JBAT 7(1) (2018) 12 – 17

p-ISSN 2303 0623
e-ISSN 2407 2370

Jurnal Bahan Alam Terbarukan

Terakreditasi: SK No.: 36b/E/KPT/2016
http://journal .unnes.ac.id/nju/index.php/jbat

Hydrothermal Liquefaction of Mahogany *(Swietenia macrophylla*) Sawdust

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DOI 10.15294/jbat.v7i1.12410

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Article Info

Article history:
Received
May 2018
Accepted
June 2018
Published
June 2018

Keywords :
Hydrothermal treatment;
Mahogany sawdust;
Coloring test;
High heating value

Abstract

Hydrothermal treatment is one of the thermochemical methods to convert complex organic compounds, such as organic waste and biomass, into upgraded solid, bio-oil, and other dissolved chemicals by utilizing the properties of water at near critical condition. Such method is very potential since the process is environmentally friendly and the products have more added values. In this research, conversion of mahogany sawdust *(Swietenia macrophylla)* using hydrothermal treatment method was studied. The experiments were conducted in a batch autoclave with temperature range of 200–300ºC and initial pressure of 1 MPa. At targeted temperature, the process was hold for 30 minutes. In addition, biomass-water ratio (B/W ratio) for experiments was varied at 1:20, 2:20 and 3:20. The liquid products, which were characterized by Gas chromatography-Mass spectrometry (GC/MS) instrument, showed the presence of furfural and several organic acids, but no flavonoid compounds. Thus, coloring potential test of hydrothermal liquid was unsuccessful; there were not any color attached on the cloth specimen. On the other hand, proximate and ultimate test results indicated that solid products had high heating value (HHV) of 4625.34–4876.25 cal/g which were comparable to that of sub-bituminous coal.

INTRODUCTION

As development progresses in Indonesia, the demand for wooden equipment such as furniture and other household appliances is increasing. In addition, the government's policy of loosening the export of sawn timber increases the sawmill activities. This is indicated from the data on sawn wood production which has increased within 2009-2013 from 710,208 m^3 to 1,217,868 m^3 (BPS, 2015). As consequence of increasing wood sawing activity, high accumulation of sawdust waste then becomes an environmental drawback.

Currently, the handling of sawdust is still a problem, particularly for big sawmills. Most are left to rot, stacked and burned, all of which can reduce the quality of the environment, and even pollute it. One of the sawdust which widely found is Mahogany sawdust *(Swietenia macrophylla)*. This sawdust comes from many wood processing industries, such as those for construction timber, furniture and other processed products. High amount of mahogany sawdust found in sawmills is due to the abundance of mahogany tree in Indonesia. Mahogany is a tropical plant that can be found in many areas, such as teak forests, beaches, as well as city streets (Harianja, 2008). In milling process, approximately 50–60% of volume of mahogany is discharged as waste.

Mahogany sawdust is one of the potential biomass sources in Indonesia. Biomass is organic material primarily derived from either living or dead plants. Generally, biomass consists of three main components, e.g. cellulose, hemicellulose, and lignin. It is believed that biomass is one of the most abundant sources of renewable energy and it will play an important role in the sustainable energy supply in the future (IEO, 2009; Toor et al., 2011).

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ISSN 2303-0623
e-ISSN 2407-2370

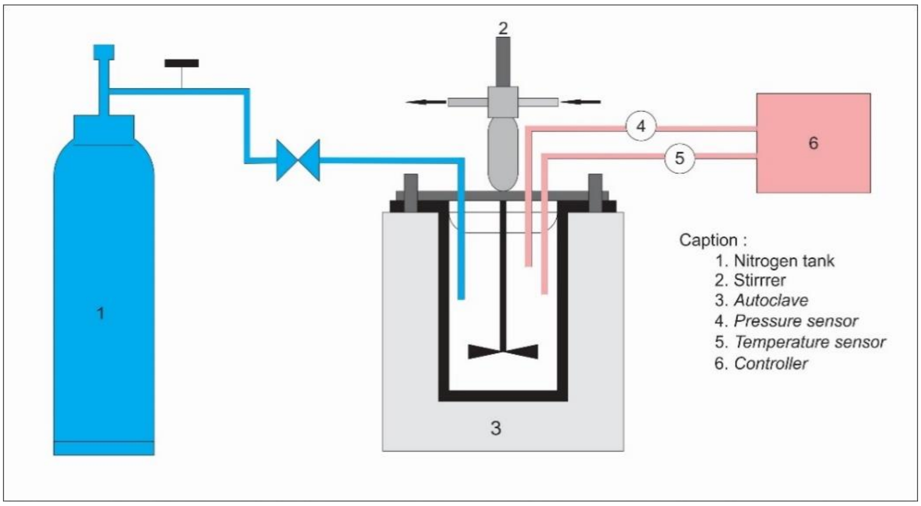


Figure 1. Experimental apparatus for hydrothermal liquefaction.

Hydrothermal treatment is a method for biomass conversion which has attracted many attentions recently. In this method, complex organic compounds of biomass are converted into upgraded solid, bio-oil, and other dissolved chemicals by utilizing the properties of water at near critical condition (Sasaki et al., 2003; Yuliansyah et al., 2010).

Many researches have been conducted on hydrothermal treatment of biomass (Tekin et al., 2014). However, most of them focused on upgrading the solid biomass for producing solid fuel. Only a few works have reported on the liquid product and its utilization. In this research, hydrothermal treatment was applied to convert mahogany sawdust into solid and liquid products. By characterizing both products, their further potential utilization will be studied. In addition, a test on the potential coloring of hydrothermal liquid as natural dye for textile will also investigated.

EXPERIMENTS

Materials

Mahogany sawdust is collected from a sawmill in Kalasan-Yogyakarta and West Lombok-West Nusa Tenggara. The mahogany sawdust is air dried, pulverized, and sieved with particle size of -32 +65 mesh. The material was then analyzed for its fixed carbon, volatile matter, moisture content, ash content, calorific value, as well as its chemical composition (cellulose, hemicellulose, and lignin)

Equipment

The equipment used in these experiments is illustrated in Figure 1.

Experimental Procedure

Hydrothermal treatment Process

Hydrothermal treatment was carried out by loading 15 g of mahogany sawdust and 150 mL of water into the autoclave. After tightly closed, the air inside of autoclave was then purged for 3 (three) times using N_2 gases with a pressure of 5 bar. Afterward, the process is started at an initial pressure of 10 bar and the setting temperature of 200 ^oC. Once the temperature was reached, it was held for 30 minutes. The experiments were conducted in various temperatures and biomass-water (B/W) ratios. Temperature for treatment was varied at 240 ^oC, 270 ^oC, and 300 ^oC, while B/W ratio was 1: 20, 2:20, and 3:20. This procedure was similar with that had been conducted with Prasetya *et al.* (2016).

Analysis

The liquid product was analyzed using gas chromatography-mass spectrometry (GC/MS) with the following operating conditions: capillary column type of Rastek RXi-5MS 30 m x 250μm, injection temperature of 290^oC, detector temperature of 250^oC, and temperature column of 45 to 250^oC with heating rate of 5 ^oC/min. Helium gas was used as carrier with flow rate of 80 mL/min and pressure of 22.0 kPa. Meanwhile, the solid products were characterized by proximate and ultimate analyses.

Test the potential of the liquid product as a dye

Coloring test was conducted by soaking a cotton cloth (approximately 10x5 cm) in liquid solution of hydrothermal treatment for 30 minutes, and continued in fixator solution (alum solution)

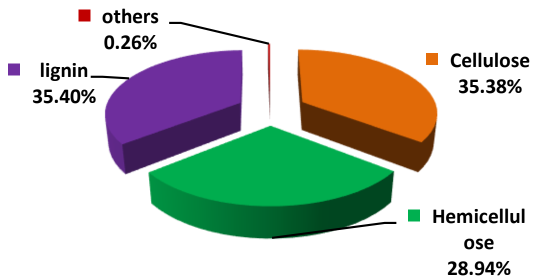


Figure 2. Composition of mahogany sawdust.

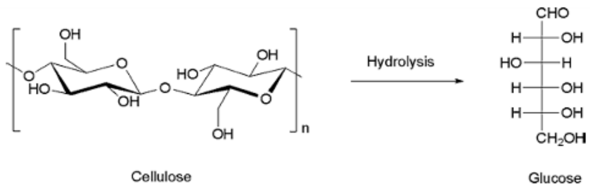


Figure 3. Illustration of cellulose hydrolysis.

Table 1. Products of hydrothermal treatment of mahogany sawdust with variation of temperature and biomass-water (B/W) ratio.

No	Temperature (°C)	B/W ratio	Biomass Sample (g)	Liquid product (mL)	Liquid yield (vol%)	Solid product (g)	Solid yield (wt%)
1	200	1 : 20	7.52	125	83.33	5.18	68.88
		2 :20	15.19	81	54.00	10.66	70.18
		3: 20	22.51	74	49.33	17.93	79.65
2	240	1 : 20	7.50	123	82.00	5.03	67.07
		2 :20	15.03	94	62.67	9.91	65.93
		3: 20	22.54	90	60.00	18.12	80.39
3	270	1 : 20	7.56	123	82.00	4.91	64.95
		2 :20	15.13	99	66.00	9.63	63.65
		3: 20	22.52	73	48.67	17.6	78.15
4	300	1 : 20	7.54	120	80.00	4.74	62.86
		2 :20	15.12	105	70.00	9.13	60.38
		3: 20	22.51	75	50.00	17.02	75.61

for 15 minutes. Afterward, the cloth was air dried and the color appeared was observed.

RESULTS AND DISCUSSION

Proximate analysis for mahogany sawdust consisted of analysis of moisture content, ash content, fixed carbon, volatile matter, and calorific value. Laboratory analysis showed that water content, ash content, fixed carbon, volatile matter and calorific value of mahogany sawdust were 10.57%, 0.86%, 44.92%, 63.89%, and 4393.57 cal/g, respectively. Furthermore, the content of cellulose, hemicellulose and lignin was also determined. The composition of mahogany sawdust was shown in the Figure 2.

According Figure 2, lignin and cellulose dominated the composition of mahogany sawdust with 35.40 and 35.38 wt%, while content of hemicellulose was 28.94 wt%. This composition greatly affected the final product obtained. For liquid product, lignin was responsible for the emergence of phenolic compounds, as the main product of hydrolysis and decomposition reaction. Meanwhile, cellulose hydrolysis produced derivatives of sugar such as furfural and HMF. Under hydrothermal conditions, cellulose reacts with water and it is hydrolyzed into glucose or other monomers followed by breaking the C-O-C bond and accompanied by further degradation. Jin et al illustrated hydrolysis reaction of cellulose compounds in Figure 3.

Similarly, hydrolysis of hemicellulose will produce organic acid compounds such as acetic acid, carboxylic acids and other compounds such as furfural and furan.

Yield of the liquid and solid products of hydrothermal treatment of mahogany sawdust at various conditions is summarized in Table 1 and Figures 4 and 5.

According to Table 1, solid product resulting from hydrothermal treatment decreased as temperature increased. It indicates that more complex carbohydrates and lignin compounds of the biomass feed are hydrolyzed, decomposed, and further dissolved into the liquid phase. The yield of solid product relatively increased along with the increase of B/W ratio. The table showed that the highest yield of solid product was attained at B/W ratio of 3:20 for all temperature treatments. The yield as high as 76–80 wt% was obtained at this ratio. This result indicates less decomposition

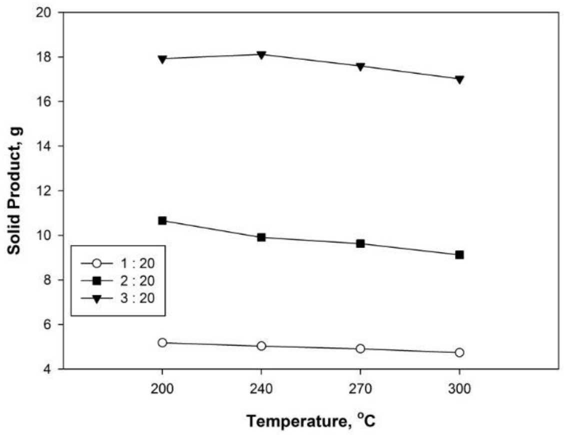


Figure 4. Solid product obtained at various temperatures.

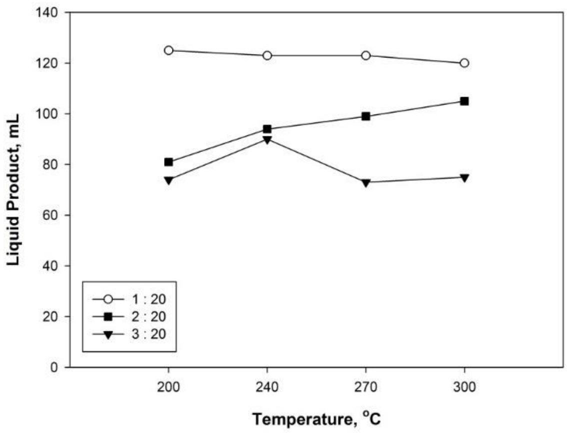
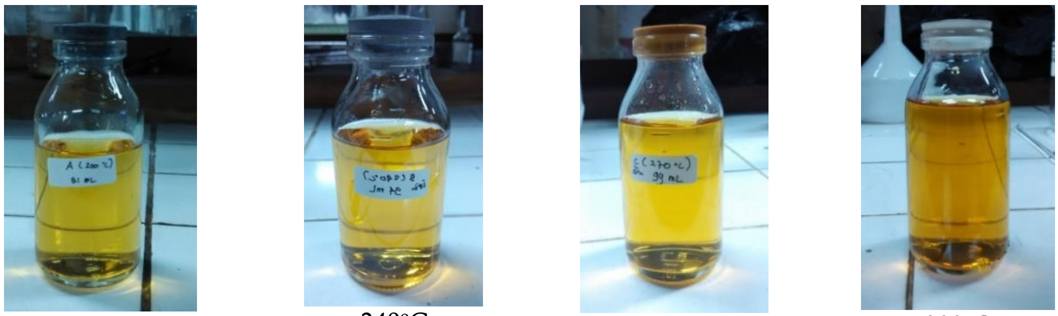


Figure 5. Liquid product obtained at various temperatures.

Table 2. Ultimate analysis results of and Higher Heating Value (HHV) of the solid products

Temperature Treatment, °C	Ultimate Analysis, wt.% (dry basis)					HHV, cal/g
	C	H	N	S	O	
200	48.60	5.94	0.15	0.10	45.21	4652.34
240	51.58	5.89	0.19	0.08	42.26	4844.83
270	52.37	5.75	0.12	0.07	41.69	4876.25
300	51.35	5.86	0.15	0.05	42.59	4825.08



200°C 240°C 270°C 300°C

Figure 6. Liquid product of hydrothermal treatment of mahogany sawdust at B/W ratio of 2:20

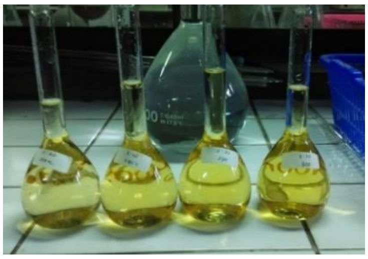
reactions occurred at B/W ratio of 3:20, so that more biomass feed materials remains unreacted and left as residue. This solid residue was then considered as "solid product". It was also shown that for B/W ratio of 3:20, the hydrolysis and decomposition reactions were not so effective to dissolve the solid; that only 4% difference of solid yield (76–80 wt%) was existed between the lowest and the highest yield.

The ultimate analysis results of and Higher Heating Value (HHV) of solid products resulting from experiments at B/W ratio of 2:20 are presented in Table 2.

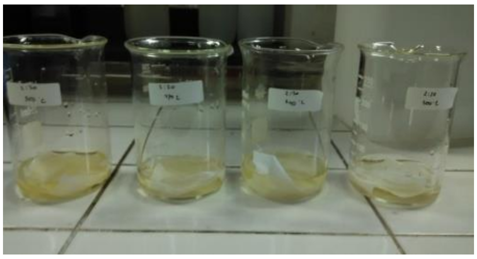
Based on Table 2, it can be seen that under hydrothermal treatment, a slightly increase of the C content, followed by simultaneous decrease in the H, O, and S content of solid products as temperature increased. As a result, the HHV was also increased. Hence, solid products resulting from hydrothermal treatment of mahogany sawdust had a HHV ranging from 4625.34 to 4876.25 cal/g. These values are high enough and comparable with that of sub-bituminous coal.

In case of liquid product, it was seen from Table 1 that for a given temperature and the same amount of feed water (150 mL), the least amount of liquid product was resulted from treatment at B/W ratio of 3:20. It explains that more water is required for hydrolysis and decomposition reactions, since more biomass feed materials are present. These reactions occurred more intensely at higher temperature. It was revealed from the color appearance of liquid product that was getting darker as temperature increased (Figure 6)

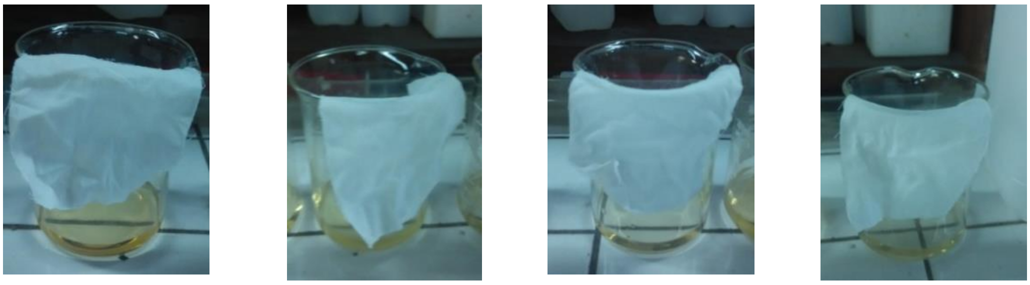
Preliminary test on coloring ability of hydrothermal liquid was done by alum solution as



Liquid product hydrothermal treatment of mahogany sawdust



Cloth specimen immersion



Cloth specimen appearance after immersion

Figure 7. Test on the potential of liquid products of hydrothermal treatment of mahogany sawdust as natural dye for textile.

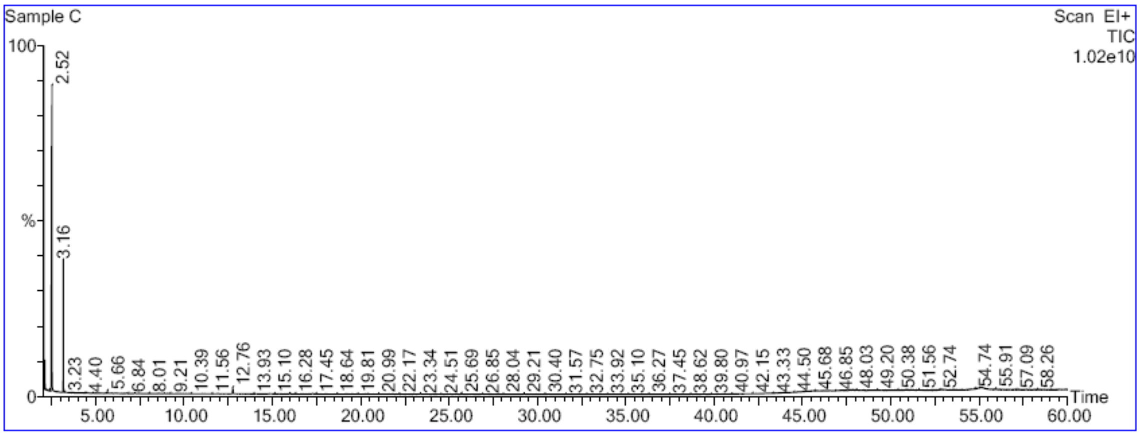


Figure 8. TIC GC/MS for hydrothermal liquid of mahogany sawdust (240°C, B/W ratio of 2:20)

fixator. As shown in Figure 7 there was no color attached on the cloth specimens. This was due to the absence of flavonoid compounds and or their derivatives which were responsible as natural dye in hydrothermal liquid. They were probably degraded when treated at elevated temperatures. The Total Ion Chromatogram (TIC) of GC/MS for hydrothermal liquid (Figure 8) had confirmed this.

Based on this TIC, approximately 40 chemical compounds were contained in the liquid, however only 4 compounds were the major ones e.g.: ethyl cyclopentane (Retention time, RT = 2.128), dimethyl formamide (RT = 2.524), furfural (RT = 3.164), and hexadecamethyl octasiloxane (RT = 55.075). Percent peak areas for such corresponding compounds were 1.543, 40.115, 10.123, and 2.005% respectively, while those for other compounds were less than 1%.

CONCLUSIONS

Based on the experimental results, it can be concluded that hydrothermal treatment could be an alternative solution to convert waste mahogany sawdust into more valuable products, in the form of liquid solution and solid fuel. In this case, liquid product that contains various chemical compounds has the potential to be utilized in many applications. However, a preliminary investigation on the potential of hydrothermal liquid product of mahogany sawdust as a natural fabric dye shows that it is not good enough because the dye compounds are degraded at elevated temperatures (above 200°C). Meanwhile, the solid product has the potential as an alternative solid fuel due to its calorific value ranging from 4625.34 to 4876.25

cal/g that are comparable with that of sub-bituminous coal.

ACKNOWLEDGMENTS

The authors are grateful for the support from the Graduate School of Universitas Gadjah Mada which has provided financial support in conducting this research.

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