointed in the increasing values with the increasing of pyrolysis temperature, however, the calorific values of tar inclined up to temperature of 500 °C, however, it would decline because the density of tar become lower. The variance in calorific values could be attributed to the chemical composition of the mahogany wood; indeed, it was known a larger amount of carbon percentage. Furthermore, the percentage of carbon tends to increase in the pyrolysis wood.

Keywords: calorific value, solid yield, liquid yield, mahogany, pyrolysis.

INTRODUCTION

There has been many research in recent years in the area of thermo-chemical conversion process of biomass into bio-fuels (bio-oil, bio-char and bio-gas). Among the biomass to energy conversion processes, pyrolysis technology has attracted more interest in producing liquid fuel product due to its several socio-economic advantages. It is an efficient conversion method compared to other thermo-chemical conversion technologies because of its advantages in storage, transport and versatility in application such as combustion engines, boilers, turbines, etc. However, this technology is not yet fully developed with respect to its commercial applications. The future application will be implemented in the alternative fuel produced by renewable energy sources. One of the renewable one replaces woody biomass as a pyrolysis feedstock.

Woody biomass has a mixture of structural elements (hemicelluloses, cellulose and lignin) which each element can be decomposed at different rates and by pyrolysis mechanism. It is believed that as the reaction progresses the carbon becomes less reactive and forms stable chemical structures, and consequently the activation energy increases as the conversion level of biomass increases [1].

The production of bio-liquids and other products (char and gas) by pyrolysis of different biomass species has been extensively investigated in the past [1-13]. Some

of these biomass species include beech wood, bagasse, straws, seedcakes, and municipal solid waste (MSW) [2, 3]. After investigating the solid waste (MSW and cow dung) of pyrolysis [2] and measuring the physical properties of char [3], it has been examined another pyrolysis feedstock, mahogany wood, producing bio-fuels; solid yield (char) and liquid yield (tar). Due to the complexity of hardwood structure, mahogany wood has the potential products to be bio-fuels. Afterward, the products were measured its calorific indicating important-physical properties of fuel. The study aims to determine the solid and liquid yields of char and pyro-oil from the mahogany wood and to analyze the influence of different temperatures on the calorific value of pyrolysis yields by means of calorimetric measurement.

EXPERIMENTAL PROCEDURES

In the investigation, before starting the pyrolysis, mahogany was shaped in the needle particles around 1 μm and dried at 100 °C around an hour to keep the biomass in dry condition. It was because the wood did not have a lot of water contained in tar produced. After the drying process was completed, the wood specimen was weighed around 200 grams for each test. Then, it was inserted in a glass beaker to be placed in pyrolyzer (furnace). After the pyrolysis run ready, Nitrogen gas was flowed into furnace to eliminate O₂ content until it was ± 2% of the volume of furnace. To measure the pyrolysis temperatures, at each



investigation, the thermocontrol was conducted in pyrolysis temperatures of 250 °C, 350 °C, 450 °C, 500 °C, 600 °C, 700 °C, 800 °C. At each pyrolysis experiment, it was used the same heating rate 0.44 °C/sec categorized as slow pyrolysis. The each pyrolysis process was accompanied to proceed for 3 hours. When the process accomplished, the pirolizer was turned off and the weight

and volume of solid yields (char) were measured. Afterward, the char produced was tested to determine the calorific value at each pyrolysis temperature. In parallel way, tar produced was condensed into cold trap containing

RESULTS AND DISCUSSIONS

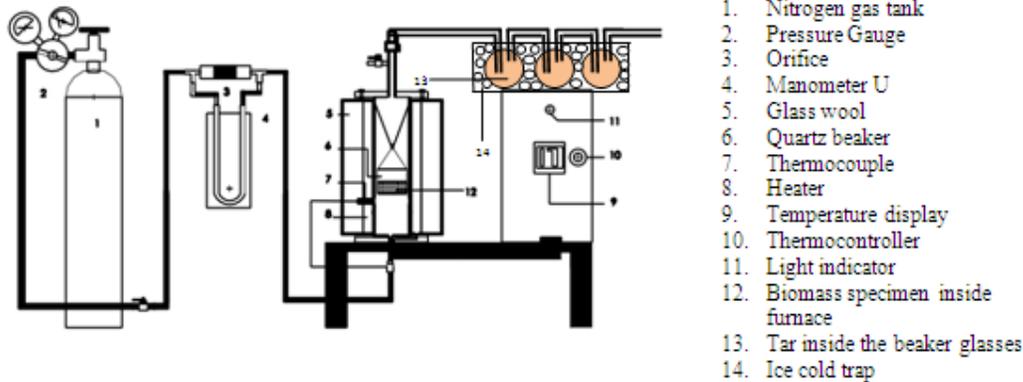


Figure-1. Pyrolysis experimental run.

glass beaker inside ice rig, then it was also tested to observe its calorific value. Both the calorific values; char and tar, were measured.

The investigation of study was proposed to obtain the calorific value of fuel that one of the properties that will be placed in the governing equation in equation. 1 to solve the energy equation in the pyrolysis process. The calorific value is also named the calorific value value of the measurement process during the pyrolysis process. Although each data points were taken at one temperature pyrolysis as like 250 °C, 350 °C, 450 °C, 500 °C, 600 °C, 700 °C, 800 °C, but the overall results of the study explained that the pyrolysis are able to be assumed as the changes process that occur in overall pyrolysis process from $T=25\text{ °C}$ (before the pyrolysis process begins) to $T=800\text{ °C}$.

The investigation only observed the measured calorific value of char and tar (bio-oil), however, the calorific value of gas generation will to be measured / calculated in the next work.

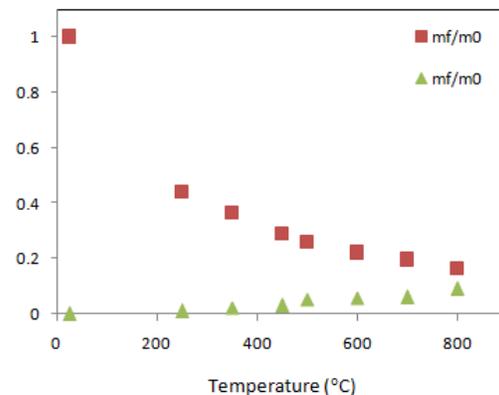


Figure-2. The mass of char and tar yields in pyrolysis temperatures of 250 °C – 800 °C.

As pyrolysis is a thermochemical process, before heading to the acquisition values of the calorific value, the effect of temperature means an important factor in the heating process. It will greatly affects the yields of pyrolysis, so that it, firstly, before measuring the calorific value values obtained, the effect of temperatures on the yields will be observed firstly. Initially, the observations will be carried out by measuring the mass and volume were formed at the end of the process.



Effect of the Pyrolysis Temperatures on Mass and Volume of Pyrolysis Yields

The pyrolysis process was conducted by using a slow heating rate (slow pyrolysis) with a heating rate of 0.44 °C/sec. Since the heating rate was slow, the yield product was formed predominantly the char. It can be illustrated in Figure 2 and 3. In the graphs, it can be seen that the mass and volume of char yield had a greater percentage than the mass and volume of tar. The data shows that the products of pyrolysis char yield of 40% and 2 % for tar in the low-temperature range, 26 % for char and 5 % for tar in the middle-temperature range, as well 16 % char and 9 % tar in high-temperatures range.

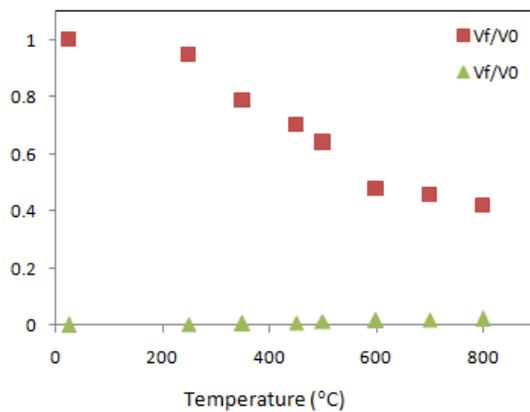


Figure-3. The volume of char and tar yields in pyrolysis temperatures of 250 °C – 800 °C.

Thus, the lowest char yield was produced at the highest temperature $T=800$ °C that accompanied by an increasing in tar yield generated. It could be argued that the higher the temperature, the less the char produced. In otherwise, the higher the temperature, the much more the tar produced. As a result, the pyrolysis process showed an inverse ratio between solid yields (char) and liquid products (tar). It is due to the fact that the greater the pyrolysis temperature, the components/compounds in the mahogany wood would be decomposed sharply. The biomass decomposition would cause shrinking of wood particles due to evaporation of moisture and volatile matter. The volatile matter later on atmospheric conditions would result in tar (liquid) and gas (which will be observed in subsequent studies) phase.

Therefore, as more components were decomposed, as less the mass of char, however, as much the tar mass produced. In addition, the main component of mahogany wood consists of cellulose, hemicellulose, and lignin. Based on the component reason, the mahogany wood includes hemicellulosa in major component, so it includes the hardwood type of wood. Cellulose decays in the fastest decomposition of the compound at low temperatures, whereas lignin is the slowest compound that

will decompose at high temperatures. The hemicellulose will begin to crumble the component at the pyrolysis temperature of 200 °C – 280 °C. In Figures 3 and 4, it can be seen that the decomposition was characterized by degeneration of the most significant biomass occurs at a temperature of 250 °C – 450 °C. It is because all three compounds decomposed simultaneously, thereby causing the decomposition of compounds with the cellulose, hemicellulose, and lignin.

The increasing of mass and volume of tar were begun at a temperature of 450 °C due to the hemicellulose and cellulose decomposition [5]. Meanwhile, the lignin was partly but more than in the previous temperature that cause amount of tar produced after 450 °C for more.

Effect of Mass and Volume Yields on the Yields of Apparent Density

Furthermore, a large amount of mass and volume of char yields will be compared with tar yields as shown in Figure 4 and 5 to understand the apparent density of char and tar products, which can be seen in Figures 6 and 7.

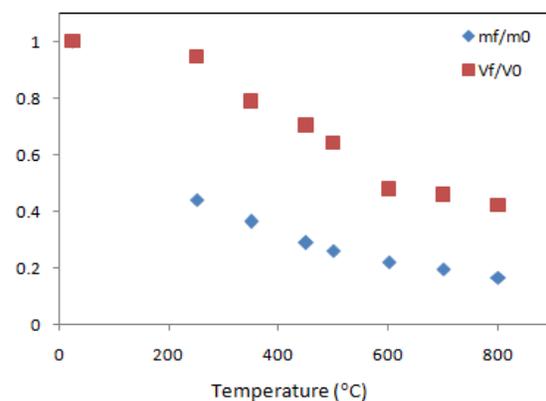


Figure-4. Char yields produced in elapsed temperature of 250 °C – 800 °C.

The Apparent Density of Char

In Figure-4, it could be described that the comparison between the mass and the volume of char tends to produce the same trends. In other words, it could be said that the density occurs during pyrolysis for solid yields had a constant value.

If it was compared with the previous study (Tanoue, 2010) which states that the apparent density significantly changes occurred in the range of pyrolysis temperature of 250 °C-350 °C, it was not seen in this study. It was due to the magnitude of the pyrolysis heating rate was not the same, in which in the previous study, the heating rate was 0.11 °C/sec, whereas in this study, the heating rate was conducted in 0.44 °C/sec causing more rapid decomposition of biomass happened at a low temperature pyrolysis. As a result, the apparent density of



char was found in Figure-6, with the average apparent density about 0.075 g / ml.

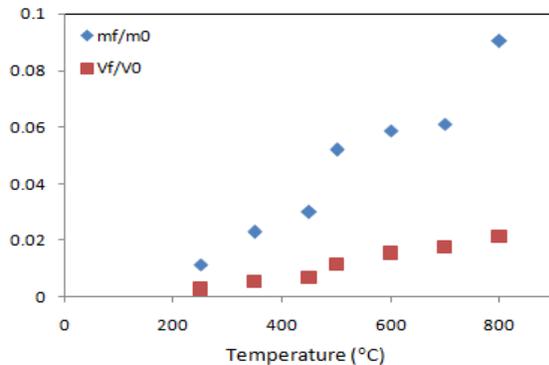


Figure-5. Tar yields produced in elapsed temperature of 250 °C – 800 °C.

The Apparent Density of Tar

In tar yield, as illustrated in Figure 5, the higher the pyrolysis temperature caused the larger volume of tar. However, the ratio of volume and mass had the different ratio, expressed at figure 5 and 7. As a result, at temperatures among 250°C to 500°C, there was a significant increasing in their apparent density. In contrast, at the pyrolysis temperature between 500°C and 700°C, a decreasing of the tar apparent density was very large. The greater pyrolysis temperature caused the volume ratio of future large extensible. It was probably due more tar was condensed at higher pyrolysis temperature. However, at a temperature of 800°C, the apparent density jumped very significantly. It seems to be liked an anomaly, which occurs very significant increasing the apparent density. The research needs to be confirmed again in the next work to find out what the exact reasons. It is because it will be associated with the process of gas generation during the process.

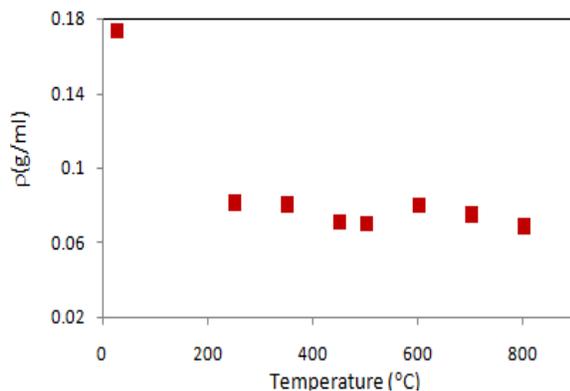


Figure-6. The apparent density of char yields in temperatures of 250 °C – 800 °C.

In general, at the low temperature pyrolysis, the mass loss of biomass has occurred significantly, but the shrinking volume of one decreased was not as much as the mass loss. For char, the condition of the atomic structure was very hollow. For tar, the low density indicated conditions produced lighter-tar oil. However, the magnitude of intermolecular cavities and voids among particles of biomass remained to be investigated again.

Effect of Temperatures on the Calorific Values on the Mahogany Wood

The calorific value value suggests the potential energy content of pyrolysis products in which in the research, the product were solid fuel (char) and liquid fuel (tar). In each pyrolysis temperatures, the char and tar were tested with the calorific value values using bomb calorimeter. The results of the study in the form of gaining the calorific value values for could be expressed in Figure-8. In the char products, the greater the pyrolysis temperature, the higher the values of the calorific value. It was because the higher the heating, the more pure-char was formed. That was, at low temperature, the solid product was not only char formation, but also a mixture of wood and char produced. The higher the heating temperature, the more components of wood was decomposed to be char.

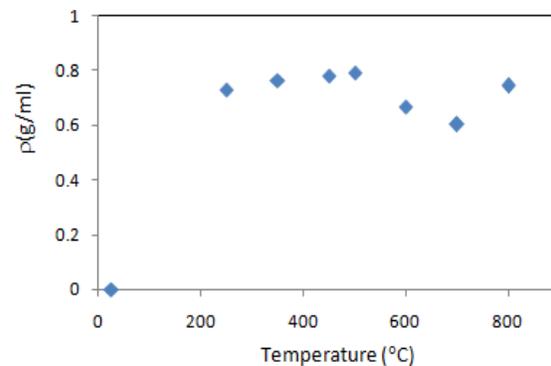


Figure-7. The apparent density of tar yields in temperatures of 250 °C – 800 °C.

The same trend occurred in the formation of tar in which the higher the pyrolysis temperature, the greater the heating value of tar pyrolysis results. The calorific value values of tar inclined up to temperature of 500°C, after that, it would decrease very significant. It was associated with the decreasing in the apparent density occurs. It was due the elements having a high calorific value, such as CH₄ and H₂ began to decompose to gaseous phase products. Consequently, the heating value of tar was low, and it would predict that the calorific value of the gas generation would increase.

In overall pyrolysis yields, the calorific value of char increased with the increasing temperature, while the



calorific value of tar rose to 500 °C, afterward, it would decrease due to its liquid getting into lighter-oil. It also could be said that the values of the tar calorific value increased to a temperature of 500 °C. After that, the value of the calorific value of tar decreased significantly due to viscosity decreasing as a result of combustible compounds turn into gas generation.

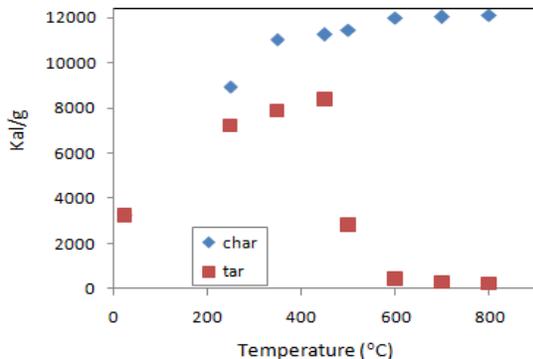


Figure-8. The calorific value of char and tar yields in elapsed temperature of 250 °C – 800 °C.

CONCLUSIONS

The study aimed to obtain the values of the calorific value of char and tar yields summarized as follows:

1. Temperature affects the calorific value values that also influenced by mass, volume, and the apparent density.
2. The higher temperatures, the larger the char obtained, but it was accompanied by the larger amount of tar.
3. The char calorific values increased with the increasing temperature, while the increasing of the tar calorific value reached up to 500°C. After that, the values decreased significantly due to viscosity decreasing as a result of combustible compounds turn into a gas.

REFERENCES

- [1] A. Demirbas. 2004. Determination of calorific values of bio-chars and pyro-oils from pyrolysis of beech trunkbarks, *J. Anal. Appl. Pyrolysis*. 72 (2004) 215-219
- [2] W. Wijayanti. 2014. Gaining the Calorific value of Solid Yields Formation in the Process of Waste Pyrolysis, *Applied Mechanics and Materials*. Vol. 493, pp. 179-185
- [3] W. Wijayanti. 2014. The Physical Properties (Calorific value and Thermal Conductivity) of Mahogany Wood Induced by Pyrolysis Temperature Process, *Applied Mechanics and Materials*. Vol. 664, pp. 215-220.
- [4] Di Blasi, C. 2008. Modeling Chemical and Physical Processes of Wood and Biomass Pyrolysis, *Progress in Energy and Combustion Science*. 34, pp. 47-99.
- [5] Koufopoulos, *et al*, 1991, Modelling of the pyrolysis of biomass particles. Studies on kinetics, thermal and heat transfer effects, *The Canadian Journal of Chemical Engineering*. Vol. 69, Issue 4, pp. 907-915.
- [6] Babu, B.V., *et al*. 2004. Heat transfer and kinetics in the pyrolysis of shrinking biomass particle, *Chemical Engineering Science*, Vol. 59, Issue 10, May 2004, Pages 1999-2012.
- [7] Tanoue, K., T. Hinauchi, T. Oo, T. Nishimura, M. Taniguchi, and K. Sasauchi. 2007. Modeling of heterogeneous chemical reactions caused in pyrolysis of biomass particles, *Advanced Powder Technology*. 18, 825-840.
- [8] Tanoue K., Widya W., *et al*. 2009. Numerical Simulation of Heat Transfer through the Pyrolysis of Woody Biomass, 9AICHE - 2009 AICHE Annual Meeting, Conference
- [9] Tanoue, K., Widya, W., Yamasaki, K., Kawanaka, T., Yoshida, A., Nishimura, T., Taniguchi, M., Sasauchi, K. 2010. Numerical Simulation of the thermal conduction of packed bed of woody biomass particles accompanying volume reduction induced by pyrolysis, *J. Jpn. Inst. Energy*. 89(10): 948.
- [10] Tanoue K., Widya W., *et al*. 2010. Effect of the Volume Reduction on the Thermal Conduction through the Pyrolysis of the Biomass, 10AICHE - 2010 AICHE Annual Meeting, Conference Proceedings.
- [11] Widya W, Tanoue, K., *et al*, 2011, Rule of thumb for simulating biomass pyrolysis in packed bed reactor, 11AICHE - 2011 AICHE Annual Meeting, Conference Proceedings.
- [12] Mohan *et al*. 2005. Pyrolysis of wood/Biomass for Bio-oil: A Critical Review; Department of Chemistry, Mississippi State University, USA.
- [13] Y.S Kim *et al*. 2003. *J. Anal. Appl. Pyrolysis* 70 (2003).