Increased Cellulose Levels in Organosolv Pretreatment Process in Bioethanol Production

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Abstract. Bioethanol is one type of biofuel that is present as an alternative fuel that is more environmentally friendly and produced from starch-containing foods such as oil palm fronds (PKS). Some methods of processing lignocellulose materials for the manufacture of bioethanol such as organosolv pretreatment which is a key process and determine the next stage, namely hydrolysis, and fermentation in the manufacture of bioethanol. The aim of the study was to extract lignin and improve the accessibility of cellulose. The research method in this study was influenced by variables used, namely operating time (60; 120; 180 minutes), ethanol concentration (35; 55; 75% v/v), operating temperature (100; 120; 150°C), size of coconut midrib 250 mesh palm oil and 1% sulfuric acid concentration (as a catalyst). Research shows that, successfully reducing lignin levels by 3.4% and increasing cellulose levels by 15.11%. Before the treatment of organosolv pretreatment on oil palm fronds, the composition of lignin was 19.8% and 34.3% cellulose content. After treatment of organosolv pretreatment in oil palm fronds, lignin levels became 16.4% and 49.14% cellulose levels. The optimum value is found at 75% ethanol concentration with an operating time of 180 minutes.

1. Introduction

Oil palm frond (OPF) is one type of lignocellulose material that is produced mostly from oil palm plantations and has not been used optimally as an alternative fuel. Oil palm frond can be prioritized in developing lignocellulose biomass-based bioethanol, given the area of land and the number of products that continues to increase every year. Each hectare of land can be produced as much as 1,640 kg of palm oil midrib dry weight [1]. Oil palm frond have a high holocellulose content of 83.5% and palm fronds can be harvested 1-2 midribs throughout the year along with harvesting fresh fruit bunches [2].

Solid waste in the form of shells, empty bunches, midribs and oil palm stems contain 45% cellulose and 26% hemicellulose. This waste produces an unpleasant odor and when burned it produces pollution that can pollute the air. The availability of various raw materials certainly needs to be accompanied by our mastery of bioethanol production technology. Currently, the production
technology of bioethanol from lignocellulose is still in the development stage in both developed and
developing countries. Some of the main obstacles faced by this technology are the presence of lignin
which can inhibit the rate of hydrolysis by blocking the access of enzymes to cellulose, there are at
least strains of microorganisms that can convert hemicellulose to ethanol, the presence of inhibitors,
and the price of expensive enzymes [3].

Bioethanol technology has experienced rapid development in recent years. The pretreatment stage
is a key stage in the production of bioethanol with lignocellulose ingredients and has a variety of
technologies. One of the lignocellulose pretreatment methods is with organosolv (organic solvents).
The success of the research from organosolv pretreatment was carried out by [4] on enzymatic
biomass hydrolysis and [5] carried out on pine fiber. As well as the success of other studies the
organosol process carried out by [6] on the utilization of coffee skin waste and [7] calculated the
feasibility of organosolv processes using aspen plus where the results of organosolv process
optimization were very favorable. The choice of the type of organic solvent used in the organosolv
process depends very much on the economic value of the material. The use of ethanol, methanol,
diethylene glycol, acetone and butanol solvents which give the best results is acetone but when viewed
from an economical perspective acetone is much more expensive than ethanol [8].

Citing from Sanchez [9] organosolv pretreatment is more advantageous in terms of easy
process, not too large pretreatment costs, easy solvent conversion, partially hydrolyzed
hemicellulose and high yield of xylose because almost all of the lignin is colonized and breaks
lignin internal bonds and hemicellulose in making bioethanol. Therefore it is necessary to
develop the best pretreatment method of oil palm lignocellulose using organosolv which is
easy, inexpensive and effective.

2. Methodology

In the form of oil palm fronds (OPF), Merck (100%) Ethanol, Merck 96% Sulfuric Acid, Sodium
Hydroxide (99%) Merck and Aguadest.

2.1 Preparation of Raw Materials

Oil Palm frond obtained from PT. Fajar Baizuri& Brother in Nagan Raya District, Aceh Province. The
midrib is cut from the stem and the outer part of the midrib is peeled to obtain fibrous parts which are
used as raw material in the study. The fibrous raw material is cut into small sizes (2 cm²) to facilitate
the drying process. The drying process of the material was carried out in an oven at 105°C and left for
24 hours to get a constant weight and crushed until it became a powder measuring 250 mesh.

2.2 Process Pretreatment Organosolv Oil Palm Frond

Dry oil palm frond powder is weighed a predetermined amount of weight with a ratio of 1:10
(mass/volume of solvent), then delignified in white liquor (ethanol) with variations in ethanol
concentration, process time and temperature. Furthermore, the holocellulose solids from the process
are separated from the cooking liquid using filter paper and the separated solids are washed using hot
water to clear the filtrate. Pulp (holocellulose) which has been washed and released from the cooking
solution is then dried in an oven at 105°C until a constant weight is obtained.

2.3 Analysis of Lignin Content

Testing the levels of lignin using the Klason method, the procedure for testing lignin levels refers to
SNI 0492: 2008. The principle of testing lignin levels in the pulp is the pulp material dissolved in
sulfuric acid solution and the determination of the level where the lignin deposit results are compared
with the weight of the dry sample in grams.

2.4 Analysis of Cellulose Content

Cellulose content testing was carried out according to SNI 0444: 2009, the principle of testing pulp
was extracted using 17.5% sodium hydroxide solution and heating was carried out at 25°C then the
dissolved part was oxidized using volumetric potassium dichromate solution.

3. Result and Discussion

3.1 The Result From Analysis of Lignin Content and Cellulose Content
The results from the analysis of lignin content and cellulose content with variations in operating temperatures, ethanol concentrations and different processing times are described in Figure 1 and Figure 2 below:

**Figure 1.** The results from analysis of lignin and cellulose content at 100°C for 60 minutes

The results from the analysis in the picture above can be seen that at the operating temperature of 100°C with an operating time of 60 minutes, lignin content and cellulose content contained in the oil palm midrib sample after organosolv pretreatment at the ethanol concentration of 35% which was 17.4% lignin and 41.15% cellulose content. At 55% ethanol concentration decreased lignin content to 17.1% and increased cellulose content to 42.78%, and at 75% ethanol concentration the content of lignin also decreased to 17.0% and increased cellulose to 43.83%. Lignin content at ethanol concentrations was 75% lower than lignin content at 55% ethanol concentration, which decreased by 0.1% and higher cellulose content which increased by 1.05%. This is caused by the high ethanol concentration and the length of operating time which affects the content of lignin content and cellulose content in the sample [10].

**Figure 2.** The results from analysis of lignin and cellulose content at 150°C for 180 minutes

At high process conditions for operating temperatures of 150°C with an operating time of 180 minutes can reduce lignin content and increase cellulose content gradually. The process conditions
with time and operating temperature from 35% ethanol concentration to 75% ethanol concentration succeeded in reducing lignin content by 0.7% and were able to increase cellulose content by 1.63%. The results of the analysis after organosolv pretreatment in oil palm midrib samples, succeeded in reducing lignin content in the sample with the optimum value of the lowest lignin content and the highest cellulose content at an operating temperature of 150°C and operating time of 180 minutes with a 75% ethanol concentration of 16.4% and 49.41%.

3.2 Optimization of the solvent concentration and time of operation

In this study, it was known that the concentration of organic solvents and operating time greatly influenced the content of lignin and cellulose levels in the pretreatment of oil palm frond organosolv for the manufacture of bioethanol. The decrease in lignin levels and an increase in cellulose levels which occur along with the addition of organic solvent concentration and operating time. According to [10], an increase in cellulose levels occurs because the longer the contact time of solvents with the structure of lignocellulose in the material, it will increase the accessibility of cellulose and extract lignin. In figure 3, the effect of ethanol concentration and optimum operating time on bioethanol is shown as follows:

![Figure 3. Effect of solvent concentration and optimum operating time on bioethanol](image)

Regarding the results in Fig. 3 above, it can be seen that lignin and cellulose content without treatment have the high lignin content of 19.8% and low cellulose content of 34.3%. While after treatment with 75% ethanol concentration and operating time of 180 minutes, it can reduce lignin content to 16.4% and increase cellulose content to 49.41%. Based on these results, it can be concluded that the operating time and ethanol concentration greatly influences the content of lignin and cellulose in the oil palm midrib sample, because of the length of operating time and the high ethanol concentration, the lower the lignin content and the greater cellulose content in the midrib sample. Oil palm compared without treatment with operating time and ethanol concentration.

4. Conclusion

From the results of this research that has been carried out with the process conditions that have been applied to the research, some conclusions can be drawn as follows:

1. Ethanol concentration and process time greatly affect the content of lignin and cellulose in oil palm midrib samples, the higher the ethanol level and the longer the processing time, the lower the lignin content and the higher the cellulose content.
2. The lignin content of the organosolv pretreatment process in oil palm midrib decreased by 3.4% from 19.8% to 16.4%.
3. Cellulose content from the results of organosolv pretreatment on oil palm midrib increased by 15.1% to 34.3% to 49.4%.

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