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Effects of Torrefaction Process on Chemical Properties of Small Diameter *Acacia mangium* Wood

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Abstract. Torrefaction refers to a thermal process that involves the processing of biomass in a torrefied to produce a "charred" product that can be utilised as a fuel or as a soil amendment. People need energy sources to meet their basic needs and live the kind of life they want. *Acacia mangium* was selected in order to produce biochar and determine the lignocellulosic affected by the holding temperature and residence time. The chemical properties of torrefied *Acacia mangium* biochar were investigated at different holding temperatures and residence times. Torrefaction were carried out at several process temperatures, ranging from 200 to 300°C, with residence time ranging from 30 to 90 minutes. According to the findings, the effects of holding temperature and residence time on the chemical properties of torrefied *Acacia mangium* biochar was carried out. The results show that the chemical properties decreased with an increase in both the holding temperature and residence time except for the lignin percentage content. It shows that as the holding temperature and residence time increased, the lignin content increased. The results shows that the chemical properties are decreased, except for the lignin content, which is not affected by the factors. The chemical bond in lignin content is hard for breaking down. Hence, torrefaction is accountable for the decrease of chemical properties and the breaking of chemical bonds in chemical properties.

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1 Introduction

Biomass sources is one of the alternative and renewable sources that should been considered to provide heat and power to the domestic and industrial sectors especially its woody materials and it coincides to the advantages of woody materials related for high energy content, and relatively high fixed carbon content, plus easy handling [1]. There are about 9% of the total energy consumption had been obtained from woody material as well as 65% contribution from total renewable energy produced previously [2].

Advantage of woody materials as high energy content, as well as the chemical properties make woody materials as an option and attraction as renewable source for bioenergy production [3]. Therefore, torrefaction is one of the innovative methods that may be used on those woody materials to produce biochar that can enhance the raw biomass sources [4].

A small diameter of *Acacia mangium* was chosen as the material for the torrefaction process for the purpose of this investigation, through the differences caused by the process at varying holding temperatures and residence time. This species is a fast growing tree species and native to Australia, Indonesia, including Papua New Guinea. Nowdays, this species are widely planting in Malaysia as one of the forest plantation species for various forestry wood based product. However, there are a lot of this species that grow haphazardly as wild and cause disturbance to the original species

Acacia mangium contains high lignocellulose content, which makes it a potential feedstock for energy recovery through various biomass conversion technologies such as combustion, gasification, or pyrolysis [5]. However, the outlined technologies are prone to problems such as low carbon conversion efficiencies, low gas yield, and tar formation [6].

In this study, chemical properties were studied based on different holding temperature and residence time which is among the main variables of the torrefaction process. There are three major components to biomass: cellulose, holocellulose, and lignin. Depending on the type of biomass, the cellulose, hemicellulose, and lignin concentration can range from 40 to 60%, 15 to 30%, and 10 to 25%, respectively [7]. Biomass feedstock parameters and product quality would be greatly influenced by the attributes of the three biomass components. As a result, considerable research into the torrefaction of cellulose, holocellulose, and lignin should be undertaken.

2 Material & Method

2.1 Material

Acacia mangium samples with small diameters between 5 to 10cm were randomly selected around Jeli, Kelantan in good condition which is straight bole and free defect for this study. A furnace, a shaker water bath, and a Soxhlet extractor are used to prepare the extraction from torrefied *Acacia mangium*. Preparation of a non-torrefied sample *Acacia mangium* is required.

2.2 Method

These experimental methods describe the torrefaction process of *Acacia mangium* and are followed by extraction of chemical properties including extractive, holocellulose, cellulose, and lignin content.

2.2.1 Torrefaction process

The torrefaction process started with the process of chipping and grinding of the wood sample *Acacia mangium*. Five samples were collected, one of them was non-torrefied and the rest was torrefied *Acacia mangium*. By using an electrical furnace (muffle furnace of WiseTherm), *Acacia mangium* were undergoing a torrefaction process by holding temperatures at 200 and 300°C with 30 and 90 minutes of residence times in the absence of oxygen (O2) under a low heating rate of about 10°C/min.

2.2.2 Extraction process

The extraction method was used on a total of five (5) biomass samples of *Acacia mangium*, including a raw material sample of *Acacia mangium*, two (2) samples from torrefied *Acacia mangium* biochar at holding temperature of 200°C for residence time of 30 and 90 minutes, and two (2) samples from torrefied Acacia mangium biochar at holding temperature of 300°C for residence time of 30 and 90 minutes.

Extractive's extractions were done first as it is necessary to extract the desired chemical components from the substance for further characterization. The percentage of the extractive is calculated by Equation (1).

$$\text{Extractive content (\%)} = (\text{Weight of Extractive (g)})/(\text{Weight of oven dried samples (g)}) \times 100\% \quad (1)$$

Holocellulose had been determined by following the Wise method which has been modified [8]. For the determination of holocellulose, sodium chlorite ($NaClO_2$), acetone (C_3H_6O), acetic acid (CH_3COOH) and distilled water were used. The percentage of holocellulose is calculated by Equation (2).

$$\text{Holocellulose content (\%)} = (\text{Weight of Holocellulose (g)})/(\text{Weight of extractive free powder (g)}) \times 100\% \quad (2)$$

The cellulose is the leftover that does not dissolve in 17.5% of natrium hydroxide (NaOH) when the reaction is done under certain circumstances. For the determination of cellulose, 17.5% and 8.3% of NaOH were used. The percentage of cellulose is calculated by Equation (3).

$$\text{Cellulose content (\%)} = (\text{Weight of Cellulose (g)})/(\text{Oven dried holocellulose (g)}) \times 100\% \quad (3)$$

According to Klason method [8], sulphuric acid (H_2SO_4) is used to determine lignin content at first, which is as an amorphous and aromatic substance that contains methoxyl phenolic, hydroxyl and other types of elements according to TAPPI 244 cm-11 (2011) [9]. For the determination of lignin, H_2SO_4, raw material sample and torrefied biochar samples of *Acacia mangium* and distilled water were used. The percentage of cellulose is calculated by Equation (4).

$$\text{Lignin content (\%)} = (\text{Weight of Lignin (g)})/(\text{Weight of samples (g)}) \times 100\% \quad (4)$$

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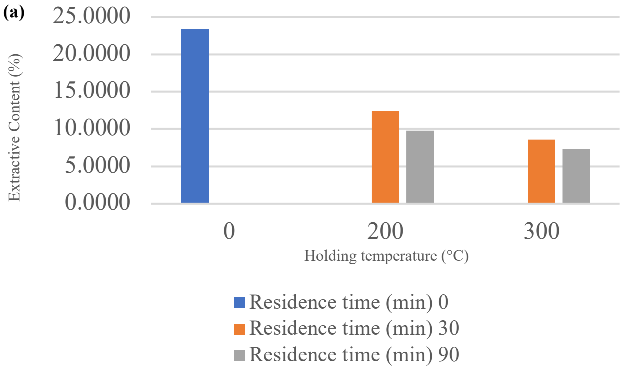
3 Results & Discussion

3.1 Extractive content

Figures 1(a) and (b) show how the extractive content goes down as holding temperature and residence time going up. The raw *Acacia mangium* has an extractive content of less than 25%, while the torrefied biomass has an extractive content of 2-15%. Figure 1(a) shows that the extractive content at 300°C for 90 minutes shows the biggest drop (7.3108%) compared to the extractive content of raw *Acacia mangium* (23.3080%). As the figures show, there is also a significant drop at other holding temperatures and residence times. After the sample has been dried and put through the torrefaction process, it needs to go through the Soxhlet extraction process with the ratio of 2:1 (ethanol:toluene) to get rid of any lignin or polyphenol compounds that might be in the free extractive.

Figure 1(a) depicts the decrease from 200 to 300°C, indicating that the extractive content produced by the extraction process is greater at 200°C than at 300°C. As shown in Figure 1(b) for 30 and 90 minutes, the extractive content decreases gradually as the holding temperature rises. It has been discovered that the extractive content of biomass decreases as holding temperature and residence time increase. The total extractive content of biomass samples torrefied at high holding temperature and residence time was the lowest. Extractives consisting of a variety of volatile substances, such as terpenes, resins, fats, waxes, tannins, lignans, and carbohydrates, extracted from biomass [5]. They impart colour, odour, and flavour to biomass. Extractives can safeguard biomass against microbial and insect attack. Moreover, extractives provide biological activity in biomass with energy.

(a)



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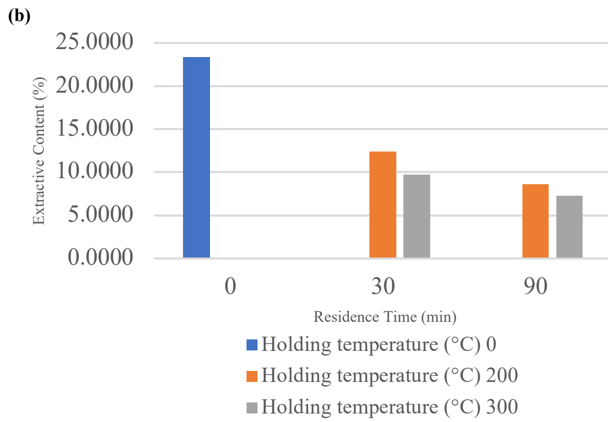
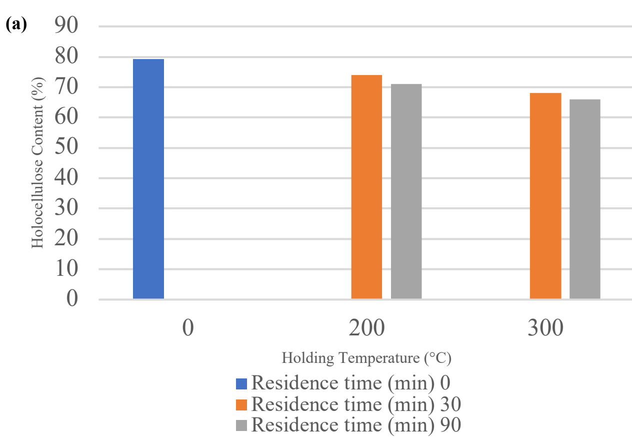


Fig. 1. (a) Effect of holding temperature on extractive content of raw and torrefied *Acacia mangium* biochar; (b)Effect of residence time on extractive content of raw and torrefied *Acacia mangium* biochar

3.2 Holocellulose content

Figure 2(a) shows that the raw *Acacia mangium* has 79.25% holocellulose, which drops to 66.00% when heated to 300°C and left for 90 minutes in the torrefaction process. Chemically, holocellulose is a mixture of cellulose and hemicellulose in *Acacia mangium*. It is the remaining fibre residue after extractives, lignin, and ash-forming elements have been removed. Holocellulose has 75–80% of the chemical content of all *Acacia mangium* compositions. In this study, the highest amount of holocellulose was found in raw *Acacia mangium*, as shown in Figures 2(a) and (b). After torrefaction, the amount of fixed carbon in holocellulose went up, while the amounts of hydrogen, oxygen, and volatile carbon went down. Also, water and light volatiles were taken away from the holocellulose, but a lot more carbon was kept. During torrefaction, the ratio of H/C to O/C kept going down [10].

The sample at 300°C, 90 minutes has the least amount of holocellulose at 66.00%. Holocellulose decrease because hemicellulose breaks down and the amount of cellulose in raw and torrefied samples goes up when the temperature increased. The holocellulose content depends a lot on the temperature and time. As seen in Figures 2(a) and (b), the amount of holocellulose decreases based on the holding temperature and residence time increased.



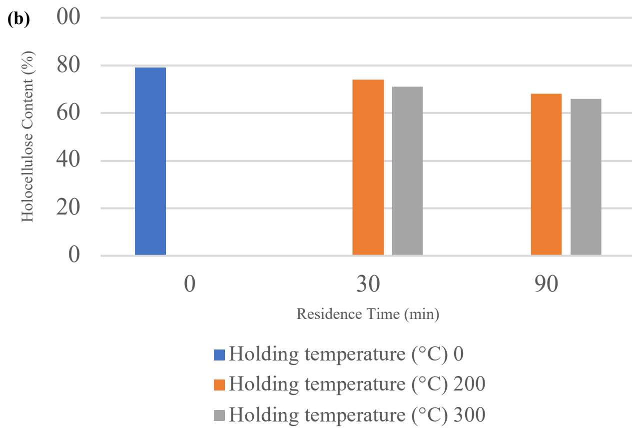
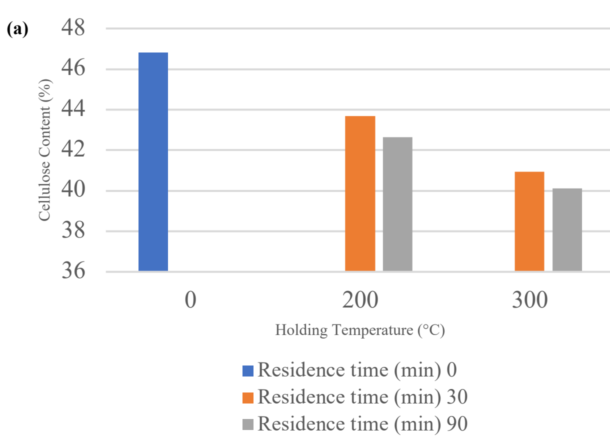


Fig. 2. (a) Effect of holding temperature on holocellulose content of raw and torrefied *Acacia mangium* biochar; (b) Effect of residence time on holocellulose content of raw and torrefied *Acacia mangium* biochar

3.3 Cellulose content

Figures 3(a) and (b) show holding temperature and residence time affect the amount of cellulose in raw and torrefied *Acacia mangium* biochar. Figure 3(a) shows that there is a drop in the cellulose content of raw and torrefied *Acacia mangium* biochar at different holding temperatures and residence times. The decrease in cellulose content can be explained by the fact that cellulose breaks down and loses water at temperatures between 200 and 300°C, forming anhydrous cellulose and levoglucosan in the process.

As seen in Figures 3(a) and (b), the decrease in the percentage of cellulose is affected by the holding temperature and residence time. During the torrefaction process, hydroxyl, carbonyl, methoxyl, and phenolic compounds are made when heat is used to change them [11]. So, biomass acts because these compounds usually form when torrefaction happens at high temperatures and time. Torrefaction could make cellulose and hemicellulose have less oxygen and a lower O/C ratio [12]. So, the weight loss of cellulose during torrefaction could be predicted by adding the weight losses of the different parts in a linear way. As the holding temperature increased, the amounts of H/C and O/C in hemicellulose gradually decreased.



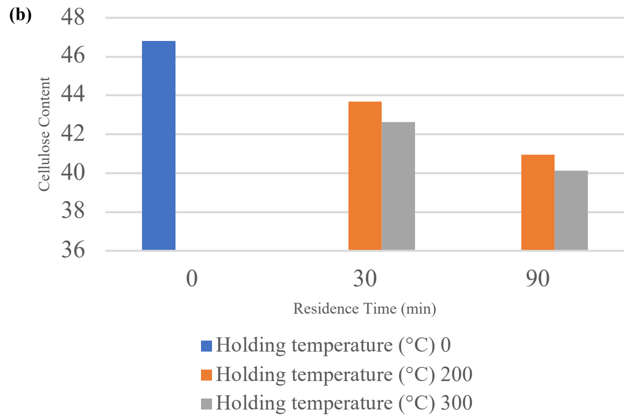


Fig. 3. (a) Effect of holding temperature on cellulose content of raw and torrefied *Acacia mangium* biochar; (b) Effect of residence time on cellulose content of raw and torrefied *Acacia mangium* biochar

3.4 Lignin content

Based on Figures 4(a) and (b), raw *Acacia mangium* has the highest lignin content at 21.98%, whereas the sample of 300°C, 90 minutes has the lowest lignin content at 13.64%. The degradation of lignin began at 200°C based on the effect of increasing holding temperature and residence duration as shown in Figures 4(a) and (b), which exhibit a decreasing trend. At 300°C for 90 minutes, the percentage trend of lignin breakdown is readily visible in comparison to other minutes. Lignin is a polymer created by randomly joining three phenylpropane units (guaiacol, eugenol, and p-hydroxybenzyl) with C–O–C ether linkages (-O-4, -O-4, and -O-4) and C–C bonds (5-5, -1, and -5). As shown in Figures 4(a) and (b), the drop in lignin concentration within 90 minutes is not excessive [13]. Decisively, lignin is hard to break down and depolymerize because it has a complicated structure.

Lignin is the most challenging to thermally degrade because it decomposes across a higher temperature range than cellulose or hemicellulose. Depending on the type of wood, lignin is varying. Lignin is known as a binding agent because it cements the cell components of biomass together. The high lignin content of *Acacia mangium* is the primary cause for its alkaline treatment. With this pretreatment, lignin will be eliminated, and its composition will be diminished. During torrefaction, the holding temperature (200 and 225°C) can produce polycondensation and de-methoxylation of the aromatic units of lignin, and the removal of oxygen increased the amount of C-C and C-H bonds in lignin while decreasing the amount of C-O and O-H bonds.

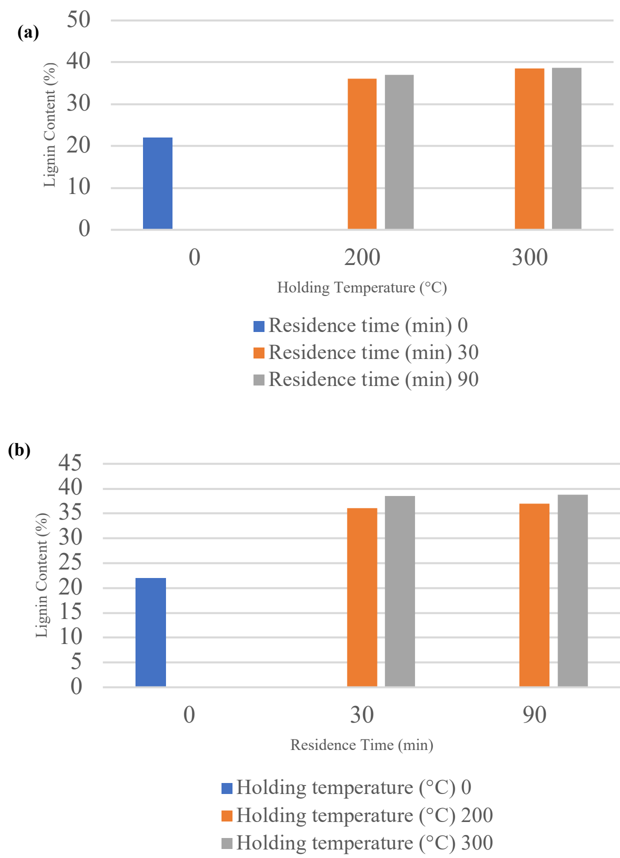


Fig. 4. (a) Effect of holding temperature on lignin content of raw and torrefied *Acacia mangium* biochar; (b) Effect of residence time on lignin content of raw and torrefied *Acacia mangium* biochar

4 Conclusion

As conclusion, the holding temperature and residence time of the torrefaction process could influence the chemical properties of *Acacia mangium*. The yield percentage of torrefied chemical properties decreases as holding temperature and residence time were increased. The oxidising environment also reduces the chemical properties of torrefied samples. When the torrefaction temperature is increased, the compact structure of raw *Acacia mangium* becomes looser and fractures into smaller particles with more cavities. In addition, the results demonstrated that the chemical bond between raw and torrefied *Acacia mangium* biochar was decomposed as holding temperature and residence time increased. Oxygen content and hydrogen content decreased as holding temperature and residence time increased in torrefied *Acacia mangium* biochar.

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