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Effect of Time and Concentration of Sulfuric Acid on Yield Bioethanol Produced In Making Bioethanol from Peat Soil

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Abstract. The depletion of petroleum reserves, the price of fuel oil (BBM) which tends to increase, and environmental safety reasons encourage the search for other materials to be made as raw materials for making bioethanol. One of the most potent ingredients as raw material for making bioethanol is lignocellulosic biomass. Lignocellulosic biomass consists of three main components, namely: lignin, cellulose, and hemicellulose. Cellulose and hemicellulose are sugar polymers which can be broken down / hydrolyzed to produce sugar and then fermented into bioethanol. One of the lignocellulosic biomass that can be used as a substrate for bioethanol production is peat. This study will review the effect of the delignification process and hydrolysis of the yield percent of ethanol produced in bioethanol production from peat soil.

Keywords: Peat; delignification; hydrolysis; fermentation; bioethanol

1. Introduction

Peat is a layer of earth's crust which consists mostly of organic material with water-saturated conditions from the results of incomplete decomposition of plant material that occurs anaerobically [1].

Indonesia ranks the fourth largest peat swamp land after Russia, Canada, and the United States with an area of 14.9 million Ha. Whereas in South Sumatra itself the area of peat land reaches 1.2 million Ha [2].

The function of peat ecology is actually a storehouse of carbon, water storage, climate regulators and sources of biodiversity. The transfer of the function of peatland into agricultural land and plantations will result in changes in its ecological function so as to cause environmental impacts, especially the increase in CO_2 emissions released by peatlands. This is believed to be one of the factors causing global warming, climate change and rising sea levels [3]. Many tropical deposits are actively accumulating peat or are in a steady state[4]. Therefore, peat soils need to be used in other ways, one of which is to produce bioethanol.

Peat soil has a lignocellulose composition which is a potential raw material for the manufacture of ethanol from cellulose fibers which have low emission levels. Cellulose is a material that is rich in carbon. The carbon contained in cellulose can be utilized in the process of microbial

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fermentation. Peat contains organic material that cannot be directly utilized because it is still in the form of complex compounds, one of which is cellulose. In this case, cellulose can be used to produce ethanol by fermentation using Saccharomyces cerevisiae.

1.1 Peat

Peat is formed by the accumulation of tropical vegetation residues that are rich in lignin and cellulose content (Brady, 1997) [4]. Peat contains organic material that cannot be directly utilized because it is still in the form of complex compounds, one of which is cellulose. Cellulose is a linear polymer that is greater than 1000 long glucose subunits with a 1.4b-β bond [5].

Peat soils formed from tropical swamp forest vegetation that have the heterogeneous composition, consisting of logs, twigs and coarse roots that are still similar to the original plants.

Figure 1. Peat Soil

1.2 Bioethanol

Bioethanol is ethanol derived from biological sources. Bioethanol is a liquid produced by the fermentation process of sugar from carbohydrate (starch) sources using the help of microorganisms. The production of bioethanol from plants containing starch or carbohydrates is carried out through the conversion of carbohydrates into sugar or glucose by several methods including acid hydrolysis and enzymatically [6].

Ethanol is an organic compound consisting of carbon, hydrogen, and oxygen, so that it can be seen as a compound of hydrocarbons that have a hydroxyl group with a formula C_2H_5OH.

Ethanol is a liquid, colorless, odor-specific, combustible and volatile, can mix in water with all comparisons.

Ethanol combustion is cleaner than fossil fuels which means reducing greenhouse gas emissions. This is the most significant advantage of ethanol for the environment compared to fossil fuels [7].

a. Bioethanol Formation

$$\underset{\text{(Glucose)}}{C_6H_{12}O_6} \xrightarrow{\text{ENZYM}} \underset{\text{(Ethanol)}}{2\,C_2H_5OH} + \underset{\text{(Carbon dioxide)}}{2\,CO_2} \qquad (1)$$

b. Bioethanol Combustion

$$CH_3CH_2OH + 3O_2 \longrightarrow 2\,CO_2 + 3\,H_2O + \text{Energy} \qquad (2)$$

1.3 Bioethanol Formation

The stage of making bioethanol is carried out through a process of delignification, hydrolysis, fermentation, and purification. Raw material preparation is done to get glucose. Glucose is obtained through 2 stages, namely delignification and hydrolysis. At the delignification stage, it will produce cellulose. Cellulose will be processed further by the process of hydrolysis so that glucose will be produced.

1.3.1 Delignification.

Lignocellulose ingredients generally consist of cellulose, hemicellulose, and lignin. Cellulose is naturally bound by hemicellulose and protected by lignin. This lignin-binding compound causes lignocellulosic materials to be difficult to hydrolyze [8]. In making ethanol from the peat, the cellulose is used so that lignin in the wood must be removed. The process of separating or removing lignin from cellulose fibers is called delignification or pulping. Delignification is done using alkaline solutions (chemically) NaOH solutions can attack and damage the structure of lignin in the crystalline and amorphous parts and separate part of hemicellulose [9]. The OH- ion of NaOH will break the bonds from the basic structure of the lignin while the Na + ion binds to lignin to form sodium phenolate. This phenolic salt is soluble. Dissolved lignin is marked in black in a solution called black liquor.

1.3.2 Hydrolysis.

Hydrolysis aims to break down the lignin bond, eliminate lignin and hemicellulose content, damage the crystal structure of cellulose and increase the porosity of the material (Sun and Cheng, 2002). [10] Damage to the cellulose crystal structure will make it easier to break down cellulose into glucose. In addition, hemicellulose also decomposes into simple sugar compounds: glucose, galactose, mannose, hexose, pentose, xylose and arabinose. Furthermore, these simple sugar compounds which will be fermented by microorganisms produce ethanol [11]. The parameters of acid concentration, temperature and hydrolysis time are very crucial in the process of hydrolysis so as to minimize the product inhibitor which can ultimately increase the yield of ethanol in the fermentation process [12].

In the method of acid hydrolysis, lignocellulosic biomass is exposed to acids at certain temperatures and pressures for a certain time and produces sugar monomers from cellulose and hemicellulose polymers. Some of the acids commonly used for acid hydrolysis include sulfuric acid (H_2SO_4), perchloric acid, and HCl. Sulfuric acid is the most studied acid and is used for acid hydrolysis. Acid hydrolysis can be classified into concentrated acid hydrolysis and dilute acid hydrolysis [13].

Cellulose hydrolysis using acids was first commercialized in 1898 [14]. The main advantages of hydrolysis with dilute acids are no need for acid recovery, and no acid loss in the process [8]. Generally, the acid used is H2SO4 or HCl [12] in the range of 2-5% concentration [8,10] and reaction temperature ± 160 ºC.

Solving sugar molecules, complex carbohydrates and cellulose into monosaccharide molecules are done by boiling solutions containing carbohydrates with acidic solutions:

$$\underset{\text{Cellulose}}{(C_6H_{10}O_6)n} + \underset{\text{Water}}{nH_2o} \longrightarrow \underset{\text{Glucose}}{nC_6H_{12}O_6} \qquad (3)$$

1.3.3 Fermentation.

Fermentation is the process of breaking organic compounds, especially sugar (fat) by microorganisms in anaerobic conditions to produce simpler organic products [15].

Ethanol fermentation is a biological process that involves microorganisms to convert organic matter into simpler components. Microbes that are often used in the fermentation process are Saccharomyces cerevisiae.

$$C_6H_{12}O_6 + \textit{Saccharomyces} \longrightarrow 2C_2H_5OH + 2\,CO_2 \quad (4)$$

Fermentation occurs due to microbial activity. The size of this microbial life activity determines the amount of ethanol that will be produced and this activity is also influenced by several factors. These factors are generally closely related to the supply and use of nutrients that are used to support life.

1.3.4 Purification (Distillation).

To separate ethanol from fermentation can be done by distillation. Distillation is a separation method based on boiling point differences. Distillation separates components - volatile components of a liquid mixture by evaporating them (separating the heating agent) followed by steam condensation that forms and holds the condensate produced. The vapors released from the mixture are called free vapors, the condensate which falls as a distillate and the mixture that does not evaporate is called residue [16]. This process is carried out to extract alcohol from fermentation. Distillation can be carried out at 80°C because the boiling point of alcohol is 78°C while the boiling point of the water is 100°C.

1.4 Previous Research

Making bioethanol from peat soil with hydrolysis and fermentation processes, by Dr. Kiagus Ahmad Roni, ST., MT., Merisha Hastarina, ST., M.Eng. and Rully Masriatini, ST., MT., Palembang Muhammadiyah University [17]. The method used is dilute acid hydrolysis followed by fermentation on peat soil. Hydrolysis uses sulfuric acid (H_2SO_4) and ferments using bread yeast (Saccharomyces cerevisiae).

1.5 Research Design

1.5.1 Peat Soil Sample Preparation. Peat soil is taken from the peatland and then washed with water to separate the soil and peat. After washing, the peat is dried in the sun and in an oven with a temperature of 70°C to remove the water content. Then reduce the size by blenders up to 3 mm or 3-6 mesh.

1.5.2 Delignification Process

a. Addition of NaOH to Peat Soil

A hundred (100) gr of dried peat soil was treated using 200 ml of 0%, 5%, 10% and 15% NaOH solution for 30 minutes at 120 °C.

b. Washing Peat Soil Deposits with Aquadest

From the results of the delignification of peat soil, the peat dregs are found to be wet with pH 9. The peat soil is then washed with aquadest until the pH of the peat soil becomes neutral (pH 6.5 - 7.5).

1.5.3 H_2SO_4 Acid Hydrolysis.

At this stage peat soil dregs that have been washed with distilled water to neutral levels, then hydrolyzed with 200 ml of H_2SO_4 solution with a concentration of 0.5%, 1%, 1.5% and 2% during (30, 60, 90, and 120 minutes) with a temperature of 120°C, then filtered. In this process, you will get acidic peat soil with pH 2. Then add NaOH until it reaches pH 5.

1.5.4 The Bioethanol Production Procedures. The process of making bioethanol is done by fermentation. At this stage, peat soil dregs will be fermented with bread yeast and as much as urea as nutrients. In this process, the fermented peat soil will be left for 3 days.

2. Research Method

2.1 Experiment Implementation

Peat soil samples from the Talang Keramat Palembang area were washed with water, dried in the sun and in an oven at 70°C for 20 minutes to remove the water content. The dried peat is reduced in size and then treated using NaOH solution. After that the dried peat is filtered and washed using distilled water. Then hydrolysis using H_2SO_4 acid and continued with fermentation using bread yeast.

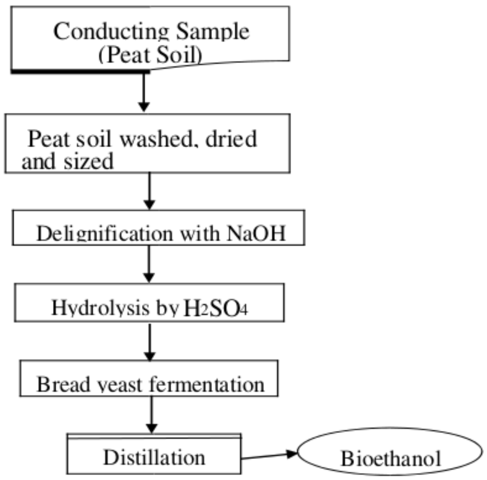

Figure 2. Flow Chart of Bioethanol Making Process from Peat Soil

3. Result and Discussion

3.1 Preparation Step

The peat soil which is taken from Talang Keramat Palembang is processed by washing, drying and grinding it into flour.

3.2 Treatment Stage

3.2.1 Addition NaOH to Peat Soil. A total of 100 g of dried peat soil was treated using 200 ml of NaOH solution (0%, 5%, 10%, and 15%) for 30 minutes at a temperature of 120 °C then filtered. In the above process can produce peat soil with a wet level with a pH of 9 and wet peat soil is obtained with a pH of 9.

3.2.2 Washing of Peat Soil Deposits with Distilled water.

In this process the treated peat soil using 200 ml of NaOH solution and obtained wet peat soil with pH 9 will be washed with distilled water 10 times to the level obtained on peat soil to neutral (pH 6.5-7, 5).

3.2.3 H_2SO_4 Acid Hydrolysis.

At this stage the peat soil has been washed with distilled water to a neutral level, then the peat soil is hydrolyzed with 200 ml of H_2SO_4 solution with a concentration of 0.5%, 1%, 1.5% and 2% during (30, 60, 90 and 120 minutes) then filtered. In this process, you will get acidic peat soil with pH 2. Then add NaOH until it reaches pH 5.

3.2.4 Fermentation.
The process of making bioethanol is done by a fermentation process. In this process peat soil which has gone through the delignification stage, hydrolysis with acid will be fermented with 10 grams of bread yeast and 10 grams of urea accompanied by nutrients. Fermentation will be carried out for 3 days (72 hours).

3.2.5 Distillation.
After the fermentation stage, the purification stage (distillation) is carried out. At this stage the hydrolyzed peat soil that has been fermented will be distilled with a temperature of 80 °C. In this process, the solution will be obtained from the fermentation of peat soil as bioethanol.

3.3 Effect of Sulfuric Acid Concentration and Hydrolysis Time on Percent Yield of Ethanol Produced.
The effect of sulphuric acid concentration and hydrolysis time on percent yield of ethanol produced can be seen from figures below.

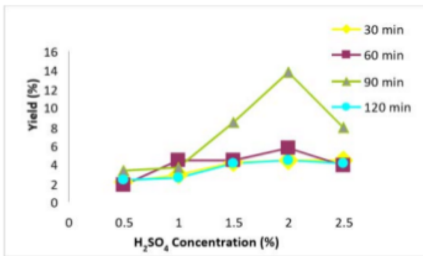

Figure 3. Graph of Effect of time and H_2SO_4 concentration on yield produced (0% NaOH Delignification)

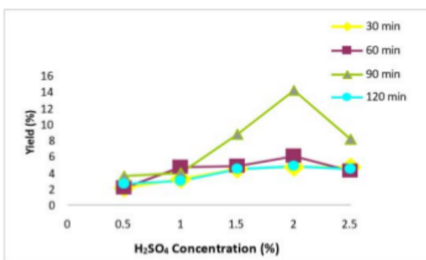

Figure 4. Graph of effect of time and H_2SO_4 concentration on yield produced (5% NaOH Delignification)

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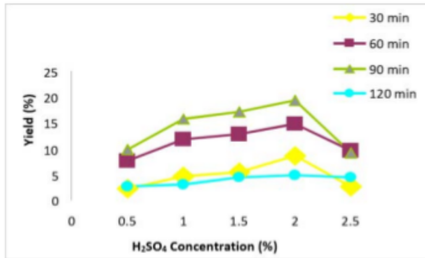

Figure 5. Graph of effect of time and H_2SO_4 concentration on yield produced (10% NaOH Delignification)

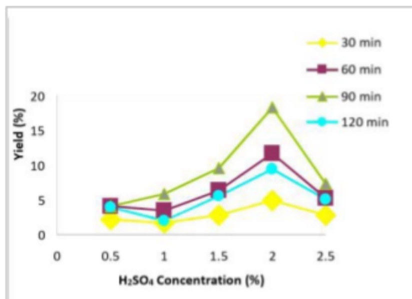

Figure 6. Graph of effect of time and H_2SO_4 concentration on yield produced (15% NaOH Delignification)

In the graphical picture, the relationship between hydrolysis time and variation of sulfuric acid concentration on the yield percentage above can be drawn a statement that the optimum point for the hydrolysis process of bioethanol production from peat soil is at 90 minutes hydrolysis time with 2% sulfuric acid concentration. The longer the hydrolysis time, the more cellulose which is converted into simple glucose so that when a lot of simple glucose fermentation process can be converted by Saccharomyces cerevisiae into bioethanol, but at a time longer than 90 minutes, yield tends to decrease this is due to the cellulose may start to burn.

Likewise with variations in sulfuric acid concentration, the higher the concentration of sulfuric acid in the hydrolysis process, the more cellulose which is converted into simple glucose. However, sulfuric acid concentrations of more than 2% are considered economically not optimum because they can be seen from the graphs above that the concentration above 2% of the graph shows the results with the tendency of decreasing yield although not too significant.

Whereas shown in the figures (from 3 to 6) the hydrolysis compared to yield percent time with the variation of sulfuric acid concentration above, the highest yield of ethanol produced in delignification with 10% NaOH concentration yields ethanol yield up to 19.16%. From the graphic, it was also found that the higher the NaOH concentration the greater the ethanol yield produced, but the NaOH concentration above 10% was considered uneconomical because the increase in yield was not too significant.

4. Conclusion

Peat can be used as raw material for bioethanol production because peat contains cellulose which can be converted into glucose by using acid in the process of hydrolysis and yeast in the

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fermentation process. In the delignification process with NaOH, the optimum conditions are obtained at 10% NaOH concentration

At the stage of the hydrolysis process, the optimum operating conditions occur at 90 minutes hydrolysis time and 2% Sulfuric Acid concentration by a yield percentage of 19.16%

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