Thermal Characterization of Crude Natural Polymer Recovered from Bioethanol Pretreatment Process

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Abstract. The natural polymer was isolated from black liquor as the product of bioethanol pretreatment process by means of precipitated method. The method was carried out by addition of sulfuric acid to obtain various pH conditions of the mixtures at room temperature. The precipitated then was characterized by Thermo Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA), and Energy Dispersive Spectroscopy Scanning Electron Microscope (EDS-SEM). The results showed that there were different amount of precipitates between the sample preparations. The TGA results shows lignin at pH 1 and 12 start to decompose at around 200^{o}C. The decomposition temperature of natural polymer at pH 1 and 12 is approximately temperature at 450^{o}C. The information of their purity was also identified by EDS. The additional elements such as Na, Mg, K, Zn, and Fe and higher percentage of mass Al, Si, Ca, and Cu elements were established in the lignin precipitated in basic media.

Keywords: natural polymer; black liquor; isolation; thermal characterization

Introduction

Currently, the second-generation bioethanol produced from various lignocellulosic materials such as wood, agricultural or forest wastes, has the prospective to be a valuable substitute for gasoline [1]. The utilization of lignocellulosic materials as feedstock for bioethanol conversion produces in considerable reduction of greenhouse gas emissions and in the increasing of economic profit due to low cost raw materials. Lignocellulosic materials can be grouped based on the source: wood (softwoods and hard woods) and shrubs, non food agricultural crops (kenaf, reed, rapeseed, oil palm empty fruit bunch, etc) and residues (olive stones, wheat straw, corncobs, rise husks, sugarcane, etc) and municipal solid wastes related to thinning, gardening, road maintenance, etc [2]. The second-generation bioethanol production disposes huge amount black liquor as a waste which has certain content of lignin.

Lignin is a phenolic polymer constructed by oxidative coupling of three major phenylpropanoid units, namely, 4-hydroxyphenylpropane (H), guaiacylpropane (G), and syringylpropane (S) resulting from the enzymatic polymerization of p-coumaryl, coniferyl,

and sinapyl alcohol, respectively, that form a randomized structure in a three dimensional networks inside the cell wall [3,4]. The additional effort is carried out to improve economics of bioethanol production by isolation of lignin and developing value-added lignin as coproduct [4]. Various method have been developed to isolate a desirable lignin such as organosolv fractionation, steam explosion, enzymatic hydrolysis, and alkaline delignification [5,6]. Major use of lignins is based on their function as dispersants, emulsifiers, binders, and sequestants. Utilization of lignin has been widespread in the several products application such as carbon black and pigment dispersion, cement and concrete, dyestuff formulation, gypsum wallboard, wettable pesticides, oil well drilling, corrosion inhibition, industrial cleaner, micronutrients, adhesives for board, ceramic, foundry sands, asphalt emulsion, wax stabilizer, soil conditioning, etc [5].

Since lignin contains elements of C, H, O, the solid lignin will be decomposed to CO_2, CO, H_2O, and CH_4 by heating at its melting point. When the lignin contains inorganic impurities, the inorganic impurities will be still remained by heating its melting point. Therefore, in this experiment the thermal characteristic and impurities of the precipitate will be investigated. The thermal stability of crude lignin was studied using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Meanwhile, the impurities analysis of precipitate was determined by energy dispersive spectroscopy analysis (EDS-SEM)

Experimental

Materials

Black liquor was generated as by product from hydrolysis of oil palm empty fruit bunch in the bioethanol production pilot plant located in Research Centre for Chemistry-Indonesian Institute of Sciences. Black liquor produced in this bioethanol process has pH 14, density 1.03 (g/mL), and total solid content 6.5% (dry matter content 66.9 g/L). Deionized water was produced using a Milli-Q water purified system (Millipore Corp) and used in all experiment runs. Sulfuric acid (98%) was purchased from MERCK Chemical, Germany.

Methods

Determination of Ash Content and Dry Residue of Black Liquor

The method was referred to Indonesia Standard Method (SNI: 06-1839-1990 black liquor, total solid content, total alkali and total active alkali). About 10 mL of black liquor was

dried at 105°C in crucible for 4 hours to constant weight. The dry residue was accurately weighed by analytical balance.

The ash content of black liquor was determined by heating the residue from ambient temperature to 575°C and followed by accurate weighing. The ash content is calculated by means of ratio between weight residue after and before heating.

Determination of total solid from black liquor precipitated at pH 1 and 12

The pH of black liquor was adjusted to pH 1, and 12 by adding drop wise of 2 N of sulfuric acid solution. The mixture was stirred at 100 rpm for 1 h to complete the precipitation process. Subsequently, the mixture was centrifuged at 3000 rpm for 15 min to separate the precipitated total solid and supernatant solution. Afterward, the precipitated total solid was washed several times by deionized water until obtaining neutral filtrate. Later, precipitated total solid was dried in the oven vacuum at 50°C for 24 h. The yield of total solid from the precipitation process was calculated by the equation 1 as follows.

$$\%\ yield = \frac{weight\ of\ total\ solid\ precipitate}{weight\ of\ black\ liquor \times \%total\ solid} \times 100 \qquad (1)$$

Charactherization of lignins

Determination of Thermal Properties

The thermal properties of precipitated lignin was investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The thermogravimetric analysis was carried out using TA instrumental analysis TGA Q50. Approximately of 25 mg of lignin sample placed in platinum pan was heated at temperature from ambient to 600°C. The experiment was performed at heating rate 5°C/min under air atmosphere. Weight loss and heating rate are continuously monitored along the experiment to examine the different decomposition process. Differential thermal analysis (DTA) was performed using DTA instrument developed by Research Center for Physics-Indonesian Institutes of Sciences. The instrument was operated at the heating rate of temperature 5°C/min. The samples are heated from ambient to 600°C under air atmosphere.

Determination of impurities by Energy Dispersive Spectroscopy (EDS-SEM)

The impurities analysis of lignin precipitate was studied using JEOL 6510(LA) energy dispersive spectrometer (EDS-SEM). Lignin sample was coated with a very thin layer of Au prior to analysis. The EDS parameters are 20 kV of voltage, 1 nA of probe current, 0-20 keV of energy range and 7026 cps of counting rate.

Results and Discussion

Ash Content and Dry Residue of Black Liquor

The results of determination of ash content and dry residue of black liquor are presented in Table 1. From the Table 1, it can be concluded that the lignin content in the black liquor is around 46% (w/w).

Table 1. Ash content and dry residue of black liquor.

	% (w/w)
Ash content	3.52
Dry residue	6.49

Precipitation of total solid from black liquor at pH 1 and 12

The yield of total solid precipitated at pH 1 and 12 from black liquor are shown in Table 2. From the table 2, it can be estimated that there is a significant difference between total solid yield at pH 1 and 12. It indicated that the total solid at pH 1 contain such impurities together with the lignin. Meanwhile, the total solid at pH 12 contain the undissolved particles such as metal precipitates at basic condition. In addition, from the Table 2 it can be estimated that the lignin content in the total solid is around 75% (w/w).

Table 2. Yield of total solid precipitated at pH 1 and 12 from black liquor.

Ph	% Yield (w/w)
1	30.05
12	7.45

Charactherization of Thermal Properties

The TGA and DTA curves of solid sample obtained from the precipitation at pH 1 and 12 are presented in Figure 1 and 2, respectively. The thermal degradation pattern of TGA in the figures shows that the samples were decomposed within a wide range temperature from 200 to 450^{o}C. There are two degradation stages which are difficult to identify as the individual degradation stage. There was an initial stage occurred at around 100 ^{o}C due to the weight loss of moisture [6–8]. K Wang, *et al* (2010,2012) reported that the decomposition at 180-400^{o}C was attributed to the cleavage of linkages between aromatic ring of the lignin. This stage released the volatile gases such as CO, CO_2, and CH_4. The thermal degradation of lignin at 180-400^{o}C involve several steps such as a) cleavage of α-

and β-aryl-alkyl-ether linkages around 150 to 300°C; b) aliphatic side chains begin splitting of from the aromatic ring at 300°C; c) cleavage the carbon-carbon linkage between lignin structural units happened at 370-400°C [9]. The other publications [6,11,12] added that the maximum rate of weight loss of lignin occurs between 280-350°C. Subsequently, the lignin was decomposed over a wide range of temperature above 450°C at ultimate stage. The non volatile residue at 600°C for solid pH 12 was still remained around 30%. In contrast, the residue content for solid pH1 was still remained about 10%. It means that the decreasing of pH value from 12 to 1 is decreased the nonvolatile residue three times relatively.

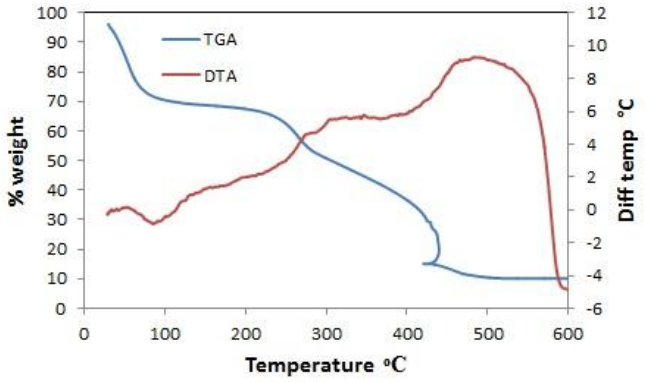

Figure 1. TGA and DTA curves of solid precipitated at pH 1.

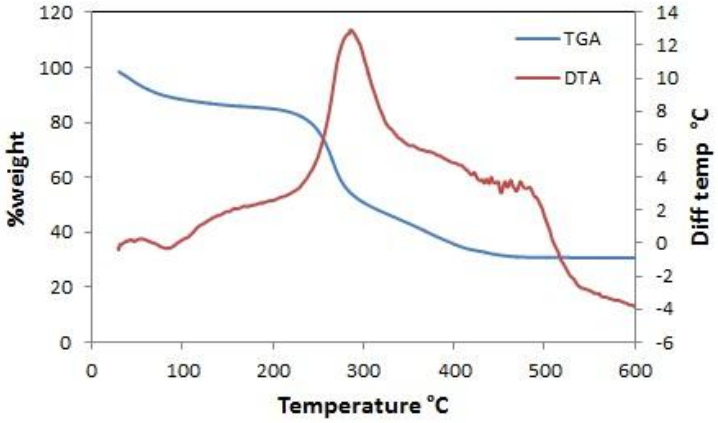

Figure 2. TGA and DTA curves of solid precipitated at pH 12.

Determination of impurities by Energy Dispersive Spectroscopy (EDS-SEM)

Figure 3 and 4 illustrates the result of EDS-SEM of metal content measurement in total solid at pH 1 and 12, respectively. The metal content in total solid pH 1 and 12 are recorded together in Table 3.

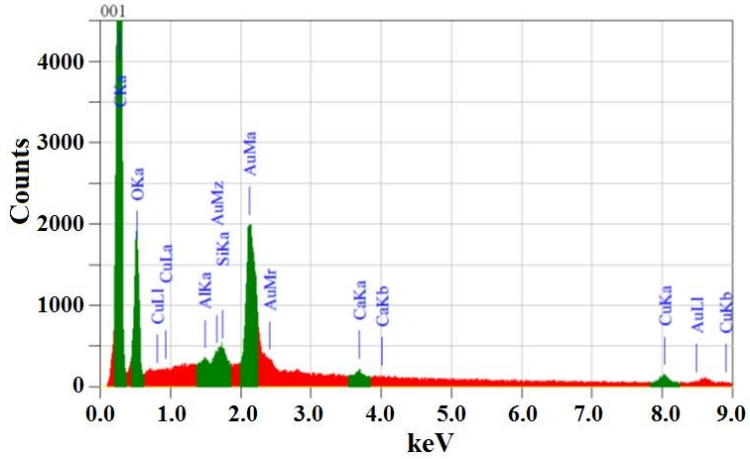

Figure 3. EDS analysis of total solid at pH 1.

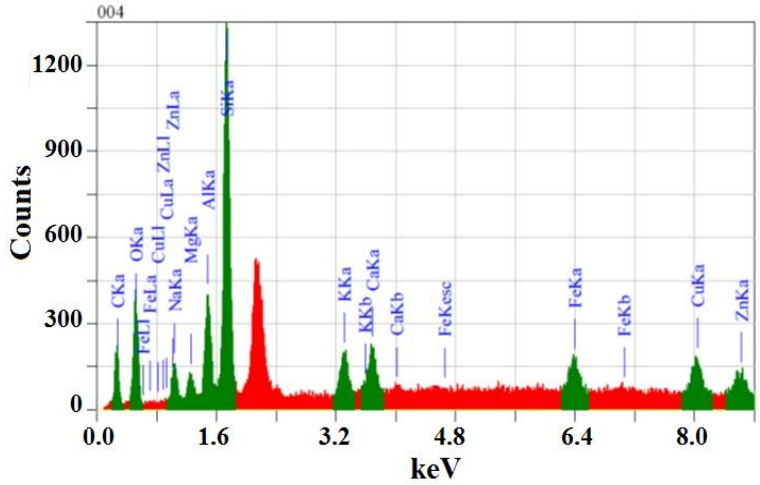

Figure 4. EDS analysis of total solid at pH 12.

Table. 3. Elemental analysis of solid precipitated at pH 1 and 12 using EDS.

Element	% mass	
	Solid pH 1	Solid pH 12
C	60.5	25.6
O	28.7	23.0
Na	-	2.3
Mg	-	1.3
Al	0.2	5.3
Si	0.4	18.0
K	-	2.4
Ca	0.2	2.4
Fe	-	5.1
Cu	1.8	13.8
Zn	-	8.7

From Table 3, the amount of elements identified in solid at pH 12 was greater than solid at pH 1 except C and O. The content of Na, Mg, K, Fe, and Zn at solid pH 12 was eliminated by decreasing the pH value of mixture from 12 to 1. The remaining elements such as Al, Si, Cu, Ca was decreased significantly approximately 93%. Therefore, the solid at pH 1 contains lignin with the small impurities. These EDS data confirms to the result of the thermal characterizations above.

Conclusion

The result of thermal characterization of crude natural polymer and metal content in the solid by EDS analysis indicates that the precipitation process of solid by decreasing the pH value from 12 to 1 could be acted as the purification step of the sample.

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[1] M. Galbe, G. Zacchi, *Adv. Biochem. Engin/Biotechnol.* **2007**, *108*, 41.
[2] D. L. A. Fernandes, S. R. Pereira, L. S. Serafim, D. V. Evtuguin, A. M. R. B. Xavier, *Bioethanol*, Marco Aurelio Pinheiro Lima (Ed.), InTech, Rijeka Croatia, 2012, p.123-1523.
[3] R. Sun, J. Tomkinson, J. Bolton, *Polym. Degrad. Stabil.* **1999**, *63*, 195.
[4] F. Monteil-Rivera, M. Phuong, M. Ye, A. Halasz, J. Hawari, *Ind. Crop. Prod.* **2013**, *41*, 356.
[5] F. Lu, J. Ralph, *Lignin*. *Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels* Elsevier, Amsterdam, **2010**, 169.
[6] A. Moubarik, N. Grimi, N. Boussetta, A. Pizzi, *Ind. Crop. Prod.* **2013**, *45*, 296.
[7] X. Yang, Y. Zeng, X. Zhang, *Bioresources* **2010**, *5*, 488.
[8] M. Carrier, A. Loppinent-Serani, D. Denux, J. M. Lasnier, F. Ham-Pichavant, F. Cansell, C. Aymonier. *Biomass Bioenerg.* **2011**, *35*, 298.
[9] K.Wang, F. Xu, R. Sun, *Int. J. Mol. Sci.* **2010**, *11*, 2988.
[10] K. Wang, H. Y. Yang, X. Yao, R. C. Sun, G. L. Jones, *Cellulose Chem. Technol.* **2012**, *46*, 185.
[11] P. Methacanon, U. Weerawatsophon, Kasetsart J. (Nat. Sci.) **2010**, *44*, 680.
[12] R. Sun, J. Tomkinson, *Sep. Purif. Technol.* **2001**, *24*, 529.