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Delignification and Adsorption Research on Bioethanol Process using Pseudostem of *Musa balbisiana* as the Blending Raw Material for Gasohol

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Abstract

This research is focused on the study of delignification and adsorption on the bioethanol process using pseudostem of banana as the blending raw material to gasohol. The process started with the pre-treatment and delignification of the pseudostem with using 10, 20, and 30% NaOH at 100, 125, 150, 175, and 200 °C. In delignification, treatment using 10% NaOH on 150 °C temperature produced the finest cellulose and lignin content with the amount of 81.3% cellulose and 10.1% lignin. The pseudostem fibers that have gone through delignification, hydrolyzed and fermented to produce bioethanol. The resulting bioethanol separated from reaction mixture through distillation. Furthermore, bioethanol was purified in adsorption and distillation process. In adsorption, the 5, 10, 15, 20, and 25 g adsorbent was added to the bioethanol. The result showed that the highest rate of purified bioethanol is 99.11% bioethanol content using 20 g adsorbent. The 99.11% bioethanol content blended with Pertalite with ratio of 5:95, 10:90, 15:85, 20:80, and 25:75, thereafter it was analyzed the RON content, which obtained the highest point that is 97.48 on 25:75 ratio.

Keywords: Bioethanol, Delignification, Adsorption, Pseudostem, and RON

Abstrak (Indonesian)

Pada penelitian ini dilakukan studi delignifikasi dan adsorbsi pada pembuatan bioetanol dari batang pisang sebagai bahan baku blending menjadi gasohol. Pertama, melakukan proses pratreatmen dan delignifikasi pada batang pisang klutuk dengan variasi konsentrasi NaOH 10, 20, 30% dan temperatur pemanasan yaitu 100, 125, 150, 175, dan 200 °C. Pada tahap delignifikasi ini konsentrasi NaOH 10% dan temperatur 150 ºC, menghasilkan kadar selulosa dan lignin terbaik, dengan kadar selulosa 81.3% dan kadar lignin 10.1%. Serat batang pisang yang telah di delignifikasi, selanjutnya akan dilakukan proses hidrolisis dan juga fermentasi untuk menghasilkan bioetanol. Bioetanol yang dihasilkan kemudian didistilasi untuk memisahkan bioetanol dan air. Bioetanol dimurnikan lebih lanjut dengan proses adsorbsi. Pada proses adsorbsi dengan campuran adsorben 5, 10, 15, 20, dan 25 g terhadap bioetanol. Hasil adsorpsi untuk kemurnian bioetanol tertinggi pada adsorben 20 gr dengan kadar bioetanol 99.11%. Bioetanol dengan kadar 99.11% selanjutnya diblending dengan pertalite pada perbandingan 5:95, 10:90, 15:85, 20:80, dan 25:75, lalu dianalisa kadar RON (*Research Octane Number*). Pada analisa RON diperoleh nilai tertinggi yaitu 97,48 di perbadingan 25:75.

Kata Kunci: Bioetanol, Delignifikasi, Adsorpsi, Batang Pisang, and RON.

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INTRODUCTION

The world's largest fuel sources are rapidly and unpredictably diminishing as a result of rising population. Fossil fuels are the primary, but not renewable source of energy. The indiscriminate utilization of fossil fuels leads to environmental impacts, poor air quality, and global climate change.

The demand for fossil fuels is anticipated to grow 40% from 2010 to 2040 [1].

The energy constraints from the fuel oil can be countered by the using of new and renewable energy. Renewable energy sources are environmentally friendly energy sources that do not pollute the environment and do not contribute to climate change and global warming [2]. Among the promising alternatives to fossil fuels, various biomasses have shown significant progress and can become a potential environmentally friendly basic product, namely bioethanol [3].

Bioethanol is deemed as one of the excellent energy resources that attribute for the spark-ignition internal combustion power plant. It contains higher octane and higher heat associated with vaporization, causes alcohol better to be a 100% pure energy resource than gasoline [4].

Musa balbisiana is one of the major harvested plants of numerous places around the world and the second-largest cultivated fruit in Malaysia. The tender core of the banana pseudo-stem is densely packed in the center (core) of the banana stem, tube-like shape with a diameter of approximately 5–6 cm. After the banana collection, mostly the wastes are either left for natural degradation as fertilizer/soil conditioner for the purpose of nutrition and mulching or thrown to the barren land and that contributes to environmental pollution and troubles further replanting operations [5]. Pseudostem has cellulose 34.5%, hemicelluloses 25.6%, and low lignin 12% [6].

Bioethanol is one of the liquid alcohol based biofuels, which can be produced by anaerobic conversion of carbohydrates extracted from various types of feedstocks such as food waste, woody biomass, agricultural residual, and edible crops using microorganisms and bacteria [7]. According to the alcohol content, ethanol is divided by three grades namely industry grade with the content of 90-94%, liquor and pharmaceutical raw material grade with the content of 96-99.5% and fuel oil with the content of 99.5-100% [8]. Ethanol has its characteristics: 35% lower calorific value than petrol, clear and colorless liquid, the range of boiling points of bioethanol fuel is approx. 5 ^oC, very low vapour pressure, and 7077 Cal/gr of the caloric value [9].

Delignification is a process of removing lignin of the lignocellulose materials therefore the result of this process getting the high purified cellulose. In the process of making bioethanol, delignification is the initial stage which aims to reduce the lignin content in lignocellulose materials. Delignification will open up the lignocellulose structure to make the cellulose more accessible. The delignification process will dissolve the lignin content in the material so as to facilitate the process of separating lignin from cellulose fibers [10].

Adsorption is a case which a solid and liquid that are plugged at one certain condition. In the adsorption process an adsorbent is used, the use of an adsorbent in the adsorption process has several advantages, including having large pores, hydrophobicity, stability at high temperatures, no catalytic activity and easy regeneration [11]. There are several factors that affect the adsorption power, namely the nature of the adsorbent, the nature of the absorption, the temperature, the degree of acidity (pH), and the contact time [12]. Here we reported *Musa balbisiana* process through delignification and fermented to produce bioethanol, which was purified by adsorption using zeolite.

MATERIALS AND METHODS

Research Materials and Site

Primary materials that were used in this research namely pseudostem of *Musa balbisiana*, zeolite, NaOH, HCl and Saccharomyces Cerevisiae. This research was conducted in Politeknik Negeri Sriwijaya, Energy Laboratories.

Delignification Instrument

The instrument that is made for this research is delignification instrument that is for the processes of delignification and hydrolysis. The instruments was used for delignification of pseudostem is shown in **Figure** 1.

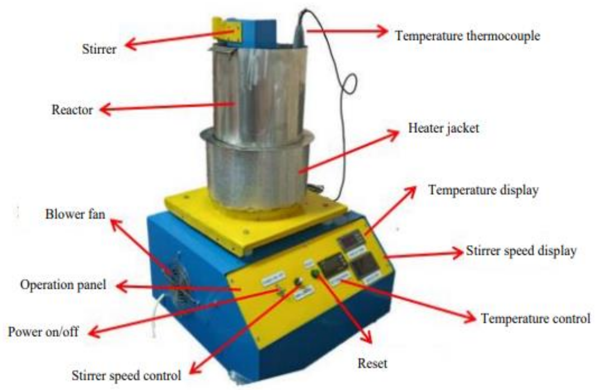

Figure 1. Delignification Instrument

Delignification Stages

First step is pseudostem of *Musa balbisiana* was cleaned. Afterwards, pseudostem cut into small measurements and was dewatered about 3-5 days in the sun to drip-dry. Then, the pseudostem blended to fine and heated in the oven for 2 hours at ± 105 ^oC.
100 g of pseudostem that was already fine and dry was put to the delignification instrument. Onward, 300 mL

NaOH 10% was added, then was heated and mixed for about 30 minutes at 100 °C. Following this, the solvent was filtered and the residue was rinsed using water (Aquadest/a brand) to get the neutral PH. Then, it was dried in the oven for about 2 hours at 105°C and was ground to fine. These stages were done for the following concentration of NaOH such as 20% and 30%, as well as the temperature 125, 150, 175, and 200 °C.

Producing Bioethanol

The pseudostem that has been processed through delignification weighed to 300 g and HCl 1% for about 900 mL was added to it. Following this, it was heated for 90 minutes at 80 °C and was agitated with speed of with 50 rpm. Then, it was refrigerated to room temperature and was filtered to separate the water. Onward, NaOH 0.7% was added to it until its PH reached 4-4.5. Further, 3 g of Saccharomyces, 3 g of Urea, and 0.5 g of NPK fertilizer were added to it. Then, it was sealed and kept for 5 days at 27-30 °C. A fermented was put into Erlenmeyer and placed on the evaporator (distillation). It was heated to 1 hour at 78 °C.

Purifying Bioethanol

100 mesh of Zeolite was soaked to "Mixture" (1 g Zeolite: 10 mL NaOH 2 M solvent) for around 3 hours. It was mixed using magnetic stirrer without the heating process. Following this, it was filtered and rinsed with water (Aquadest/a brand) to its neutral pH. Then, it was dried in the oven around 4 hours at 110 °C. 5gr zeolite was added to 40 mL of bioethanol that was from distillation. Onward, it was put into boiling flask 2 neck and was mixed for 5 minutes to fine. It was kept for 30 minutes. Concludes with the distillation at 78 °C. The steps repeated for 10, 15, 20, and 25 g of Zeolite.

Blending Gasohol

The solvent of purified ethanol was retrieved and put into 1000 mL Erlenmeyer. It was mixed to gasoline and they were covered with aluminum foil, it was done for 5:95, 10:90, 15:85, 20:80, and 25:75. Then, the stirrer was put into Erlenmeyer and it stirred around 10 minutes to its solvent homogeneous.

RESULTS AND DISCUSSION

Result of Raw Material Analysis

The result of drained *Musa balbisiana* that has been analyzing and listed in **Table** 1.

Delignification Analysis of Musa balbisiana

The outcome delignification used 10, 20, and 30% NaOH at 100, 150, and 200 °C, is shown in **Table** 2 and the decreased lignin and the increased cellulose content to the materials is shown in **Table** 2 and 3.

Table 1. Data of the Result of Raw Material

Concentration NaOH (%)	Heating Temperature (°C)	Increased Cellulose (%)	Decreased Lignin (%)
10	100	12.7	40.0
	125	14.7	44.6
	150	17.2	48.2
	175	16.4	46.2
	200	11.1	44.6
20	100	13.8	35.9
	125	16.0	39.5
	150	16.8	40.5
	175	15.7	41.0
	200	15.2	37.4
30	100	14.0	34.4
	125	15.7	41.0
	150	16.5	42.6
	175	16.4	44.6
	200	16.1	40.5

Table 2. Data of the Result of Delignification

Concentration of NaOH (%)	Heating Temperature (°C)	The Pulp Quality Analysis	
		Cellulose Content (%)	Lignin Content (%)
10	100	14.0	34.4
	125	15.7	41.0
	150	16.5	42.6
	175	16.4	44.6
	200	16.1	40.5
20	100	78.1	12.5
	125	80.1	11.8
	150	80.9	11.6
	175	79.8	11.5
	200	79.4	12.2
30	100	78.3	12.8
	125	79.8	11.5
	150	80.6	11.2
	175	80.5	10.8
	200	80.2	11.6

Table 3. Data of the Results of the Decreased Lignin and the Increased Cellulose Content to Raw Materials

No	Type of Analysis	Percentage (%)
1	Cellulose Content	67.3
2	Lignin Content	19.5

Bioethanol Analysis

The data of bioethanol of the raw materials that was done delignification and was not is shown in **Table** 4.

Table 4. Data of the Result of Bioethanol Analysis

No	Type of Analysis	Bioethanol (%)
1	Bioethanol was done delignification	53.97
2	Bioethanol was not done delignification	80.34

Adsorption Analysis of Bioethanol

The data of the analysis of bioethanol that was adsorbed with zeolite is shown in **Table** 5.

Tabel 5. Data of the Result of Adsorption Analysis of Bioethanol

No	Natural Zeolite (g)	Bioethanol (%)
1	5	91.28
2	10	92.89
3	15	97.38
4	20	99.11
5	25	98.89

Gasohol Analysis

The data of blending analysis of bioethanol and pertalite is shown in **Table** 6.

Tabel 6. Data of Blending Gasohol

No	Ratio (Bioethanol and Pertalite)	RON	Density (Kg/m^3)	IBP (°C)
1	05:95	92.37	755.8	39
2	10:90	93.85	744.8	38
3	15:85	95.42	740.2	37
4	20:80	96.81	731.3	36
5	25:75	97.48	723.5	35

Raw Materials

Analysis has done for figuring out if the raw materials are decent as the materials of producing bioethanol. There are data of the result of *Musa balbisiana* as the material for the research that can be seen in **Table** 1. Based on the result, *Musa balbisiana* has 67.3% cellulose content and 19.5% lignin content.

This point is reinforced in "Building Material and Technology Promotion Council" Report, which claims that the cellulose content in *Musa balbisiana* is about 60 - 65%, and the lignin content is about 5 - 10%. Therefore, the result indicated that *Musa balbisiana* is decent to use as the raw material due to the cellulose content that is quite enough. The high content of cellulose is expected to produce the fine quality of bioethanol.

Cellulose and Lignin Content

In this stage, *Musa balbisiana* was used for delignification using 10, 20, and 30% NaOH at 100, 125, 150, 175, and 200 °C. The yield of the fibers was analyzed to find out the cellulose and lignin content. It can be seen in **Figure** 2.

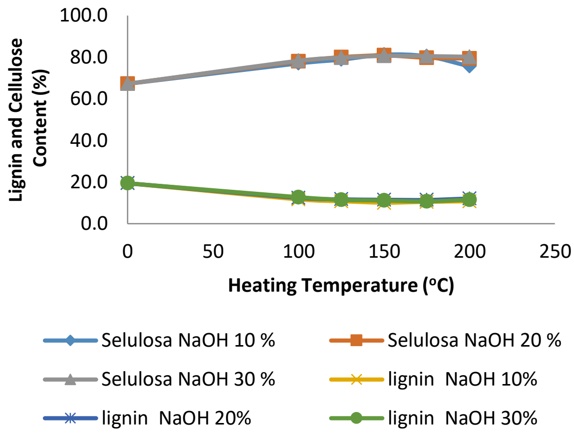

Figure 2. Cellulose and Lignin Content of *Musa balbisiana*

Its essentials are shown in **Figure** 2, which showed that the rise and fall of the cellulose and lignin contents encountered from the kinds of heating temperatures that were applied to. The highest cellulose content occurred in 10% NaOH at 150°C with the result 81.3% and the lowest cellulose content occurred at 200 °C with the result 75.7%. The highest lignin content obtained at 100 °C with the result 11.7% and the lowest lignin content obtained at 150 °C with the result 10.1%.

In summary of 20% NaOH, the highest cellulose content occurred at 150 °C with the result 80.9% and the lowest cellulose content occurred at 100 °C with the result 78.1%. The highest lignin content obtained at 100°C with the result 12.5% and the lowest lignin content obtained at 175°C with the result 12.2%.

In summary of 30% NaOH, the highest cellulose content occurred at 150 °C with the result 80.6% and the lowest cellulose content occurred at 100 °C with the result 78.3%. The highest lignin content obtained at 100 °C with the result 12.8% and the lowest lignin content obtained at 150 °C with the result 11.2%.

The Increased Cellulose Content

Figure 3 illustrated the result of the cellulose content that obtained in fibers of *Musa balbisiana* once delignification.

Once having delignification of *Musa balbisiana* using NaOH 10, 20, and 30% NaOH at 100, 125, 150, 175, and 200 °C, there were the rise and fall of cellulose content. Increasing in cellulose content can be happened since more degradation that occurred to polysaccharide of the raw materials to produce cellulose at the optimum temperature. Decreasing in cellulose content can be happened since the bond of saccharide weakened due to the high heating temperature hence the cellulose content dissolved with the solvent and was defective.

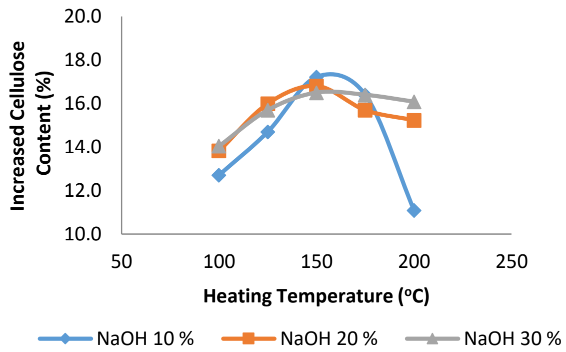

Figure 3. The Increased Cellulose Content

The Decreased of Lignin Content

Figure 4 showed the decreased lignin content that was obtained to the fibers of *Musa balbisiana* once delignification to its materials.

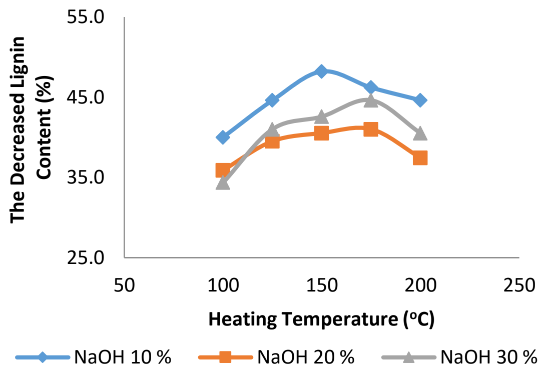

Figure 4. The Decreased of Lignin Content

Once having delignification of *Musa balbisiana* using NaOH 10, 20, and 30% at 100, 125, 150, 175, and 200 °C, there were the rise and fall of lignin content. Decreasing in lignin content can be happened since the dissociation lignin from the cellulose due to the optimum temperature. Increasing lignin content to the materials can be happened since there were more monomer due to the breaking in lignin. The monomers reacted to polymers that impregnated to the materials led to the formation of more lignin thus the lignin increased.

Delignification Analysis of Bioethanol Content

There were two sorts of raw materials that used for, the materials that once in delignification and the materials that not. This is designed to figure out the essential of delignification to the materials before having fermented to bioethanol.

As shown in **Table** 4, bioethanol from the materials that had not delignification is about 53.97% and bioethanol from the materials that had delignification is 80.34%. It showed that bioethanol content from the delignification materials is higher than the other one. This was due to the less lignin content that obtained in delignification materials thus it helped microbe to convert cellulose to bioethanol. Lignin is the third principal component of lignocellulose biomass, constituting about 15–30% of its dry mass. Lignin is covalently bonded to hemicelluloses and part of cellulose, serving as a cement between the fibers, supporting the mechanical properties of the cell walls, and protecting the structural polysaccharides from enzymatic microbial degradation. The lignin restricts the free access of hydrolytic enzymes to cellulose micro fibrils and hemicellulose chains. On the other hand, lignin acts as an adsorbent that binds the enzyme molecules on its surface, thus causing their irreversible inactivation. Therefore, lignin has to be removed in the pretreatment step [13].

Adsorbent Analysis of Bioethanol Content

Bioethanol from delignification materials was adsorbed using natural zeolite as the absorber. There were sorts of masses that were used 5, 10, 5, 20, and 25 g. Prior to it, adsorbent was activated using NaOH. Zeolite was activated for omitting the impurities thus can enhance the ability of zeolite as adsorbent to absorb water. This was done using NaOH solvent. Zeolite is structurally porous that can trap water and act as a water reservoir. Owing to its high porosity and high surface area, zeolite has a good adsorption effect on liquid adsorbates such as water.With a low Si/Al ratio, the zeolite becomes more hydrophilic due to an increase in the number of Bronsted acid sites. This property is desired since it enhances the trapping of smaller water. However, it also contributes to the trapping of water [14].

Once having adsorption using natural zeolite, bioethanol was distillated for getting the more purified yield. Following this, purify bioethanol was analyzed using GCMS (Gas Chromatography and Mass Spectroscopy). Once being analyzed, the data is shown in **Figure** 5.

It illustrated that the highest purity of bioethanol using 20gr adsorbent obtained 99.11% bioethanol and the lowest purity of bioethanol using 5 g adsorbent obtained 91.28%. As shown in **Table** 5 and **Figure** 5, adsorbent increased the purity of bioethanol. This owed the capability of zeolite to adsorb water deep in bioethanol and owed by more forces of attractions of the zeolite surface than in enduring the water deep in the bioethanol. Zeolite activated by sodium hydroxide and Si/Al ratio. The zeolite obtained showed excellent adsorption properties for water. With a lower Si/Al ratio, the zeolite becomes more hydrophilic due to the increased number of Brönsted acid sites. This property is desirable because it increases the trapping of smaller water [15].

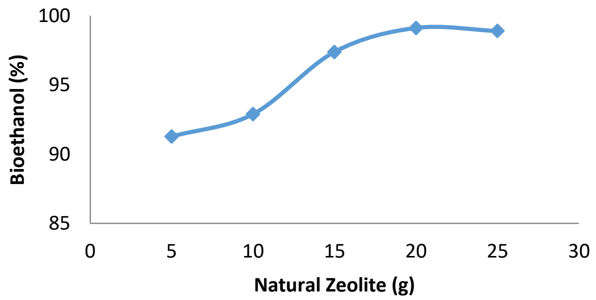

Figure 5. Adsorbent Mass to Purity of Bioethanol

Gasohol Analysis

Gasohol is one of alternative fuel oils that derived from the mixed of gasoline and ethanol using the certain ratios. In this research, it has done by blending ethanol and pertalite to increase the octane value in pertalite. The mixed-content of bioethanol and pertalite used ratios that were 5:95, 10:90, 15:85, 20:80, and 25:75, that can be seen in **Figure** 6.

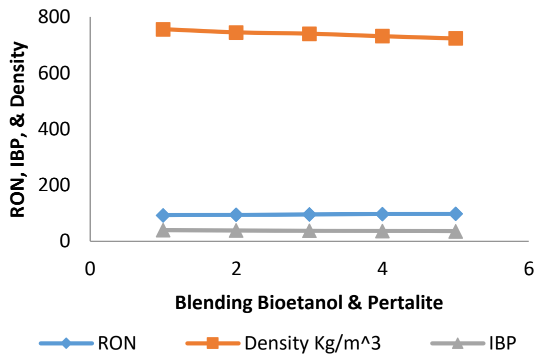

Figure 6. Blending Bioethanol and Pertalite to Gasohol of RON, IBP, and Density Value

From **Figure** 6, it can be shown that increasing in bioethanol was directly proportional to octane value, more bioethanol adding, and more octane value in gasohol. This was because bioethanol that was in gasohol can increase the octane value and oxygen that was in fuel oil. The ideal ratio is 25:75 using 35ºC IBP, 723.5 Density and 97.48 RON.

CONCLUSION

It is widely held that after having delignification to *Musa balbisiana* using 10, 20, and 30% NaOH at 100, 125, 150, 175, and 200ºC, the ideal yield of cellulose and lignin was using 10% NaOH at 150 °C. The cellulose content is 81.3% and the lignin content is 10.1%. It may be said that in blending adsorbent to bioethanol resulted the ideal purity bioethanol using 20 g adsorbent with 99.11% bioethanol. To sum up, in blending bioethanol and pertalite to gasohol, resulted the ideal one at 25:75 ratio using IBP 35 °C, Density 723.5 and RON 97.48.

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