Functional Group Structure of Bamboo and Pine Wood Biochar
Due to Differences in Pyrolysis Temperature

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Abstract – The quality of biochar produced through the pyrolysis process depends on the combustion temperature, duration of combustion, and the raw materials used. Biochar is a carbon-rich product resulting from the thermal decomposition of organic matter. Biochar from bamboo and pinewood was produced at 400°C and 800°C using a closed chamber where the temperature could be set. Biochar is made through carbonization with pyrolysis. This study aimed to find out the functional group characteristics of two types of raw materials, bamboo and pine wood. This research was conducted at the Environmental Soil Physics Laboratory, Universitas Syiah Kuala. Two types of feedstocks, bamboo, and pinewood, were used as sample experiments. The feedstocks were burned inside a closed chamber with no oxygen present (Thermo scientific thermolyne F4820-33). The temperature was at 400°C and 800°C, and a burning time of four hours. Fourier Transform Infra-Red (FTIR) was used to characterize the functional groups of biochar tested. Our research showed biochar from pinewood burned at a temperature of 400°C gave the characteristics of the functional groups OH, CH, and C=O with strong intensity. It indicates that there was decomposition of organic matter into organic compounds taking place.

Keywords: Biochar, Functional Groups, FTIR.

Introduction
Biochar is a solid material derived from the thermochemical conversion of biomass in an environment with no or limited oxygen (International Biochar Initiative, 2012), resulting in the volatile substances contained in the biomass being released. Biomass is a renewable energy source that is abundant and easily available. As a carbon source, biomass (derivatives of living organic matter) can be converted by pyrolysis into gas, liquid, and solid forms (Van der Stelt MJC, et al., 2011). Lignocellulosic and non-lignocellulosic materials are classified as biomass. Lignocellulosic groups such as timber, and plant/forest residues, while non-lignocellulose such as animal waste and organic parts of the solid waste city (Demirbas, 2001). The content of lignocellulose or non-lignocellulose will require different pyrolysis temperatures. High lignin content results in high biochar yield (Demirbas, 2004). Therefore, information on the pyrolysis temperature for each feedstock is imperative to investigate. In general, feedstocks containing cellulose require a temperature of 240-350°C, while hemicellulose at a temperature of 200-260°C for being decomposed, and lignin begins to decompose at a temperature of 500°C (Babu, BV, 2008; Goyal et al., 2008). Biochar is rich in carbon and high in micropores (Darusan et al., 2021). Pyrolysis at high temperatures could produce various characteristics of biochar, such as an enormous specific surface area so that carbon sequestration takes place in the soil. It can absorb carbon and has a high adsorption capacity (Chan et al., 2009). In addition, biochar is able to facilitate the supply of nutrients for plants through its ability to exchange...
cations as a habitat for microorganisms and fungi and has strong aggregate stability (resistant to decomposition). Nessa et al. (2021) found that burning feedstocks at the temperature of 600 – 700 °C influenced cumulative nitrification and N mineralization in soil. He also pointed out the importance of biochar pyrolysis temperatures for their use as a soil conditioner to increase soil N retention.

Biomass is easy to obtain and abundant. Thus the production of biochar is relatively cheap and easy to implement. The effectiveness and quality of biochar depend on the characteristics and morphology of the biochar produced by combustion. Raw materials, pyrolysis temperature, and residence time affect the effectiveness of biochar. A higher combustion temperature of 400°C changes the nature of the biochar from hydrophobic to hydrophilic (Jien, 2019) so that the pH of the biochar increases to around 9.5. (Johnston, 2017) stated that the dominant biochar structure consists of aromatic carbon with varying condensation due to increasing pyrolysis temperature. Pyrolysis combustion is different from general combustion, which requires air as the main element. In pyrolysis combustion, the required air is limited because the presence of air will result in a large amount of ash, resulting in a small amount of biochar. During the pyrolysis reaction, heat is required for the carbonization process. Initially, latent heat is required to dry and remove water from the biomass. Then, a sensitive heat is necessary to raise the temperature to the desired pyrolysis treatment temperature at which decomposition and devolatilization occur. The conditions of the pyrolysis process determine the nature of the resulting product. When biomass undergoes thermolysis, the original polymer molecules are broken down and transformed to produce three products, namely syngas (CO, H₂, CH₄), bio-oil (acetic acid, phenolic compounds, alcohol, H₂O, etc.), and solid (biochar). In general, pyrolysis products consist of three types, namely: (1) solid products: in the form of solid residues rich in carbon content (char), (2) Liquid products: in the form of (tar, hydrocarbons, and water), (3) Gas products: in the form of gases (CO, H₂O, CO₂, C₂H₂, C₂H₄, C₆H₆), and others (Van der Stelt MJC et al., 2011). The pyrolysis temperature determines the decomposition of organic material. It causes some changes in the biomass’s chemical structure (functional groups), which can indicate the functional properties of the biochar produced.

Biochar has an organic carbon composition that is mostly bound in six rings of C atoms, and the aromatic structure makes biochar stable in the soil. Various previous research has shown that applying biochar to soil is a practical method for long-term maintenance of organic carbon and soil fertility (Lehmann, 2007). According to (Chen X et al., 2011), biochar has a relatively structured carbon matrix with a high level of porosity and a specific surface area. The characteristics and morphology of biochar play an important role in its function, including improving soil quality. The characterization aims to determine the basic properties of biochar, including functional group analysis and its proximate.

One method to detect these changes is using Fourier-transform infrared (FTIR) analysis. FTIR is an instrument that uses the principle of spectroscopy. The spectroscopy used is infrared spectroscopy equipped with Fourier transform for the detection and analysis of the spectrum results. Infrared spectroscopy is useful for the identification of organic compounds because of its very complex spectrum consisting of many peaks (Prayogo, 2012). The use of FTIR is better known as a simpler and faster approach to observing changes in functional groups of organic components. The process of making biochar through the pyrolysis method causes the decomposition of organic material into organic compounds that can be detected using FTIR. The vibration spectrum on FTIR can provide predictions about the structure and chemical bonds between biochar and soil when applied. The main spectral region of biochar can absorb infrared radiation in the 4000-2700 cm⁻¹ region, which includes the OH and CH groups of biochar and bound water. Spectral region 1800-1000 cm⁻¹ from carboxylic, aliphatic, and aromatic acids, while carbonates and Si-O groups from ash and clay (inorganic) content sometimes appear in biochar with spectral bands <1000 cm⁻¹. The spectral features of biochar depend on the pyrolysis temperature, the type of raw material used, the heating rate, and the content of inorganic components. Among these variables, pyrolysis temperature is the most important factor in determining the quality of the biochar produced (Singh et al., 2017) (Spokas et al., 2012). The functional groups contained in biochar are in Table 1(Singh et al., 2017).

Several studies have been developed for the production of various biomass biochar. In this study, the characteristics of biochar produced from bamboo (non-woody) and pinewood (woody) were observed using variations in pyrolysis temperatures, namely 400°C and 800°C at 4 hours duration.
### Table 1. Biochar Functional Groups

| Band Range (cm⁻¹) | Functional group | Band Description               |
|-------------------|------------------|--------------------------------|
| 3670-3630         | OH               | Non-hydrogen bond              |
| 3600-3200         | OH               | H₂O adsorbed, hydrogen bond    |
| 1390-1310         | OH               | Phenol                         |
| 3080-3020         | CH               | Aromatic                       |
| 2990-2840         | CH               | Aliphatic                      |
| 1740-1650         | C=O              | Esters, Ketones, Carboxylic Acids |
| 1610-1580         | C=C              | Aromatic                       |
| 1590-1520         | COO              | Carboxylic acids, amides       |

Source: Singh, 2017

### Table 2. Biochar Treatment Arrangement

| No. | Type of Biochar | Biochar Temperature (°C) |
|-----|----------------|--------------------------|
| 1   | Bamboo         | 400                      |
| 2   | Bamboo         | 800                      |
| 3   | Pine Wood      | 400                      |
| 4   | Pine Wood      | 800                      |

### Materials and Methods

#### Time and site

This research was conducted at the Environmental Soil Physics Laboratory, Universitas Syiah Kuala, Banda Aceh; FTIR analysis was carried out at the Instrument Laboratory of the Faculty of Chemical and Environmental Engineering, Universitas Syiah Kuala. This research was carried out from March to May 2021.

#### Materials and Tools

The materials used in this study consisted of bamboo (*Bambusa blumeana*), pinewood (*Casuarina equisetifolia*), H₂O, and other related materials. The tools used consisted of a biochar grinder, chamber muffle furnace (Thermo scientific thermolyne F4820-33) with temperature setting, 100 mL crucible, conductivity meter, pH meter, oven, shaker, mortar and pestle, sieve (149 µm size), camera, Fourier Transform Infra-Red (FTIR), stationery and other laboratory equipment. The arrangement of treatments is presented in Table 2.

#### Biochar manufacturing process

The process of making/burning biochar took 4 hours for each treatment, and the combustion temperature of biochar consists of temperature 400°C and 800°C. We assumed that the temperature of 800 °C may significantly change the characteristics of tested samples, especially feedstocks containing cellulose. Combustion of biochar using a combustion chamber muffle furnace (Thermo scientific thermolyne F4820-33).

#### Biochar sampling and storage techniques

The sampling technique is carried out on each biochar that has gone through the process of homogenizing and filtering. Biochar samples were taken randomly from homogeny samples and then composited. Storage of biochar was done by putting the biochar in an airtight container and stored in a room that is not exposed to direct sunlight.

#### Biochar parameter analysis

The functional group of biochar as a function of wavelength is analyzed with Fourier Transform Infra-Red (FTIR) to convert the identification of organic compounds/elements in woody (pine) and non-woody (original bamboo) biochar by the DRS-8000 method. A Prestige-21 IR spectrometer (Shimadzu Corp.) with a resolution of four was used. The solid sample was mixed with KBr powder (5-10% sample in KBr powder) and then placed on a sample pan for analysis.

### Results
Pyrolysis of bamboo (*Bambusa blumeana*) at temperatures of 400°C and 800°C

Bamboo is a potential and abundant source of raw materials. Bamboo belongs to the family of grasses (*Gramineae*) in the form of clumps (sympodial). Many types of bamboo are widespread in Indonesia. According to Nasendi (1995), the use of bamboo is possible to be developed for biochar production because bamboo is a fast-growing plant that can be maintained and renewed so that it is more environmentally friendly. Bamboo is one of the lignocellulosic materials that produce cellulose per 2-6 larger than pine. Bamboo biochar is a micro-porous material that has excellent adsorption and a large specific surface area. The composition of chemical compounds in bamboo stems consists of cellulose 42.4-53.6%, lignin 19.8%-26.6%, and hemicellulose 1.2%-4-3.77% (Widya, 2006).

The type of bamboo used in this study is ori bamboo (*Bambusa blumeana*) which has thorns, especially on the bulkheads between branches and twigs. The original bamboo was pyrolyzed at 400°C and 800°C for 4 hours, following the results of the characteristics of the functional group of ori bamboo biochar with the difference in pyrolysis combustion temperature (Table 3).

The results of FTIR analysis on bamboo biochar with different temperatures of 400°C and 800°C are given in Figure 1 and Table 3. The table shows an increase in the intensity of the OH functional group originating from the decomposition of cellulose at peak 3338.78 – 3658.96 cm⁻¹, while the functional group CH (aromatic ring) decreased from peak 2885.52 – 2881.65 cm⁻¹. It is presumably due to the contribution of biochar characteristics where there is an increase in the aromatic structure of biochar as the pyrolysis temperature increases (Troeh, 2005). According to (Prasetyo, 2021), the effect of pyrolysis temperature >530°C can eliminate functional groups such as HO, CO, and C=C along with the increasing presence of aromatic structures. OH and C=O are active organic compounds in biochar.

| Peak (cm⁻¹) | Bond | Type of Compound     | Frequency Range (cm⁻¹) |
|-------------|------|----------------------|------------------------|
| 3338.78     | OH   | Alcohols             | 3200 - 3670            |
| 2885.51     | CH   | Aromatic Rings       | 2840 – 3080            |
| 1589.34     | C=O  | Carboxylic Acid      | 1580 – 1610            |

Table 3. Peak position and chemical bonding of ori bamboo biochar at temperatures of 400°C and 800°C

![FTIR spectrum of original bamboo biochar at temperatures of 400°C and 800°C](image)
Pyrolysis of Pine wood (Casuarina equisetifolia) at 400°C and 800°C

Pine is a group of plants in the genus Casuarina. Pine is another name for the Casuaricaceae plant. This group of plants consists of 70 species and is primarily found in the southern hemisphere, especially in tropical countries such as Indonesia, Malaysia, the Pacific Islands, and Australia. The evergreen tree produces brown, oval-shaped fruit. Pinewood is pink to reddish in color. Pinewood has high quality for fuel (charcoal). The chemical composition of pine consists of 44% cellulose, 26% lignin, and 29% hemicellulose (Artz, 2008). Based on its chemical composition, pine is classified as biomass that can be used as biochar. The results of characteristic analysis for pinewood biochar functional groups using FTIR with different pyrolysis combustion temperatures are listed in Table 4.

FTIR results on pine wood biochar with a temperature difference of 400°C and 800°C can be seen in Figure 2 and Table 4, which show the stretching of each functional group, including the OH functional group from peak 3624.25 – 3633.89 cm⁻¹, the CH functional group from peak 2881.65 – 3030.17 cm⁻¹, and the functional group C=O from peak 1680.00 – 1681.93 cm⁻¹. The functional group represents OH, CO, CH C=O, C=C (Johnston, 2017). While in pinewood biochar, there are no CO and C=O compounds. The functional groups in biochar containing oxygen are affected by the pyrolysis temperature, which also affects the adsorption properties of the biochar.

Discussion

The pyrolysis of bamboo (Bambusa blumeana), specifically pyrolysis at 400°C showed a sharp OH peak at the absorption 3338.78 cm⁻¹ which comes from the decomposition of cellulose into smaller monomers, namely glucose. Cellulose is a polymer formed from D-glucose monomers through (1→4) glycosidic bonds. Chain lengths vary from hundreds to thousands of glucose units. When cellulose is decomposed, it will split into smaller monomers, namely glucose which is detected as aliphatic OH or H₂O which is adsorbed through free air during product storage. The pyrolysis stage that occurs is at a temperature of 100°C-120°C there has been evaporation of water, a maximum at a temperature of 220°C the bound water content has evaporated from the biomass until
the temperature increase of 270°C began to occur evaporation of cellulose and obtained a distillate containing organic acids, glucose, alcohol, and their derivatives.

At the pyrolysis temperature of 800°C, the OH absorption band was detected to be very wide and flat (without a peak). The aliphatic OH group (glucose) has evaporated at a temperature > 220°C. This is confirmed by the OH bond spectrum that appears at 3658.96 cm⁻¹ absorption which shows aromatic OH bonds, which can come from the decomposition of lignin and hemicellulose. This indicates that there is strong evidence that biochar is an organic material that is resistant to extreme temperature rises. Identification of the presence of OH groups in biochar is very important, because this group can show the ability to bind water from the resulting biochar. At the two different pyrolysis temperatures, showing a large adsorption ability (Chandel et al., 2007).

On the pyrolysis temperatures of 400°C and 800°C, the aromatic group CH shows a strong and sharp spectrum. Aliphatic CH groups appear at absorptions of 2885.51 and 2881.65 cm⁻¹, indicating a very strong strain originating from organic acids originating from the decomposition of organic materials into aromatic compounds derived from lignin or hemicellulose because at temperatures > 400°C, organic materials it is decomposed. Use of pyrolysis > 400°C on bamboo biomass. Another aromatic bond is C=O which only appears at 800°C pyrolysis at an absorption of 1685.79 cm⁻¹, in contrast to the C=C aromatic bond which only appears at 400°C pyrolysis at an absorption of 1589.34 cm⁻¹. Biochar produced by or bamboo biomass at a temperature of 800°C showed a higher number and type of aromatic groups than biochar with a pyrolysis temperature of 400°C. The presence of high aromatic compounds from weak to strong absorption indicates the resistance of biochar to degradation when applied to soil. This is due to the characteristics of aromatic compounds that have very low solubility in water, which makes biochar resistant to degradation but can bind water through its carbon content.

The pyrolysis of pine wood (Casuarina equisetifolia), particularly at a pyrolysis temperature of 400°C, the OH band at an absorption width of 3624.25 cm⁻¹ indicates the decomposition of organic matter into aromatic compounds. Similar to pyrolysis at a temperature of 800°C, thermal decomposition of cellulose occurs as shown in the absorption band 3633.89 cm⁻¹ to 3500 cm⁻¹. These two OH absorption bands indicate that this biochar is neutral because of the wide OH absorption band formed. However, the OH absorption band at a pyrolysis temperature of 400°C showed a wider and sharper absorption than biochar at a pyrolysis temperature of 800°C. The wide OH absorption band comes from the decomposition of cellulose into glucose monomers which are detected as aliphatic OH (alcohol) in the range of 3000 cm⁻¹ to 3200 cm⁻¹.

The CH spectrum at both 400°C and 800°C pyrolysis temperatures showed adjacent absorption bands. This indicates the decomposition of organic material into aromatic compounds derived from lignin and hemicellulose. Evaporation of water bound to the biomass is maximal at a temperature of 220°C, while at a higher temperature, namely at a temperature of 220°C-315°C, hemicellulose decomposition occurs, and at a temperature of 315°C-400°C cellulose decomposition occurs and at temperatures above 400°C lignin decomposition occurs. The aromatic spectrum of C=O is also in the adjacent absorption range, namely 1680 cm⁻¹ and 1681.93 cm⁻¹. The sharp peak of C=O in pyrolysis is influenced by the sharp peak of C=C at <1500 cm⁻¹ absorption, while at 800°C pyrolysis, the aromatic group C=O shows a weak peak. This indicates that at the pyrolysis temperature > 400°C, there has been an over-decomposition of the aromatic compounds which causes weak functional groups that FTIR can detect. However, pine wood biomass sources provide more decomposition of organic compounds, namely OH, CH and C=O due to the high content of cellulose, lignin and hemicellulose (Downie et al., 2009).

When compared to bamboo, pinewood has a greater chance of being used as a source of biochar biomass. At a lower pyrolysis temperature, which is 400°C and a pyrolysis time of 4 hours, a strong organic compound intensity has been obtained. This indicates a large fixed carbon ratio in the biochar produced.

**Conclusion**

Biochar derived from bamboo and pinewood with different pyrolysis temperature differences at 400°C and 800°C showed different biochar qualities based on functional group analysis. Biochar from pine wood which is pyrolyzed at a temperature of 400°C gives the characteristic aromatic functional groups OH, CH, C=O. The high cellulose composition in a pinewood has a significant effect on the amount of organic compounds that can be decomposed into aromatic compounds.
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