Study of final temperature and heating rate variation to pyrolysis of Acacia (Acacia mangium W.) wood waste

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Abstract. The research pyrolysis of acacia wood waste has been carried out. This research was conducted to determine the optimal conditions that can be used for the pyrolysis process of acacia sawdust and the effect of the pyrolysis products. The pyrolysis process was carried out on the principle of slow pyrolysis using a batch type reactor. Pyrolysis was carried out by varying the final temperature of pyrolysis 375°C, 475°C, and 575°C and variations of heating rates 5°C/min, 10°C/min, and 15°C/min with a holding time of 20 minutes. The content of cellulose, hemicellulose and lignin at raw material was determined with the van soest method and the values are 32.75%, 35.16%, and 16.81%, respectively. The result of the pyrolysis process in the form of char at the final temperature of 575°C with a heating rate of 5°C/min produces a calorific value of 6.816 cal/gram. In the tar (oil) tested using GCMS, the acacia tar contains quite high phenol, acetic acid, 2 propanone. The results of pyrolysis can be seen that the highest activation energy value is found in the pyrolysis process with a variation of the heating rate of 15°C/min and the final temperature of the pyrolysis 575°C which is 49.56 kJ/mol.

1. Introduction
Population in the world from year to year was continues to increase. According to ESDM, consumption of energy in Indonesia reached 1.23 billion Barrels Oil Equivalent (BOE), which means an increase of 9% from the previous year. Energy consumption which continues to increase every year is not balanced with the existence of energy reserves in Indonesia, so it is necessary to renew energy. Renewing energy can be done by utilizing a biomass. Biomass can come from plants, animals, and industrial waste from agriculture, estate, forestry, farm and fisheries.

One of the biomass was potentially in Indonesia and has not been utilized properly is waste from the wood processing industry. The wood processing was produces 12–15% sawdust, 25–35% small ends, and 5–10% defective wood, with a total waste of 50.8% of the total raw material used [1]. Acacia (Acacia mangium W.), is wood that is widely used by wood industry in Indonesia. Acacia sawdust is a lignocellulotic waste containing about 32.8% cellulose, 34.32% hemicellulose and 14.65% lignin [2]. These compounds are compounds that have the potential to be converted into degraded biomass.

Energy conversion from biomass can be carried out by biochemical and thermochemical processes. Pyrolysis is one of the thermochemical biomass conversions. Pyrolysis is considered as the easiest technology to use for biomass conversion because pyrolysis has a high conversion ratio and easier control of the conversion process. Pyrolysis produces which have a high energy content [3].
Pyrolysis is a heating process that degrades biomass into char (charcoal), tar (oil) and gas [4]. Factors that influence the pyrolysis process include the final temperature of the pyrolysis, heating rate, holding time, particle size, and particle weight [5]. Majedi et al. [6] have conducted research on mahogany sawdust pyrolysis by varying the final temperature of pyrolysis. The pyrolysis process is carried out with temperature variations of 350°C, 450°C, 500°C, and 600°C at a heating rate of 6°C/min and a heating rate of 1°C/min. The results showed that the percentage of mass reduction at a heating rate of 14°C/min with a final temperature of 600°C experienced a mass reduction of 75.24% with a little char product. In this study, it is known that variations in heating rate and final temperature affect pyrolysis products, but it is not explained what percentage of pyrolysis products and the character of pyrolysis products are formed so that it needs to be studied further about the character of pyrolysis products. Saddawi et al. [7] said that one of the things that affects the conversion of biomass using the pyrolysis method is the kinetics of the thermal decomposition reaction. In this study, it is said that the activation energy produced by a pyrolysis process can be seen from the mass degradation during the combustion process. Activation energy can be calculated using the Arrhenius equation, the Murray and White equation, Doyle, Senum and Yang, and Flynn Wall Ozawa and Criado using the reaction order of one. This research describes the calculation of the activation energy that occurs in the pyrolysis process but does not explain the effect of thermal degradation on the kinetics that occurs in the pyrolysis process.

Based on the problems regarding biomass waste, this research was carried out to determine the effect of the final temperature and heating rate of the pyrolysis process based on the yield of the resulting product, the decrease in mass during the pyrolysis process and the character of the pyrolysis products produced so that it can be used as energy conversion of acacia sawdust.

2. Research method

2.1 Equipment
The equipments used in the research are container raw material, furnace diameter 20 cm, electronic scale A&D GF-300, ADAM thermoreader, thermocontroller, thermocouple type K, condenser, container of the tar product, stopwatch, sets of Fourier Transform-Infra Red (FTIR) (Shimadzu type FTIR-8201 PC), set of Gas Chromatography-Mass Spectrometer (GC-MS).

2.2 Materials
The materials of the research is acacia sawdust obtained from Kedungombo, Sragen (7°25'32.8"S 110°48'48.9"E).

2.3 Research procedure

2.3.1 Preparation of the materials
Acacia sawdust is sieved to pass 20 mesh.

2.3.2 Pyrolysis of materials
The pyrolysis process of acacia sawdust is carried out by weighing 200 grams of material. The material laid on the furnace. Pyrolysis is carried out by varying the heating rate and final temperature. Pyrolysis of acacia sawdust was carried out by varying the final temperature were 375°C, 475°C, and 575°C. The heating rates used for acacia sawdust pyrolysis were 5°C/min, 10°C/min and 15°C/min. The holding time was carried out for 20 minutes. The addition of heating temperature is done every minute using a thermocontroller.

2.3.3 Testing the raw materials
The raw material to be used for the research is the van soest test (use to check the contents of cellulose, hemicellulose and lignin) and the proximate test to determine the chemical content of the raw material.
Raw materials are also tested using FTIR to determine the functional groups contained in the raw materials.

2.3.4 Testing the pyrolysis product

The pyrolysis process produces products in the form of char (charcoal) and tar (tar). In the two pyrolysis products, several tests were carried out. Char products are subjected to proximate test, calorific value test and characterization of functional group by FTIR. Meanwhile, the tar product was tested by FTIR and GC-MS characterization.

3. Result and discussion

3.1 Identification of acacia sawdust

3.1.1 Van Soest analysis

Based on the results of the tests that have been carried out, it is known that the acacia sawdust used has high levels of cellulose, hemicellulose, and lignin. According to Yang et al (2007), a biomass can be said to be good if it has a hemicellulose content of 20-30% of the total mass, so that acacia sawdust used in this study is biomass which is very good for energy conversion raw materials.

| Table 1. Van Soest analysis result of sawdust Akasia. |
|---------------------------------|-----------|
| Contents                       | Presentase (%) |
| Cellulose                      | 32.75     |
| Hemicellulose                  | 35.16     |
| Lignin                         | 16.81     |

3.1.2 Proximate analysis

The proximate test results showed that the acacia sawdust before pyrolysis contained high levels of fixed carbon and volatile matter. High volatile matter will result in a significant reduction in mass during the pyrolysis process [4]. The water content of acacia sawdust indicates that acacia sawdust has a relatively low water content. High water content will reduce the heating value of a biomass. The water content of acacia wood is low so that acacia wood has a high calorific value. The test results of the calorific value of the acacia sawdust sample showed a low value. Based on SNI 01-6325-2000, biomass should have a heating value of at least 5000.00 cal/g. From the results of testing the calorific value of acacia sawdust waste before pyrolysis, it only has a calorific value of 4727.56 cal/g.

| Table 2. The contents of the acacia sawdust. |
|--------------------------------------------|-----------|
| Sample                                     | Dust (%)  | Water (%) | Volatile matter (%) | Fixed carbon (%) | Calor value (kal/g) |
| Acacia sawdust                             | 1.68      | 12.81     | 60.36             | 25.52            | 4727.56             |

3.1.3 Analysis of functional group

The acacia sawdust that will be used as raw material for the pyrolysis process is carried out by FTIR test to determine the functional groups and chemical bonds contained in the sample. FTIR analysis can be seen in the FTIR spectra in figure 1. In the FTIR spectra, it can be seen that the raw material for acacia sawdust contains functional groups as in table 3.
Table 3. Analysis result of acacia sawdust by FTIR.

| Functional group | Wave number reference(cm⁻¹) | Wave number research (cm⁻¹) |
|------------------|-----------------------------|-----------------------------|
| O-H              | 3550-3200                   | 3421.87                     |
| C-H              | 2960-2850                   | 2921.32                     |
| C=O              | 1750-1630                   | 1738.87                     |
| C=C aromatic     | 1600-1500                   | 1509.36                     |
| C-O eters        | 1275-1200                   | 1239.32                     |
| C-O              | 1085-1030                   | 1033.89                     |
| C-H aromatic     | 900-600                     | 896.94                      |

From table 3, it can be seen that acacia sawdust has O-H bonds which can be seen as the content of cellulose and hemicellulose. The known O-H bonds from the range of wave numbers are in the range 3550-3200 cm⁻¹ [7]. The O-H bond can be said to be the water content in the raw material. In the FTIR spectra which can be seen in figure 1, it has a sufficiently wide O-H absorption so that it can be seen that the raw material has a high water content. In the range 2960-2850 cm⁻¹, it is known that there are C-H bonds which are cellulose and hemicellulose. In the 1750-1630 cm⁻¹ bond there is a C=C bond that comes from hemicellulose. In the range of wave numbers 1600-1500 cm⁻¹ there is a C=C bond which is known as the C=C bond of an aromatic compound which is known as a volatile substance in the raw material. At the wave number 1275-1200 cm⁻¹, it is known that there is a C-O bond which is an ether group which is included in the lignin content. In the range of wave numbers 1085-1030 cm⁻¹, it is known that there are C-O bonds derived from cellulose and hemicellulose, and at wave numbers 900-600 cm⁻¹, it is known that there are aromatic C-H bonds [7]. From the analysis carried out on acacia wood sawdust raw material, it can be seen that acacia wood dust originating from Kedungombo, Kalijambe, Sragen is a lignocellulotic biomass that can be used for energy conversion by the pyrolysis process.
3.2 Pyrolysis product

3.2.1 Yield product
The yield in pyrolysis products can be calculated using the mass balance principle. The yield calculation of the resulting pyrolysis products is by weighing the pyrolysis products in the form of solids (bio-char) and liquid (tar), while the products in the form of gases are calculated using the principle of mass balance. Based on the research that has been done, it can be concluded that the heating rate and final temperature affect the yield of the product from the pyrolysis process as depicted in figures 2, 3 and 4.

Based on the graphs in figures 2, 3 and 4, it can be seen that the heating rate and final temperature can affect the yield of the pyrolysis product. At the lower heating rate, the less mass decrease so that the mass of char formed is more. The mass decrease is also influenced by the final temperature, the final temperature was higher used in the pyrolysis process, was the mass decrease more. This results in fewer char products being formed. At high temperatures, a perfect heating process occurs so that many bonds in the cellulose and hemicellulose in the sample are damaged and make the sample more flammable, so that the product is less [8]. At the final high temperature, the decomposition reaction is very reactive, resulting in the conversion of biomass into liquid and gas products [9].

![Figure 2. Yield graph of pyrolysis at final temperature 375°C.](image2)

![Figure 3. Yield graph of pyrolysis at final temperature 475°C.](image3)
Figure 4. Yield graph of pyrolysis at final temperature 475°C.

3.2.2 Char (Charcoal)
Char (charcoal) is a product of pyrolysis in the form of solid. Char from the pyrolysis process has the main content in the form of carbon and contains some oxygen and hydrogen.

3.2.2.1 Calor value
The calorific value analysis is carried out on the solid product resulting from pyrolysis (char) which aims to obtain data on the heat energy released by a fuel due to the reaction or combustion process. The calorific value of raw acacia sawdust is 4727.56 cal/g. The calorific value of the pyrolysis results will be affected by the pyrolysis operating conditions such as the final temperature and heating rate. The results of the calorific value test on acacia sawdust pyrolysis products are shown in table 4.

| Heating rates (°C/min) | Final temperature 375 (°C) | Final temperature 475 (°C) | Final temperature 575 (°C) |
|------------------------|-----------------------------|-----------------------------|-----------------------------|
| 5                      | 5585.38                     | 6467.72                     | 6816.36                     |
| 10                     | 5558.02                     | 6405.40                     | 6742.76                     |
| 15                     | 5429.59                     | 6281.83                     | 6643.91                     |

The heating rate affects the heating value of pyrolysis products. The higher the heating rate up to 15°C/min with a constant final temperature, the lower the calorific value. This happens because the calorific value is influenced by the moisture content and ash content in the pyrolysis products. At high heating rates, the chemical bonds are broken simultaneously while at low heating rates (<10°C/min) the weakest chemical bonds are broken. This can happen because there are still many chemical bonds that are still stable [10].

High heating rates can also predict high levels of volatile matter and a decrease in bound carbon content. The heating value will also be affected by the final temperature of the pyrolysis process. At the final temperature variation of 575°C the calorific value obtained will be higher [11].

3.2.2.2 Proximate analysis
Proximate analysis of acacia sawdust was carried out to determine the basic characteristics of the biomass after pyrolysis, such as the physical and chemical properties of the sawdust.
a. Proximate analysis on bio-char with variation of final temperature on same heating rate.
The proximate test was carried out on the bio-char product of the acacia wood sawdust pyrolysis process based on the variation of the final pyrolysis temperature (375°C, 475°C, 575°C) with a heating rate of 5°C/min can be seen in figure 5.

![Figure 5. Graph of Proximate bio-char analysis with variation final temperature at the same heating rate.](image)

b. Proximate analysis on bio-char with variation heating rate on same final temperature
The proximate test was carried out on the bio-char product of the acacia wood sawdust pyrolysis process based on variations in heating rate (5°C/min, 10°C/min, 15°C/min) with the final pyrolysis temperature of 575°C can be seen in figure 6.

![Figure 6. Graph of proximate bio-char analysis with variation heating rate at the same final temperature.](image)

The proximate test results showed that the bio-char of acacia sawdust contained quite high fixed carbon and volatile matter even though with different heating rates. Fixed carbon increases with decreasing heating rate, this indicates that along with decreasing heating rate with high temperatures, the pyrolysis process will run perfectly. The ash content in bio-char corresponds to the content of fixed carbon. High levels of fixed carbon will increase the ash content because ash is a constituent of fixed carbon. Volatile matter levels decreased along with a decrease in the pyrolysis heating rate. This shows that at high heating rates the volatile matter is still high because the pyrolysis process occurs quickly so that the pyrolysis process has not occurred optimally. At low heating rates the pyrolysis process occurs slowly so as to maximize the evaporation process of volatile substances [6].
The water content of the proximate test results can also show how long the drying process takes on acacia sawdust pyrolysis. At a temperature of 575°C, it has a higher water content than the temperature below, so it shows that the pyrolysis process at this temperature takes a longer time. The water content of acacia sawdust indicates that the water content in this acacia sawdust is low. The water content of acacia wood is low, so this acacia wood has a high calorific value.

3.2.2.3 Functional group analysis
a. Bio-char functional group analysis with variation final temperature (375°C, 475°C, dan 575°C) at heating rate 5°C/min.
Analysis functional group with instrument FTIR on bio-char can be seen on spectra FTIR on figure 7. In the FTIR spectra, it can be seen that the bio-char from the pyrolysis of acacia sawdust contains functional groups as in table 5.

![Figure 7](image)

**Figure 7.** Spectra FTIR bio-char on same heating rate with variation final temperature pyrolysis.

**Table 5.** Result of functional group analysis of pyrolysis on same heating rate at variation final temperature.

| Functional group | Wave number reference (cm⁻¹) | Wave number research (cm⁻¹) |
|-------------------|-----------------------------|-----------------------------|
| O-H               | 3550-3200                   | 3391.97                     | 3428.62                     | 3453.69                     |
| C-H               | 2960-2850                   | 2919.39                     | 2923.25                     | -                           |
| C=O               | 1750-1630                   | 1726.36                     | -                           | -                           |
| C=C aromatik      | 1600-1500                   | 1510.33                     | 1598.09                     | 1593.27                     |
| C-O eter          | 1275-1200                   | 1234.50                     | 1264.39                     | -                           |
| C-O               | 1085-1030                   | 1044.50                     | 1032.93                     | -                           |
| C-H aromatik      | 900-600                     | 615.32                      | 897.58                      | 874.76                      |
From table 5, it can be seen that the bio-char from the pyrolysis of acacia sawdust has O-H bonds derived from cellulose and hemicellulose content. The O-H bond is known from the range of wave numbers, namely in the range 3550-3200 cm\(^{-1}\) [7]. The O-H functional group contained in this bio-char identifies that this bio-char still contains water. This O-H group will decrease in intensity with the increase in the final temperature of the pyrolysis process [7]. In figure 7, it can be seen that at low temperatures the absorption spectra of this O-H bond are wider than the spectra at high temperatures. In figure 7 it can be seen that the higher the final temperature of pyrolysis, the O-H absorption will be narrower. This is because the addition of the final pyrolysis temperature will reduce the water intensity in the bio-char. In the range 2960-2850 cm\(^{-1}\), it is known that there are C-H bonds derived from cellulose and hemicellulose. In figure 7, it can be seen that the C-H group absorption appears to be narrower as the final temperature of pyrolysis increases. This is consistent with the theory that cellulose and hemicellulose will decompose in the temperature range 250-500°C [12]. In the 1750-1630 cm\(^{-1}\) bond there is a C=C bond that comes from hemicellulose.

In the range of wave numbers 1600-1500 cm\(^{-1}\) there is a C=C bond which is known as the C=C bond of an aromatic compound which is known as a volatile substance in the raw material. At the wave number 1275-1200 cm\(^{-1}\), it is known that there is a C-O bond which is an ether group which is included in the lignin content. In figure 7, it can be seen that the C-O bond absorption which is the ether group of lignin looks narrower as the final temperature of pyrolysis increases. At 575°C, it can be seen that the absorption of this group is lost.

In the range of wave numbers 1085-1030 cm\(^{-1}\), it is known that there are C-O bonds that come from cellulose and hemicellulose, and at wave numbers 900-890 cm\(^{-1}\), it is known that there are aromatic C-H bonds. The aromatic C-H bond was only seen at 575°C and it is known that this compound appears at high temperatures.

Based on the spectral analysis mentioned above, it can be seen that cellulose and hemicellulose will be degraded along with the increase in the final temperature of pyrolysis and the water content in bio-char which is known from the absorption of O-H hydroxyl bonds decreases along with the increase in the final temperature of pyrolysis.

b. Bio-char functional group analysis with variation final temperature heating rate (5°C/minute, 10°C/minute, 15°C/minute) at the final temperature 575°C

FTIR analysis of the bio-char of pyrolysis products can be seen in the FTIR spectra in figure 8. In the FTIR spectra, it can be seen that the acacia sawdust sample contains functional groups as in table 6.

![Figure 8](image_url)
Based on the variation of heating rate with the same final pyrolysis temperature, it can be seen that this bio-char still contains water. As previously explained, at the high end temperature of pyrolysis, the O-H hydroxyl bond absorption at wave number 3550-3200 cm\(^{-1}\) is getting narrower, which indicates that there is still water content in the bio-char. At 1600-1500 cm\(^{-1}\) absorption, there is a C=C bond which indicates the presence of an aromatic group and at 900-690 cm\(^{-1}\) absorption there is an aromatic C-H bond. The presence of aromatic groups in the bio-char indicates that there are volatile substances from biochar which are formed at high temperatures in the pyrolysis heating process which is caused by damage to the volatiles of the bio-char material.

Based on the spectra analysis mentioned above, it can be seen that as the heating rate increases, the pyrolysis process occurs more rapidly, but the pyrolysis combustion process has not yet occurred completely. The faster heating rate also affects the hydroxyl group content, it can be seen that in figure 8, the absorption of hydroxyl groups at low heating rates looks narrow and will even disappear. This indicates that with a low heating rate a pyrolysis process will run perfectly because the water content will disappear over time.

### 3.2.3 Tar

Tar is a blackish liquid fuel produced from the conversion of biomass by pyrolysis. The largest organic components in tar are lignin derivatives, phenols, organic acids, alcohols, and carbonyl compounds such as aldehydes, ketones and esters [13]. Tar consists of molecules of different sizes derived from cellulose, hemicellulose and lignin. Tar is one of the alternative energy sources that is renewable and environmentally friendly. Tar is used for various industrial purposes, including combustion fuel and power generation to produce chemicals and can be mixed with diesel oil as fuel [14].

The tar composition varies depending on the nature of the biomass, pyrolysis temperature, heating rate, and environmental pyrolysis conditions. Generally tar consists of 51.2% water-soluble pyrolytic lignin, 25–30% water, 20–25% organic acids, 51% anhydrous sugar, 5–10% nonpolar hydrocarbons, and 10–25% other compounds. Tar has a pH between 2–4 which indicates that tar is acidic.

In this study, the tar obtained from the pyrolysis process was tested for its content using analysis by FTIR and GC-MS. This pyrolysis product tar was not subjected to heat testing and proximate test.

### 3.2.3.1 Functional group analysis

a. Functional group analysis Bio-oil with variation final temperature (375°C, 475°C, dan 575°C) at heating rate 5°C/min

Bio-oil, a product of acacia sawdust pyrolysis, is known to have brownish yellow and clear color. This bio-oil product is analyzed using FTIR to determine which chemical bonds and functional groups are present in this bio-oil. In the analysis using FTIR, it can be seen that the FTIR spectra in figure 9. In the FTIR spectra, it can be seen that the acacia sawdust sample contains functional groups as in Table 7.

| Functional group | Wave number reference (cm\(^{-1}\)) | Wave number research (cm\(^{-1}\)) |
|------------------|-------------------------------------|----------------------------------|
|                  | 5°C/min                             | 10°C/min                         | 15°C/min                         |
| O-H              | 3453.69                             | 3414.15                          | 3418.97                          |
| C-H              | 2960-2850                           | 2922.28                          | 2928.07                          |
| C=C aromatik     | 1584.59                             | 1584.59                          | 1585.55                          |
| C-H aromatik     | 874.76                              | 871.86                           | 872.83                           |

Table 6. FTIR bio-char analysis at the final pyrolysis temperature of 575°C with various heating rates.
Figure 9. Spectra FTIR tar at heating rate 5°C/minute with variation final temperature.

Table 7. The results of the FTIR analysis of tar at the same heating rate as the final temperature variation.

| Functional group | Wave number reference (cm⁻¹) | Wave number research (cm⁻¹) |
|------------------|-----------------------------|-----------------------------|
| O-H              | 3550-3200                    | 3448.87                     | 3448.87                     | 3447.91 |
| C-H              | 2900-2600                    | 2612.69                     | 2622.34                     | 2630.05 |
| C=O              | 1750-1630                    | 1637.64                     | 1713.83 &                   | 1713.83 & |
|                  |                              |                             | 1637.64                     | 1638.60 |
| C-O ether        | 1275-1200                    | 1275                        | 1274.04                     | 1273.07 |
| C-O ether        | 1085-1010                    | 1057.04                     | 1050.29                     | 1050.29 |

From table 7 it can be seen that the bio-oil resulting from pyrolysis of acacia sawdust with the same variations in the pyrolysis temperature and heating rate has O-H bonds derived from cellulose and hemicellulose content. This O-H bond is an O-H alcohol bond known from the wave number range, namely in the range 3550-3200 cm⁻¹ [7]. The O-H functional group contained in this bio-oil is known to be a hydroxyl group which identifies that this bio-oil still contains water. This hydroxyl group will decrease in intensity as the final temperature of the pyrolysis process increases [7]. In figure 9, it can be seen that at low temperatures the spectra of the O-H bond are wider than the spectra at high temperatures. At the wave number 1750-1630 cm⁻¹ there is a C=O bond that comes from hemicellulose. It is known that all the tar from the pyrolysis process of acacia sawdust contain cellulose. At temperatures between 300-500°C, it is known that cellulose and hemicellulose are differentiated.

In the range of wave numbers 1390-1340 cm⁻¹, it is known that there are C-H bonds which are known to be deformations of cellulose and hemicellulose. At low temperatures, it is known that the C-H bonds of hemicellulose are not too wide compared to high temperatures. This can occur because at high temperatures, namely above 400°C, cellulose and hemicellulose can be formed from the pyrolysis process.
At the wave number 1275-1200 cm\(^{-1}\), it is known that there is a C-O bond which is an ether group which is included in the lignin content. In figure 14 it can be seen that the higher the final temperature of pyrolysis, the more visible the stretch in the bond spectra is. This shows that lignin is difficult to degrade at low temperatures. The higher the final temperature of the pyrolysis, the more visible the stretch in the wave number is. In the range of wave numbers 1085-1010 cm\(^{-1}\), it is known that there are C-O bonds that come from cellulose and hemicellulose.

Based on the spectral analysis mentioned above, it can be seen that the higher the pyrolysis temperature is carried out, the more cellulose, hemicellulose, and lignin content is visible.

b. Functional group analysis of Bio-oil with variation heating rate (5\(^{\circ}\)C/min, 10\(^{\circ}\)C/min, 15\(^{\circ}\)C/min) at final temperature 575\(^{\circ}\)C.

In the analysis using FTIR, it can be seen the FTIR spectra in figure 10. In the FTIR spectra, it can be seen that the acacia sawdust sample contains functional groups as in table 11.

![Figure 10. Spectra FTIR tar at final temperature 575\(^{\circ}\)C with variation heating rate.](image)

**Table 8.** Analysis FTIR tar at final temperature 575\(^{\circ}\)C with variation heating rate.

| Functional group | Wave number reference(cm\(^{-1}\)) | Wave number research (cm\(^{-1}\)) |
|------------------|----------------------------------|----------------------------------|
|                  |                                  | 5\(^{\circ}\)C/min | 10\(^{\circ}\)C/min | 15\(^{\circ}\)C/min |
| O-H              | 3550-3200                        | 3347.91     | 3422.83     | 3483.59     |
| C-H              |                                  | 2645.48     | 2620.41     | 2621.37     |
| C=O              | 1750-1630                        | 1713.83 & 1638.60 | 1713.83 & 1637.64 | 1713.83 & 1638.60 |
| C-O eter         | 1275-1200                        | 1273.07     | 1274.04     | 1273.07     |
| C-O              | 1085-1010                        | 1050.29     | 1049.32     | 1017.49     |

From table 8 it can be seen that the bio-oil resulting from pyrolysis of acacia sawdust with the same variation in heating rate and pyrolysis temperature has an O-H bond derived from cellulose and hemicellulose content. This O-H bond is an O-H alcohol bond known from the wave number range, namely in the range 3550-3200 cm\(^{-1}\) [7]. The O-H functional group contained in this bio-oil
is known to be a hydroxyl group which identifies that this bio-oil still contains water. In figure 10, it can be seen that at a high heating rate of 15°C/min, it can be seen that the O-H absorption is wider than the O-H absorption at heating rates of 10°C/min and 5°C/min. It is known that at a fast heating rate the pyrolysis process has not yet occurred completely and has not been maximized. At a heating rate of 5°C/min, it can be seen that the absorption of the O-H group is narrower, which indicates that the hydrolysis group which is classified as water decreases more in the pyrolysis process and indicates that the pyrolysis process occurs optimally.

At the wave number 1750-1630 cm\(^{-1}\) there is a C = C bond that comes from hemicellulose. It is known that all bio-oils from the pyrolysis process of acacia sawdust contain cellulose. In the range of wave numbers 1390-1340 cm\(^{-1}\), it is known that there are C-H bonds which are known to be deformations of cellulose and hemicellulose.

At the wave number 1275-1200 cm\(^{-1}\), it is known that there is a C-O bond which is an ether group which is included in the lignin content. In the range of wave numbers 1085 -1010 cm\(^{-1}\), it is known that there are C-O bonds derived from cellulose and hemicellulose.

Based on the spectra analysis mentioned above, it can be seen that the higher the heating rate, the pyrolysis process will occur faster and make the pyrolysis process not optimal. The pyrolysis process which is carried out at a slow heating rate will maximize the pyrolysis process and the absorption of functional groups of cellulose, hemicellulose and lignin can be seen.

3.2.3.2 Analysis GC-MS

For pyrolysis products in the form of liquid (bio-oil), chemical analysis in the form of gas chromatography - mass spectroscopy (GC-MS) is carried out to determine the content of any chemical compounds contained in the pyrolysis products. The products tested were heating rate of 5°C/min, where this variation had the most yield among the variations in the pyrolysis process carried out. GC-MS results can be seen in figure 11.

From the GC-MS results which can be seen in figure 11, there are 26 peaks of the number of compounds in tar. The seven most dominant chemical compounds include: acetic acid, phenol, CAS (hexane acid), 2-propanone, 2-amino, 1-propanol, propionic acid, 1-hydroxy-2-butane, the seven dominant compounds are components in tar which is the decomposition of cellulose and hemicellulose. It can be seen that the pyrolysis product tar contains the components needed to become tar, as explained by Goyal et al (2006), where the organic components contained in tar, namely the contents of the acid, ester, alcohol, ketone groups., aldehydes, alkenes, furans and other compounds which are characteristic of tar.

In this study it can be seen that the tar produced is acidic, this is because the pyrolysis temperature used is susceptible to 375°C–575°C. In this temperature range, cellulose, hemicellulose, and lignin compounds decompose. Hemicellulose decomposes at 200°C–275°C and cellulose decomposes at 240°C–350°C [15]. This tar has a phenol content of about 40–45%. This is because phenol from tar is
obtained from lignin, where lignin can decompose at temperatures above 300℃ explaining that the formation of phenol compounds in the pyrolysis process is the result of the decomposition of lignin in biomass at temperature range 400℃–500℃. The tar produced has a fairly large phenol content, so that the tar produced from the pyrolysis of this acacia sawdust can be used as a substitute fuel for petroleum.

3.3 Activation energy

Activation energy is defined as the energy that must be met to start a chemical reaction. The activation energy value of a sample indicates the ease with which the sample can react. The calculation of activation energy carried out in this study is based on a reaction kinetics formula using the first order which is often referred to as global kinetics (global kinetic). This study is adapted to the research of Himawanto [3] regarding the determination of the amount of activation energy in global kinetics using a graphical method where the formula used is based on the Arrhenius equation.

The Arrhenius equation is a simple mathematical method and is widely used to obtain exponential factors and activation energies based on TGA experiments which depend on reaction rate constants [16]. Each variation is then plotted on a graph. The graph obtained from the Arrhenius equation is a graph of the relationship between ln(d/dt) and 1/T. The graph is then made linear regression to obtain the equation y = ax + c. The x coefficient or slope of the equation is multiplied by the gas constant (8.314 J/mol.K), so the activation energy value is obtained.

Table 9. The relationship of activation energy with variations in heating rate and final temperature

| Heating rate(℃/min) | Final Temperature 375℃ (kJ/mol) | Final Temperature 475℃ (kJ/mol) | Final Temperature 575℃ (kJ/mol) |
|---------------------|----------------------------------|----------------------------------|----------------------------------|
| 5                   | 14.48                            | 43.57                            | 47.13                            |
| 10                  | 20.36                            | 43.88                            | 47.37                            |
| 15                  | 27.97                            | 46.38                            | 49.56                            |

Table 9 shows the calculated results of the activation energy with variations in heating rate and final temperature. When viewed from the results of the calculation of the activation energy with variations in final temperature (375℃, 475℃ and 575℃) and by varying the heating rate, the results obtained in table 9 show that the higher the temperature and heating rate, the resulting activation energy also increases. Increasing temperature causes the decomposition reaction of biomass to also increase. Increased decomposition reactions will require a large amount of energy to break the bonds contained in the biomass.

The lignocellulose content contained in biomass will be decomposed through several stages, where an increase in the rate of reaction that occurs in the pyrolysis process results in the biomass being decomposed slowly. The lignocellulose content contained in the sample of this study will differentiate the heating rate of a sample when it is treated thermally. If a material has a dominant lignin content, it requires a higher temperature to reach the devolatilization point. Due to the high temperature needed to break the bonds in lignin so that the energy required is also greater. In addition, the higher the heating rate, the acceleration of heat energy provided to break down the larger biomass compounds causes the decomposition rate of acacia sawdust to be faster and bigger.

3.4 Mass degradation

According to [6], the combustion process of solid materials is divided into three stages, namely the drying stage, the devolatilization stage, and the combustion stage. The drying stage is the stage where
the sample will lose its moisture content, the devolatilization stage is the stage where the biomass conversion process chemically occurs. The biomass devolatilization stage generally occurs at temperatures around 200–500°C which is marked by a sharp decrease in the TG graph due to the decomposition of cellulose, hemicellulose and lignin [16]. Then the combustion stage on the TG graph shows a slight decrease, even closer to flat or straight because what happens is only the remaining lignin decomposition process which is getting slower. In this study, the thermal degradation analysis is divided into two variations, namely variations in heating rate and variations in final temperature respectively.

Pyrolysis in this study will be influenced by several factors. These factors include the final temperature and heating rate. The final temperatures used in this study were 375°C, 475°C and 575°C. The decomposition process of acacia sawdust with various heating rates at the final temperature of 375°C, 475°C and 575°C is depicted in figures 12, 13 and 14, respectively.

Figures 12, 13 and 14 show the influence caused by the heating rate in the biomass pyrolysis process. It can be seen from the acacia sawdust decomposition curve that the greater the heating rate, the more the graph will shift to the left, which means that the decomposition reaction occurs faster than the lower heating rate. The final temperature variations carried out in this study did not show any significant effect. This can happen because at the final temperature variation, pyrolysis takes place at the same rate as the example in figure 11 which is carried out at a rate of 5°C/min. So that the energy received by the biomass every one minute is the same.

![Figure 12. TG curve of acacia sawdust with variation of heating rate at final temperature 375°C.](image)

![Figure 13. TG curve of acacia sawdust with variation of heating rate at final temperature 475°C.](image)
Figure 14. TG curve of acacia sawdust with variation of heating rate at final temperature 575°C.

Figure 15. TG curve of acacia sawdust with variation of final temperature at heating rate 5°C/min.

Figure 15 shows the decomposition curve of acacia sawdust with variations in the final pyrolysis temperature. In general, the variation in heating rate and final temperature is intended to determine which variation is best done for the pyrolysis process of acacia wood waste biomass. Based on the data table above, it can be seen that the best temperature for the pyrolysis process of acacia wood waste is at a temperature of 575°C and a heating rate of 5°C/min, this is indicated by a significant reduction in mass that occurs in the devolatilation process and the combustion process in the range temperature 500°C to 575.

4. Conclusions
The conclusions of this study are as follows. The final temperature of pyrolysis affects the amount of pyrolysis products produced. The mass reduction at a temperature of 575°C at a heating rate of 5°C/min reached an average of 76.34%. The calorific value produced by pyrolysis product with a final temperature of 575°C reaches 6816.36 cal/g. At the final temperature of 575°C, the highest activation value was 49.56 kJ / mol. The characters of char produced at high temperature are known to contain the functional groups O-H, C-H, C = C aromatic, and C-H aromatic. Pyrolysis heating rate affects the amount of pyrolysis products produced. The mass reduction at a low heating rate of 5°C/min at a temperature of 575°C reaches an average of 76.34%. The calorific value produced by pyrolysis products with a heating rate of 5°C/min reaches 6816.36 cal/g. At a heating rate of 15°C, the maximum activation value is 49.56 kJ/mol. The characters of char produced at high temperature are known to contain the functional groups O-H, C-H, C = C aromatic, and C-H aromatic.
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