The effect of temperature on lignin purification from bioethanol production waste based on palm oil empty fruit bunch

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Abstract. In this study, the optimal condition of lignin purification from bioethanol production waste based on palm oil empty fruit bunch has been conducted. Purification of Lignin through two steps are impurities precipitation in pH 7 and lignin purification in pH 2 simultaneously with variation temperature. The concentration of lignin determines by spectrophotometer UV-Vis and thermal analysis to determine the ratio of lignin content and residual content. It was found that in lignin purification step, the lowest lignin concentration is at temperature 30°C with the concentration of lignin is 8.388% and the highest residual content is at temperature 60°C with % residual combustion is 26.652%. The optimal temperature at pH 2 for lignin purification is 50°C with a lignin concentration is 73.854% and the residual combustion is 27.956%.

1. Introduction
Indonesia is a country that has a fairly high agricultural wealth, especially in palm oil tree commodities. Palm oil tree commodity has been widely used in several industrial fields in Indonesia such as producing biofuel [1], composites [2], medicine [3] and the other utilities. Palm oil tree processing in some of its function gives a residual product in the form of Oil Palm Empty Fruit Bunch (OPEFB). In the previous growth of the palm oil industry, a large amount of palm biomass is generated every year, 23% of fresh fruit bunches become OPEFB [4]. OPEFB is the agricultural waste which has a high lignocellulose content [5]. Lignocellulose consists of lignin, cellulose and hemicellulose compounds [6]. The most abundant form of biomass is lignocellulose, with an annual production of around 170 billion metric tons [7]. The mainly components in lignocellulose materials are cellulose, hemicellulose and lignin. Among them, hemicellulose (20–30%) and cellulose (40–50%) are the polymers of C5 and C6 sugars [8]. By the main problem, we can enhance the application of palm oil waste i.e. OPEFB as the main ingredient of producing some ethanol. Lignocellulose compound can be derived into simple sugars which converted into ethanol through several processes and it is one of a potential renewable material for bioethanol conversion [9, 10]. But in bioethanol conversion there were some lack on the process, lignin contain in OPEFB can reduce the yield of the bioethanol. Therefore, we need to do some pre-treatment to relieve lignin compound.

The purpose of the pre-treatment process is to eliminate lignin content in bioethanol production. It is called delignification process that produce crude lignin [11]. Crude lignin is a waste that contains of...
lignin and a lot of impurities [5]. Lignin can be used commercially as a binder, adhesive, filler, surfactant, polymer product, dispersant and other chemical sources [12]. This crude lignin needs to be purified so that the product can be utilized [5]. Pre-treatment process can be done by lignin deconstruction between acid and alkali pre-treatment is apparent. Alkali-based pre-treatment utilizes various kinds of alkaline (e.g., sodium hydroxide, calcium hydroxide, ammonia, etc.), caused effects of lignin solubilisation or degradation [13]. Lignin purification has been carried out by the precipitation method with several of pH, by two steps at pH 7 then pH 2, and one stage at pH 2. Two-steps settling produces inorganic impurities then one-stage settling [6]. Some researcher has studied about the effect of variations in precipitation temperature on one-stage process that the percentage optimum lignin is obtained at 50°C and ash content increases followed by increasing the temperature [14]. Influence of temperature condition in two-steps precipitation process not conducted yet. Therefore, this research is focus on the effect of temperature variations on the purification of lignin by two-stage precipitation at pH 7 and pH 2. The concentration of lignin obtained using a UV-Vis spectrophotometer and thermal analysis.

2. Experimental
2.1. Materials
The materials in this research were commercially available from Merck without treatment and purification such as natrium hydroxide (NaOH), sulphate acid (H₂SO₄) 95-97% that used to control pH of solution, and 1,4-dioxane GR. Crude lignin obtained from bioethanol production waste in LIPI P2K Laboratorium, aquades.

2.2. Lignin Purification
The purification of lignin conducted at different temperatures and through two steps. First step is impurities precipitation. Crude lignin (10 gram) dissolved in 25 mL NaOH 5%. The solution stirred 15 minutes, 125 mL aquades added into solution. The solution stirred for the other 15 minutes, H₂SO₄ 1% dropped into the solution until the solution reached pH 7. The solution stirred for 1 hour in variation temperature (30°C, 40°C, 50°C, 60°C). The solution precipitated for 16 hours at room temperature. The solution was centrifuged at 10.000 rpm in 10 minutes, filtrate and precipitate were separated. Precipitate dried at 50°C for 16 hours and crushed (Compound 1). Weight all of compound 1 is measured.

The second step is lignin purification that conducted by dropped H₂SO₄ 1% into the filtrate until the filtrate reached pH 2. The solution stirred for 1 hour in the same variation temperature (30°C, 40°C, 50°C, 60°C). The solution precipitated for 16 hours at room temperature. The solution separated by Buchner using Whatman filter paper 42. The precipitate dried at 50°C for 16 hours and crashed (Compound 2). Weight all of compound 2 is measured.

2.3. Lignin Concentration Analysis
Calibration curve measured with variation concentration of standard lignin (5, 10, 15, 20, 50 ppm) by spectrophotometer UV-Vis at wavelength 280 nm. The equation of calibration curve used to calculate lignin concentration in samples (Equation 1).

\[ y = 0.024x + 0.0145 \]  

Determining lignin concentration in compound 1 and compound 2 obtained by dissolved 5 mg compound in 10 mL dioxane:water (1:1), and measured by UV-Vis at wavelength 280 nm.

2.4. Thermal Analysis
Compound 1 and compound 2 was analysed using STA Linseis PT 1600 which heating from 20°C to 600°C and heating flow rate is 10°C/minute. Concentration impurities can be obtained by % residual combustion.
3. Result and Discussion

3.1. Impurities Precipitation

Alkaline solution that commonly used as pretreatment solution is NaOH solution. During alkali-based pretreatment, the ether linkages between monolignols are partially broken [11]. Sodium hydroxide commonly used as catalysts for the base-catalyzed depolymerization of lignin. The reaction between alkaline metal hydroxides and lignin produce a mixture of simple aromatic compounds. Ether linkages (α- and β-aryl ether), being the weakest bonds in the lignin structure, are predominantly broken down during the depolymerization process [12,11].

Figure 1a is a graph of lignin concentration with variation temperature. Based on those data, it can be concluded that the higher of temperature is the most lignin is taken at the precipitate. Precipitation step is step to separate between lignin and impurities by precipitate the impurities. Therefore, the lowest lignin concentration is taken in precipitation is the best condition to separate impurities and lignin in solution. It was found that the lowest lignin concentration is at precipitation temperature 30 °C.

![Figure 1a](image1a.png)

(a) Lignin concentration (a) and residual combustion (b) in precipitation step.

Figure 1b is graph of % residual combustion in the precipitation step with variation temperature. Based on the graph, precipitation temperature at 40 °C, 50 °C, and 60 °C have not significantly different of % residual combustion that are 22.724%, 25.943%, 26.652% and 26.703% respectively. Purification temperature at 30 °C has the smallest % residual combustion that is 22.724%. Based on data, it can be concluded that purification temperature at 40 °C, 50 °C and 60 °C can precipitate more impurities.

![Figure 1b](image1b.png)

(b) Lignin concentration (a) and residual combustion (b) in precipitation step.

Figure 2. Ratio of lignin concentration of lignin and % residual combustion in precipitation step.
Ratio of lignin concentration and % residual combustion in precipitation step can be seen in figure 2. The lowest ratio is the most effective temperature because it has the lowest lignin concentration. This shows that the higher of temperature is the more lignin is taken at the precipitate. As well as from the impurity curve, it was found that the most impurity concentration at 30 °C. The most effective precipitation temperature is 30 °C.

![Figure 3. TGA spectra of precipitates in purification step.](image)

Figure 3 is TGA spectra of precipitates in precipitation step at variation temperature. Degradation of lignin occurs around 350 °C-450 °C [12]. Lignin degraded at temperature around 200 °C-600 °C [13]. Precipitation temperature at 30 °C showed mass began to decrease from 200 °C-600 °C with % mass reduction is 22.724%. Precipitation temperature at 40 °C showed that mass reduction occur at temperature 200 °C-600 °C with % mass reduction is 25.943%. Precipitation temperature at 50 °C showed that the mass reduction occurs at temperatures 200 °C-600 °C with % mass reduction is 26.652%. Based on data, it was found that the mass began to decrease around 200 °C - 600 °C with % mass reduction is 26.703% at precipitation temperature 60 °C. The mass degradation reaction that occurs at any temperature variation is an endothermic reaction.

3.2. Lignin Purification

Lignin purification has been obtained by conditioning solution at pH 2 that produced lignin precipitates as dark brown solids. Figure 4a is graph of lignin concentration in the purification step with variation temperature. Based on the graph, lignin concentration at 30 °C and 50 °C are higher than lignin concentration at 40 °C and 60 °C. Lignin concentration at 30 °C and 50 °C are 63.229% and 73.854%, respectively. Lignin has a negative charge in alkaline conditions due to dissociation of phenolic and carboxyl groups in lignin. Repulsive forces between negative charge of lignin make lignin stable in solution. Decreasing of pH caused interaction between hydrogen ion and negative charge of lignin. The interaction cause neutral charges in molecular surface of lignin so that produces lignin precipitation [5]. Based on these data it can be concluded that high lignin concentration can obtain at temperature precipitation 30 °C and 50 °C.
Residual combustion is impurities that precipitated with lignin in purification step. Figure 4b is graph of % residual combustion in the purification step with variation temperature. Based on the graph, purification temperature at 30 °C, 40 °C, and 50 °C have not significantly different with that are 27.602%, 27.012%, and 27.956% respectively. Purification temperature at 60 °C has the largest % residual combustion that is 32.655%. Based on data, it can be concluded that purification temperature at 30 °C, 40 °C, and 50 °C have low impurities.

Figure 5. Ratio of lignin concentration of lignin and % residual combustion in purification step. Ratio of lignin concentration and % residual combustion in purification step can be seen in figure 5. The highest ratio is the most effective temperature because it has the largest lignin concentration. The purification temperature at 50 °C has the highest ratio. It means that in the temperature condition 50 °C can be obtained the high concentration of lignin with the lowest impurities.

Figure 6 is TGA spectra of precipitates in purification step at variation temperature. Based on graph, each variation temperature has a relatively similar profile. It can be estimated that the contents of all samples are same. Lignin degraded between temperatures 350 °C - 450 °C, at temperature 100 °C - 200 °C is degradation of water and at temperatures 200 °C - 300 °C is hemicellulose is degradation [16]. Based on TGA spectra (Figure 6), it can be seen that mass degradation occurs at temperatures below 100 °C. The degradation is estimated as degradation of water molecules, because it is possible that the...
sample still contains water from the solvent. Mass degradation at temperatures around 350 °C - 600 °C is estimated of degradation of lignin polymers. The significant mass degradation occurs around 390 °C- 400 °C that estimated of breaking the C-C bond.

![Figure 6. TGA spectra of precipitates in purification step.](image)

4. Conclusion
The Purification of lignin as a side product from bioethanol processing can be done through two steps. Impurities precipitation step conducted by conditioning pH 7 and conditioning pH 2 for lignin uptake. Increasing of temperature is not directly increase lignin concentration that obtained. Temperature condition at 50 °C is the most effective condition to obtain high lignin concentration with low impurities.

Acknowledgement
Authors would like to acknowledge to all staff in laboratorium catalyst at Research Centre for Chemistry, Indonesian Institute of Sciences, Kawasan PUSPIPTEK Serpong, Tangerang for support through Kegiatan Magang Mahasiswa (KMM) 2015.

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