

The Addition of Zeolite Adsorbents and Calcium Oxide on Purification of Bioethanol from Sugar Palm (*Arenga pinnata* Merr)

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Abstract. Bioethanol (C_2H_5OH) is a biochemical liquid produced by microorganisms through fermentation process on sugar molecules from carbohydrates. Bioethanol is a fuel of vegetable oil that has similar properties to premium. With its main product of palm juice, Sugar palm (*Arenga pinnata*) is a potential source of sugar and carbohydrate for bioethanol production. Production of palm juice can reach up to 12-14 liters/tree/day with total sugar content in palm juice ranges from 12-15%. The purpose of this research was to produce highly-concentrated bioethanol from palm juice through fermentation process to substitute fossil fuel. This study was conducted with three stages of treatment, namely: the fermentation of palm juice, distillation of bioethanol, and purification of bioethanol with the addition of adsorbent zeolite and calcium oxide.

Keywords: Adsorption, fermentation, sugar

1. Introduction

The rapid growth on industrial and world population these days have resulted in a greater demand for energy source. Approximately 90% of the energy required is obtained from non-renewable fuel sources, such as fossil fuel [1]. Recent study reported that the amount of fossil fuel exploited continue to increase annually, and thus leading to the depleting amount of the fossil fuels itself [2]. As a result for the declining amount of fuel supply, the researchers worldwide are now intensively seeking for renewable and environmentally friendly energy sources. Some sources of renewable energy that we have discovered are solar, water, geothermal, and biomass [2].

Bioethanol (C_5H_2OH) is a biochemical liquid with the same properties as gasoline. Bioethanol itself is a product of sugar fermentation from carbohydrates with the help of microorganisms [3]. There are two forms of raw materials used to produce bioethanol: solid and liquid. The solid form includes corn, wheat, cellulose, algae and bagasse, while liquid form includes the palm juice from coconut (*Cocos nucifera*), nipa (*Nypa fructicans*), and sugar palm (*Arenga pinnata*). Between the two forms, liquid like palm juice has advantages over the solid form, mainly because that they can be directly fermented without initial processing, in which means that the time needed to produce the bioethanol will be shortened. Solid-formed materials, on the other hand, must go through a process of hydrolysis to convert starch polymers into simple sugars, whereas cellulose must be hydrolysed in order to obtain the sugar molecules [4].



One of the plants that is potential to be utilized as raw material for bioethanol production is Sugar palm (*Arenga pinnata*). Palm trees are known to have a high amount of sugar, and they grow widely in 14 provinces in Indonesia such as Papua, Maluku, North Sumatra, North Sulawesi, and South Borneo. Data from the Directorate General of Plantation in 2004 showed that the land area dominated by sugar palm reached 60,482 Ha. The sugar content of palm sugar is approximately 12-15%, while the sugar content found in coconut palm and siwalan palm is 10.27% and 10.96% respectively. This information proved that Sugar Palm has great potency to be utilized as raw material in bioethanol production [5].

Preparation of bioethanol from sugar palm was conducted through three stages of the process, that is, fermentation, distillation, and bioethanol purification process. During the fermentation process, sucrose is broken down into glucose and fructose; the glucose molecules are then converted into bioethanol by *Saccharomyces cerevisiae* yeast. Looking into details, the sugar molecule as substrate is firstly converted to pyruvic acid through glycolysis. Afterwards, pyruvic acid is then converted into acetaldehyde and carbon dioxide with the help of pyruvate decarboxylase enzyme, which is then followed by the conversion of acetaldehyde into alcohol in the presence of alcohol dehydrogenase. The purification of bioethanol are going through the principle of distillation and adsorption by using porous media to absorb water contained in the bioethanol [6]. However, in order to be used as a renewable fuel, bioethanol must have at least > 99% concentration and is anhydrous so as not to be corrosive and damage the vehicle parts [7].

2. Methods

2.1 Experimental apparatus

To perform the study, an experimental apparatus has been designed and developed including the reactor for the fermentation process, as well as distillation Apparatus. After bioethanol is repeatedly distilled, bioethanol is redistilled using calcium oxide. To be purified using natural zeolite, bioethanol must first soaked using H₂SO₄ for 2 hours, and then soaked with natural zeolite for 5 hours.

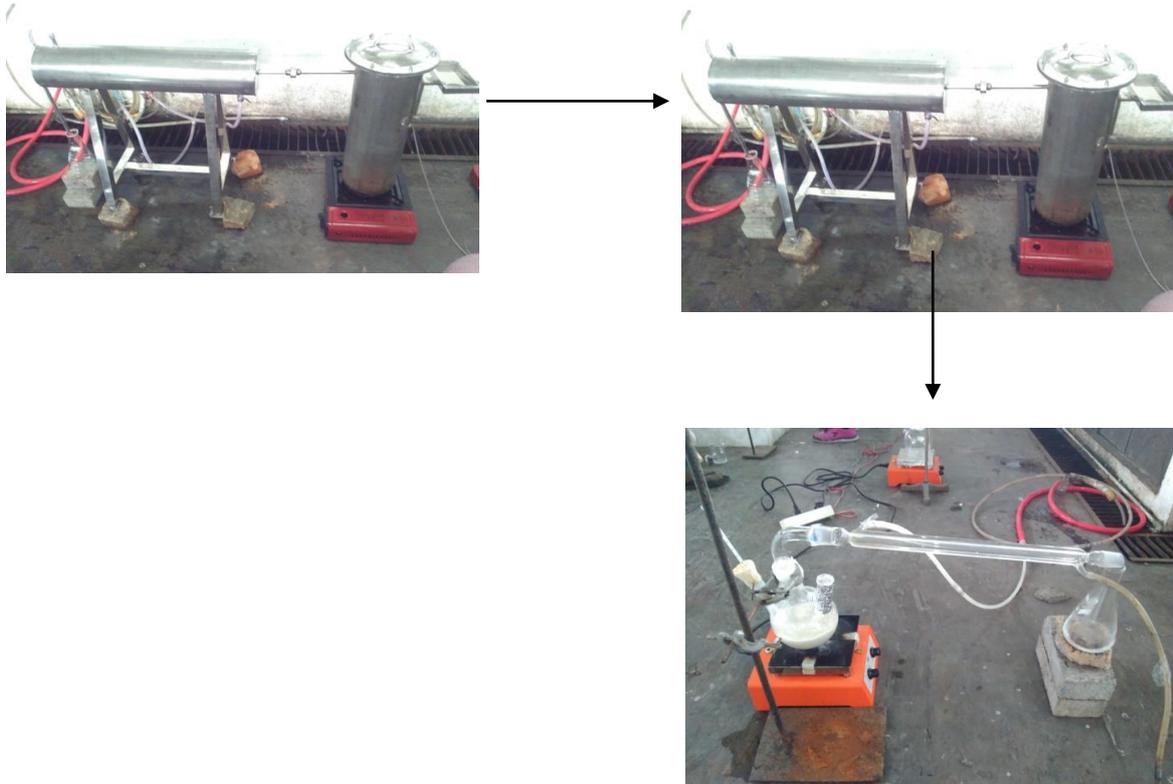


Figure 1. Distillation Apparatus for Calcium Oxide

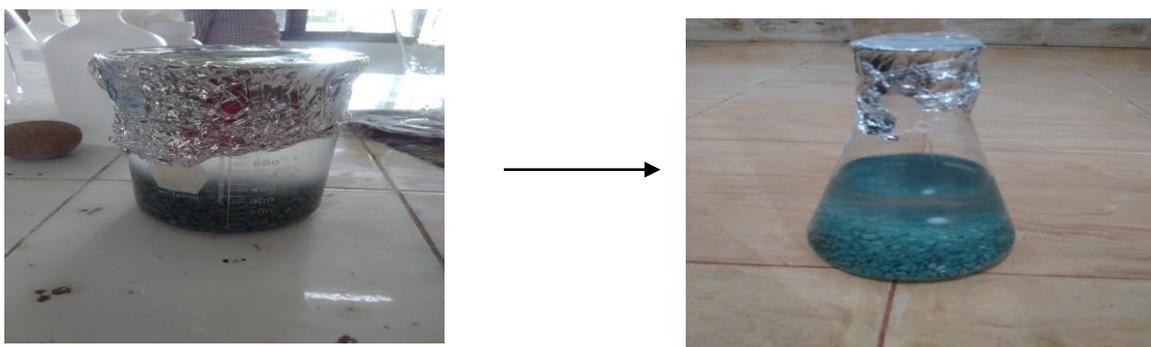


Figure 2. Experiment Apparatus for the purification of bioethanol with natural zeolite

2.2 Production of Bioethanol

Palm juice obtained from Sugar Palm (*Arenga pinnata* Merr) was inoculated with yeast *Saccharomyces cerevisiae* and left for up to 4 days to observe the optimum time for bioethanol production. The daily concentration of the bioethanol in the palm juice was measured afterwards.

2.3 Effect of Calcium Oxide Addition in Distillation Process

This process was done by adding calcium oxide powder during the distillation process of the bioethanol at 78 °C. The concentration of bioethanol obtained in this process was measured using Gas Chromatography method and then compared with the normal process without the addition of calcium oxide.

2.4 Effect of Natural Zeolite Addition in Purification Process

Natural zeolite used as adsorbent in this process was activated by soaking the natural zeolite into 1M sulfuric acid to remove other particles from the zeolite while increasing its ability so absorb water from the ethanol. The natural zeolite was then heated in the oven at 200°C for 2.5 hours to activate the zeolite pores to absorb the water in ethanol. After the activation, ethanol was soaked using natural zeolite and kept for 5 hours.

2.5 Problem formulation

Concentration of bioethanol was measured using Gas Chromatography method, while the concentration calculation was done using the formula below:

$$C_{\text{sample}} = \frac{(\text{sample areas} \times \text{sample concentration})}{\text{standard areas}} \% \quad (1)$$

3. Results and Discussion

3.1 Effect of Fermentation Time on Bioethanol Produced

The effect of fermentation time (up to 4 days) on bioethanol concentration was measured and the result can be seen in Figure 1 below.

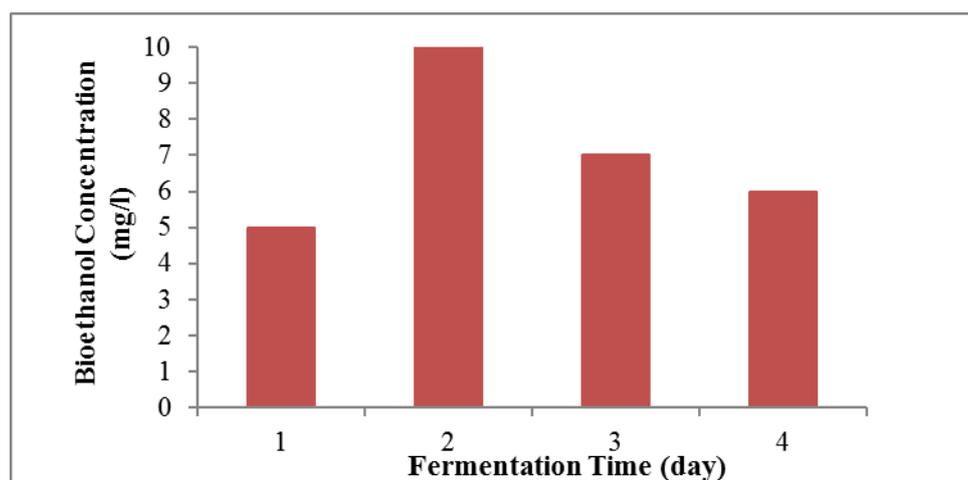


Figure 3. Effect of Fermentation Time on Bioethanol Produced

It can be seen from Figure 1 above that the concentration of bioethanol produced in the fermentation process increased from day 1 (5%) to day 2 (10%). However, the concentration dropped considerably

on the third and fourth day of the fermentation process, with 7% and 6% respectively. This means that the optimum time for *Saccharomyces cerevisiae* to multiply and produce bioethanol is approximately two days (48 hours). Subsequently, after reaching the optimum growth condition, the concentration of bioethanol in the medium will increase to about 10%, which will then start to become toxic for the cells and caused the activity of *Saccharomyces cerevisiae* to decrease [8].

The concentration of bioethanol beyond 10% is bad for yeast cell growth because they can be toxic to yeast cells, in which so that the maximum concentration of bioethanol allowed on yeast growth is 10%. This is due to that the enzymes in the yeast cells such as dehydrogenase and hexokinase are sensitive to high ethanol conditions, which then afterwards can interfere and become toxic to yeast growth activity [9].

To conclude, an appropriate fermentation time is required to produce high concentration of bioethanol [10]. The increasing fermentation time led to the further reaction of bioethanol, typically oxidation of the bioethanol itself to acetic acid. In this case, the oxidation rate of bioethanol to acetic acid is higher than the rate of glucose converted to bioethanol, and thus causing the decrease amount of the bioethanol.

3.2 Effect of Addition of Calcium Oxide (CaO) in the Distillation Process

Distillate obtained was analyzed using GC (Gas Chromatography) to calculate the percentage of the ethanol produced after the purification process using distillation by the addition of CaO adsorbents. The observational data using GC (Gas Chromatography) can be seen in Table 1 below.

Table 1. Observational Data Using GC (Gas Chromatography)

No.	Name	Areas	Information
1	Ethanol Pa (1)	2.199.609	H = 5.861.90 T = 1.896
2	Ethanol Pa (2)	80.089.032	H = 31.317.514 T = 2.001
3	Ethanol Sample + CaO (1)	3.172.001	H = 8.546.98 T = 1.889
4	Ethanol Sample + CaO (2)	84.234.345	H = 30.665.978 T = 2.002

The GC measurement was conducted with two replication, in which then the concentration can be observed by measuring the average of both the sample and standard area using the calculation below:

$$\text{Sample Area} = \frac{3.172.001 + 84.234.345}{2}$$

$$= 43.703.173$$

$$\text{Standard Area} = \frac{2.199.609 + 80.089.032}{2}$$

$$= 41.144.320.5$$

Subsequently, the bioethanol concentration can be calculated by the following formula:

$$C_{\text{sample}} = \frac{(\text{sample areas} \times \text{sample concentration})}{\text{standard areas}} \%$$

$$= \frac{43.703.173 \times 94}{41.144.320.5}$$

$$= 99.85\%$$

It can be seen that the concentration of the bioethanol produced using calcium oxide (CaO) adsorbent was 99.85%. The addition of calcium oxide (CaO) to the distillation process resulted in the increment of the bioethanol concentration, from 94% for the initial purification to 99.85%. The excellent result in this study was typically caused by the ability of calcium oxide to bind the water molecules contained in the bioethanol, which then makes it able to reach > 99% concentration.

3.3 Effects of Natural Zeolite Adsorption in Purification of Bioethanol

Data of the concentration value of bioethanol through adsorption process using activated zeolite analyzed by using GC (Gas Chromatography) method can be seen on the Table 2 below.

Table 2. Observation Data Using GC (Gas Chromatography)

No.	Name	Areas	Information
1	Ethanol Pa (1)	2.199.609	H = 5.861.90 T = 1.896
2	Ethanol Pa (2)	80.089.032	H = 31.317.514 T = 2.001
3	Ethanol Sample + Zeolite (1)	1.804.169	H = 8.546.98 T = 1.889
4	Ethanol Sample + Zeolite (2)	80.044.205	H = 30.665.978 T = 2.002

The GC measurement was conducted with two replication, in which then the concentration can be observed by measuring the average of both the sample and standard area using the calculation below:

$$\text{Sample Area} = \frac{1.804.169 + 80.044.205}{2}$$

$$= 40.924.187$$

$$\text{Standard Area} = \frac{2.199.609 + 80.089.032}{2}$$

$$= 41.144.320.5$$

Subsequently, the bioethanol concentration can be calculated by the following formula:

$$\begin{aligned}
 C_{\text{sampel}} &= \frac{(\text{sample areas} \times \text{sample concentration})}{\text{standard areas}} \% \\
 &= \frac{40.924,187 \times 94}{41.144.320.5} \\
 &= 95 \%
 \end{aligned}$$

It can be seen that the concentration of bioethanol obtained using the activated zeolite adsorbent was 95%, compared to the normal bioethanol purification which was 94%.

Research conducted by Novitasari and Kusumaningrum [6] showed that the variation of adsorption time of natural zeolite and 4A synthetic zeolite (8, 24, 32, 48 and 56 hours) showed different results at 84.34%, 81.92%, 74.49%, 72% and 74.92% respectively. This result indicated that the longer zeolite immersed in ethanol solution, the lower concentration of ethanol obtained from the adsorption process. This is due to that natural zeolite absorbs not only the water but also the ethanol produced itself. In addition, natural zeolites have varying pore sizes that more ethanol being absorbed could mean more water molecules released.

The 95% purity result obtained from this study is also in accordance with research conducted by Frita et al. [11], who purified 94% of ethanol using natural zeolite adsorbent with zeolite grain size of 50 mesh, 80 mesh, 100 mesh and 200 mesh showed increase to 95%, 95%, 95.5% and 95.5% respectively. The increment that only reached 95.5% from the initial concentration of 94% concluded that the higher concentration levels of the ethanol in the initial process to be adsorbed by zeolites, the less amount of concentration can be improved.

4. Conclusions

This study proved that the optimum fermentation time for *Saccharomyces cerevisiae* to produce bioethanol from palm sugar is approximately two days or 48 hours with 10% bioethanol concentration. The best bioethanol purification (up to 99.8% concentration) can be obtained by the addition of calcium oxide (CaO) during the process. The bioethanol produced in this research can be used as a fuel as its concentration is in line with the Indonesian Standard (SNI), which is > 99%. The success of this research proves that bioethanol obtained from palm juice can be utilized as an alternative substitute to fossil fuels.

Acknowledgments

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References

- [1] Duruyurek M, Dugun C, Fuat G, Mehmet, Zeliha S (2015) Production of Bioethanol from Waste Potato. *Turkish Journal of Agriculture Food Science and Technology*, 3(5): 331, 334, 2015.
- [2] Wijaya I Made Anom Sutrisna, Arthawan I Gusti Ketut, Sari AN (2012) Potensi Nira Kelapa Sebagai Bahan Baku Bioetanol". *Jurnal Bumi Lestari*, Vol. 12, No.1.
- [3] Gusti (2016) Pengaruh Suhu dan Volume Starter dalam Pembuatan Bioetanol dari Nira Aren (*Arenga Pinnata Merr*). Skripsi. Medan. Universitas Sumatera Utara.
- [4] Manurung MM (2016) Pengaruh Volume Starter dan Agitasi dalam Pembuatan Bioetanol dari Nira Aren (*Arenga Pinnata Merr*). Undergraduate Thesis. Universitas Sumatera Utara.

- [5] Akhir, YM, Chairul, Drastinawati (2015) *Pembuatan Bioetanol dari Fermentasi Nira Aren (Arenga Pinnata) Menggunakan yeast Saccharomyces cereviceae dengan Pengaruh Variasi Konsentrasi Nutrisi dan Waktu Fermentasi* JOM FTEKNIK 1(1).
- [6] Novitasari DD, Kusumaningrum (2012) *Pemurnian Bioetanol Menggunakan Proses Adsorbs dan Distilasi Adsorbsi dengan Adsorben Zeolit*. Jurnal Teknologi Kimia dan Industri, 1(1): 534-539.
- [7] Yuliana C, Silvia RY (2015) *Pemurnian Bioetanol Hasil Fermentasi Nira Nipah Menggunakan Proses Destilasi Adsorpsi pada Variasi Rasio Adsorben dengan Modifikasi* . JOM FTEKNIK 2(1).
- [8] Kunaepah U (2008) *Pengaruh Lama Fermentasi dan Konsentrasi Glukosa terhadap Aktivitas Antibakteri, Polifenol Total dan Mutu Kimia Kefir Susu Kacang Merah*. Thesis. Semarang. Universitas Diponegoro.
- [9] Neto, Pedro de Olivia, Claudia, Dorta, Ana F, Azevedo C, Valeria MGL, Douglas FS. (2013) *The Brazilian Technology of Fuel Ethanol Fermentation-yeast Inhibitors*
- [10] Azizah NANA, S Mulyani (2012) *Pengaruh Lama Fermentasi Terhadap Kadar Alkohol, PH, dan Produksi Gas Pada Proses Fermentasi Bioetanol dari Whey Dengan Substitusi Kulit Nanas*. Jurnal Aplikasi Teknologi Pangan. Vol. 1. No. 2.
- [11] Frita, Ornella, Ratnawulan, Gusnedi (2015) *Pengaruh Ukuran Bulir Zeolit Terhadap Kadar Bioetanol dari Tanaman Tebu (Saccharum officinarum)*. Pillar of Physics 5: 49-56
- [12] Directorate General of Plantation (2004) *The development of sugar palm in Indonesia*. Proceedings of Seminar Nasional Aren. Research Institute for Coconut and Other Palms: 138-144.