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Bioethanol Production from Coconut Coir Using Ozonolysis-Hydrolysis-Fermentation-Distillation-Silica Gel Adsorption Method

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Abstract: The utilization of coconut coir as a feedstock for bioethanol production offers an innovative approach to valorizing agricultural residues in the South Sumatra region. Given the high lignin content of coconut coir, lignin removal pretreatment was necessary to enhance cellulose accessibility for hydrolysis. This study investigated the impact of ozonolysis duration on lignin and cellulose content and, the potency of silica gel adsorption. The experimental design involved ozonolysis, hydrolysis, fermentation, distillation, and silica gel adsorption. Results revealed that 25 minutes of delignification significantly reduced lignin content by 8,3%. Cellulose content increased by 3,1%. Optimal ozonolysis conditions, coupled with pH stabilization at 4.5 using NaOH, led to enhanced 500 mL bioethanol volume after 7 days of fermentation. The application of 10 grams of white silica gel for 60 minutes showed an ethanol content of 97% from GC-MS analysis.
Keywords: coconut coir, ozonolysis, adsorption, white silica gel, bioethanol

1. Introduction

The interest in supporting the transformation towards net zero emission as climate change prevention and supporting clean energy in the future, the government has realized several principles, such as increasing the use of new renewable energy (NRE), reducing fossil energy, using electric vehicles in the transportation sector, increasing the use of electricity in households and industries, and utilizing Carbon Capture and Storage. Biofuels are a category of new and renewable fuels made from organic materials such as plants, algae, and organic waste [1].

Bioethanol is a type of biofuel produced from raw materials that are not intended for human consumption and presents a more sustainable and resource-efficient approach. In contrast to first-generation bioethanol produced from raw materials such as sugar or starch, second-generation bioethanol is produced from lignocellulosic materials, such as agricultural, forestry, or inedible plant waste such as crop residues, straw, bagasse, and coconut [2] such as young coconut waste can be utilized into bioethanol and affect CO and HC gas emission content [3]. Several regions in South Sumatra are the largest coconut producers, namely Banyuasin Regency with 46,716 tons, Musi Banyuasin with 6,350 tons, and Ogan Komering Ilir Regency (OKI) with 1,705 tons [4].

Coconut coir contains fiber, and glucose as the main component, most of which comes from alpha-cellulose [5] and can produce bioethanol through the fermentation process. The purpose of ozonification is to observe the effect of lignin dissolution in enzymatic saccharification [6]. Normal pressure and room temperature conditions in the pre-treatment do not allow the formation of inhibitor compounds that can hinder the fermentation process. The moisture content of lignocellulosic material affects the maximum rate of its reaction with ozone [7]. Important variables in ozonolysis are pH, consistency, time, temperature, and ozone concentration [8], oxygen flow and sample size also affect statistical analysis [9].

2. Material and Methods

2.1. Materials

Coconut coir from Banyuasin district was cut and crushed into powder, then sifted using a 60 mesh sieve. The sifted coconut coir was added with 1% water and then put into a chiller for 24 hours.

2.2. Methods

Coconut coir pre-treatment process with ozonolysis delignification. The coconut fiber ozonolysis process uses an ozone generator. 5 grams of dried coconut coir was put into the reactor, carried out with variations in contact time (10, 15, 20, 25 minutes), and a flow rate of 3 L/min. then removed and rinsed with water. The ozonated samples were analyzed for lignin content using the Chesson datta.

Coconut coir weighing 18 grams was put into a 1000 mL Erlenmeyer to be hydrolyzed. H_2SO_4 was added to each sample with a concentration of 8% N as much as 500 mL. Close the Erlenmeyer by using a cork.

Hydrolysis treatment is given by heating the Erlenmeyer containing the sample at 121°C using an autoclave for 60 minutes. After the process is complete, let the sample cool and then separate the substrate and solution. The solution containing reduced sugar from hydrolysis was analyzed with a DNS reagent and measured with a spectrophotometer.

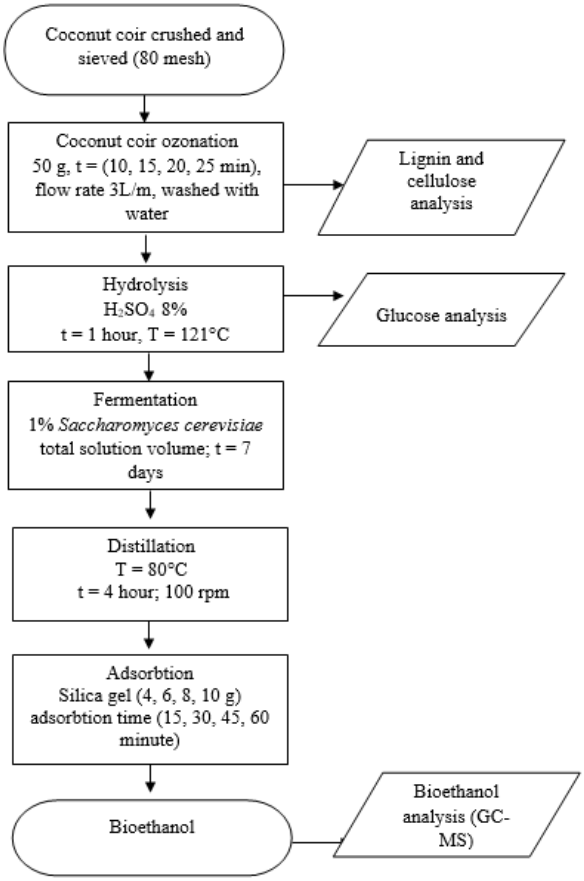

Figure 1. Bioethanol Production Flowchart

The hydrolyzed filtrate containing glucose is then fermented. Use a 500mL Erlenmeyer that has been sterilized, then add *Saccharomyces cerevisia*e yeast as much as 1% (w/v) then adjust the pH of the solution to 4.5-5. The sample that has been prepared, is closed using a cork, connect the Erlenmeyer with a bottle filled with water using a hose, and let the fermentation process takes place for 7 days.

The distillation process in this study uses a simple distillation device. This process utilizes the difference in boiling points between water and ethanol, the temperature on the heating mantle was set 80˚C. The sample was put into the distillation flask, and then steam was low into the condenser. The distillation process was carried out until the sample was collected in the receiving flask. Analysis of bioethanol content by gas chromatography method.

Silica gel was put into a glass baker with a variation in the amount of silica gel and a variation in adsorption time (15, 30, 45, 60 minutes). Then filtered using filter paper and measured the volume change. This stage is physical adsorption because there is direct contact with the absorbent (silica gel) without any chemical reaction (Figure 1).

3. Results and Discussion

3.1. Effect of Delignification Time on Lignin and Cellulose Content

The study has been conducted with variations in delignification time. The ozonolysis reaction began with the formation of the primary ozone complex when ozone was added by the double bond in Figure 2. This interaction produced Criegee intermediates, which were crucial in the subsequent reaction steps. The primary ozonide, a highly unstable three-membered cyclic compound, easily decomposes into two parts. This process involves a chemical bond break (homolytic) that produces a carbonyl oxide (Criegee biradical) and an aldehyde or ketone. The high tensitivity of the small ring of the primary ozonide initiated this cleavage. This decomposition was key in the ozonolysis reaction [10].

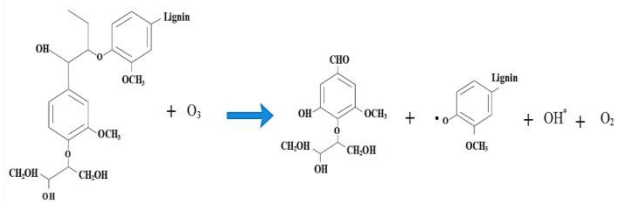

Figure 2. Lignin Degradation Reaction by Ozone [11]

Determining cellulose and lignin content using the Chesson-Datta method. The results in Figure 3. demonstrated changes in lignin content (blue line) and changes in cellulose content (red line).

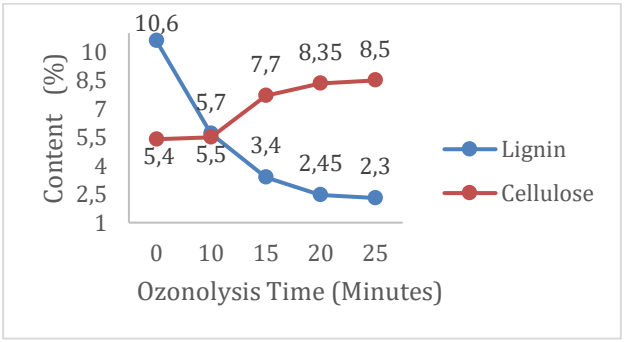

Figure 3. Graph of Ozonolysis Time, Lignin, and Cellulose Content

The reaction time of 25 minutes decreased the lignin content by 8.3 percent and the highest increased cellulose content was 3.1 percent. A sample with 60 mesh size has a significant impact on ozonolysis delignification [12], coconut coir was contaminated with O_3 then entered the pores of lignocellulose and broke chemical bonds to form new bonds which caused a decrease in lignin content and an increase in cellulose content. Lignin is more reactive with ozone than cellulose because based on the structure of lignin is more complex and irregular, with many double bonds so easily absorbed by ozone.

In hybrid ozonation-ultrasonic research [11] lignin content was up to 2.27% and cellulose 90.01% of palm mesocarp fibers at 40°C for 60 minutes. Cellulose has a more regular and linear structure, with more stable glycosidic bonds [13]. The increase of cellulose up to 7% in sugarcane amaranth occurs due to the response of reduced lignin content with ozonolysis and acid delignification [14].

There are several factors that affected the progress of the ozonolysis process, for example, raw material, reaction time, ozone generator, and particle size. The coconut coir that was analyzed has a lignin content of 10.6% of 1 g sample, this is influenced by the factor of coconut fruit growing in Banyuasin land, the age of the coconut fruit, and the coir so that it contains lignin levels that were not as high as many have studied. lignin content in ozonolysis is also related to process time, the longer ozonolysis made ozone absorbed on the surface of lignin the more electrons were degraded [15]. Ozonolysis reaction time longer than 60 minutes does not have a significant effect, because the longer the reaction time has an impact on the surface of lignocellulose and ozone would attack holocellulose causing degradation not maximized [11].

3.2. Effect of Cellulose on Glucose Content

In this study, the highest glucose content was 2.4% at 8.5% cellulose minutes, indicating that glucose content increases with increasing ozonolysis time in Figure 4. analyzed by refractometer.

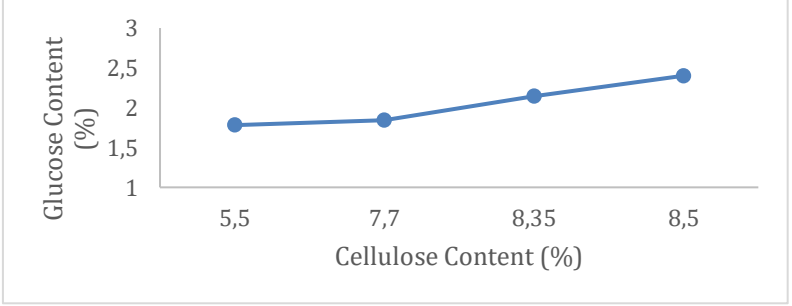

Figure 4. Graph of Cellulose on Glucose Content

Glucose is formed from the conversion of cellulose due to acids that accelerate the reaction of carbohydrate breakup [16]. Sulfuric acid 8% affects glucose content because the higher acid concentration degraded into glucose [17]. In this study, ozonolysis has an effect because two oxygen atoms become three oxygen atoms (ozone) due to the presence of electrical charges that change the structure of the cellulose chain. Ozone will increase the surface area accessible to water so as to accelerate the rate of hydrolysis and products will be formed.

3.3. *Effect of Bioethanol Purification*

After Fermentation, the distillation process continued effectively separating impurity compounds in fermented mixtures affected the physical properties of bioethanol which was clearer without any impurities/sediment. Purification with simple distillation method was chosen because it can increase ethanol levels [18]. Results of research [19] showed an increase in ethanol from 27% to 96%, in contrast to [20] using distillation and adsorption increased from 13.61% to 85.18%. Distillation was carried out for 4 hours until the ethanol did not drip anymore [21] this study obtained 400-500 mL distillate.

3.4. *Effect of Adsorption Time on Bioethanol Volume*

The graph showed several lines with different colors, each of which represents an experiment with a different amount of silica gel (4 g, 6 g, 8 g, and 10 g). Indicated that the amount of silica gel has an influence on the ozonolysis process.

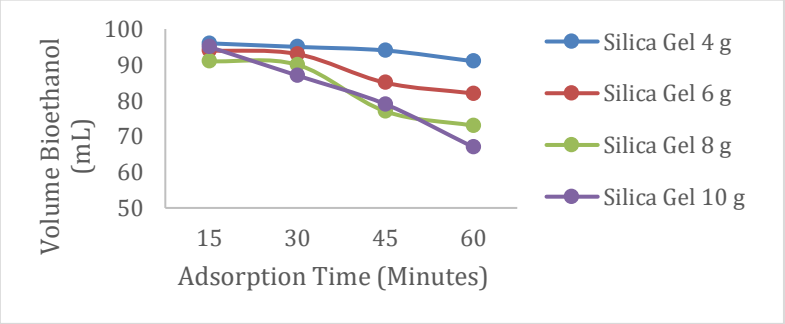

Figure 5. Effect of adsorption time on volume in 10 minutes deliginification

Figure 5. showed sample 10 minutes deliginification. Volume likely decreased with time in the variation of the amount of silica gel. This indicates several factors that cause volume decrease, such as volatilization, absorption, or chemical reactions resulted product with a smaller volume. Filtering technique, and filtering time also affect the final volume.

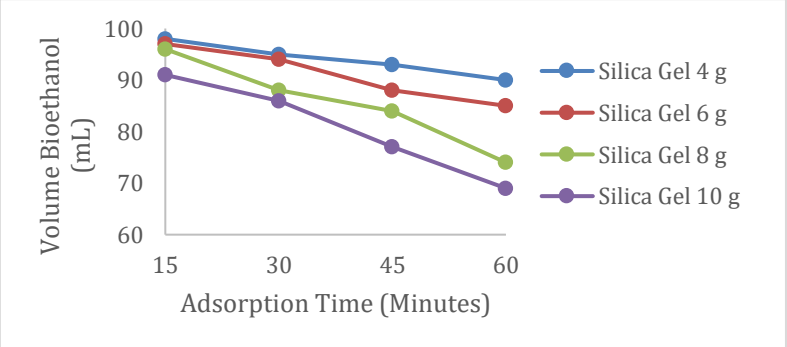

Figure 6. Effect of adsorption time on volume in 15 minutes deliginification

Figure 6. In sample 15 minutes delignification, volume tends to decrease time for all variations in the amount of silica gel, the more silica gel used, the higher the volume decreased. Silica gel served role in absorbing water molecules because it contained hydrophilic properties. Figure 7. Showed the effect of the amount of silica gel on volume change during the adsorption process. It can be seen that the more silica gel added, the faster the volume decrease occurs. The decrease seems to be stable because during the 3rd experiment the sample was closed in order to reduce the vaporization of the product, and the absorption process was optimized.

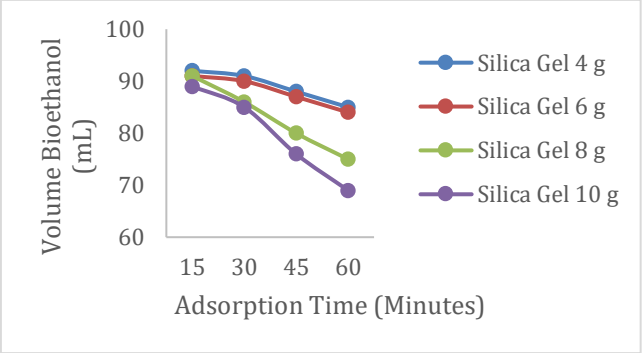

Figure 7. Effect of adsorption time on volume in 20 minutes deliginification

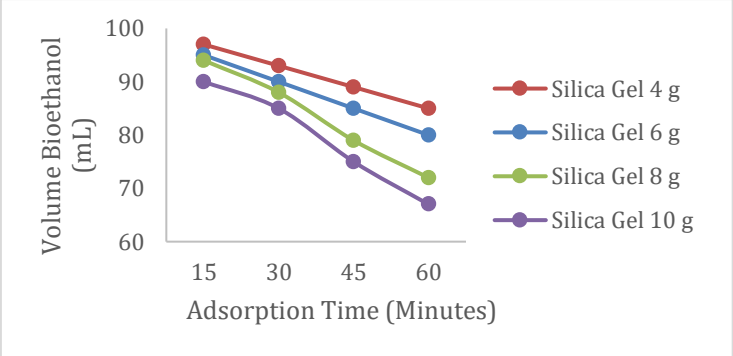

Figure 8. Effect of adsorption time on volume in 25 minutes deliginification

Figure 8. showed that the amount of silica gel has a significant effect on the change in the final volume of adsorption. Factors that influenced the adsorption volume change were accuracy in carrying out work procedures such as keeping evaporation from occurring, silica gel which was continuously renewed so that it could absorb water molecules as much as possible, and adsorbate filtration which took time until the volume could be measured properly.

Volume reduction occurs due to increased purity caused by water trapped in the adsorbent [22]. The best results at 60 minutes [23] were able to increase the bioethanol content from 39.8 ± 9.9% to 72.0 ± 1.1%. [24] conducted adsorption distillation for 60 minutes of wine with silica gel to obtain 92.65% ethanol. Adsorption in this study produced a final product of 67 mL, in a sample of 25 minutes of pre-treatment because the more the amount of silica gel, the more water was absorbed in the pores of silica gel.

Silica gel has three-dimensional structure consisting of interconnected silica networks, forming pores of various sizes. These pores act as traps for water
molecules silica gel has the potential to reduce water content along with soaking time (adsorption) to get maximum results. Based on research [25] ethanol-water adsorption distillation using blue silica gel is more effective than white silica gel because the reaction time is faster than 45 minutes.

Different from the experiments that have been carried out when blue silica gel was contacted on bioethanol from coconut fiber there was a color change from clear without color to pink, this is because blue silica gel contains Cobalt (II) chloride as a color indicator that reacts with bioethanol so that side reactions occur that can reduce the quality of bioethanol produced. When white silica gel is used as an adsorbent, no physical changes occur so it can be used to reduce water content.

3.5. GC-MS analysis

GC-MS analysis to identify and measure chemical compounds in samples with a very high level of sensitivity and accuracy.

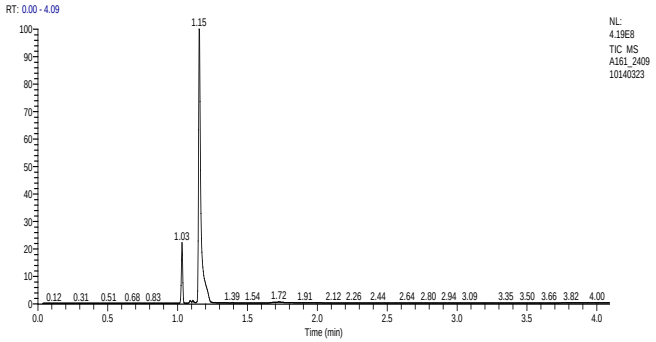

Figure 8. GC-MS Analysis Results on Sample 20 minutes delignification

Figure 9. shows the chromatogram of samples analyzed for bioethanol products (20 minutes of ozonolysis) in the retention time range of 0 to 4 minutes. Based on the results obtained, chromatographic analysis shows the detected ethanol compound 97.08% visible peak at the retention time of 1.15 minutes. Based on the results of GC-MS analysis, the retention time of 1.03 detected oxygen compounds, Hydrazinecarboxiamide. and Carbohydrazide. At retention time 1.16, ethanol (CAS 64-17-5), Hydrazine, methyl- and Dimethyl ether compounds were detected.

4. Conclusion

This study aims to produce bioethanol with a high level of purity. The results of bioethanol production indicated the great potential of coconut waste as a renewable energy source with the ozonolysis method followed by purification. Compared to previous studies, this research uses different types of waste and methods to obtain quite high bioethanol purity outcomes. However, further research needed to be conducted to optimize production methods and analysis to produce bioethanol according to Indonesian national standards.

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