Distillation-Adsorption of Bioethanol Using Natural Kaolin

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Abstract. Bioethanol has been known as one of the alternative energy sources to replace petroleum. The use of bioethanol as a fuel has requirements that must meet fuel standards or refer to as Fuel Grade Ethanol (FGE). Further refining is required to achieve this qualification. The distillation method is the most commonly used method in bioethanol purification, but the results are less than optimal and sometimes the ethanol produced will be more volatile. Distillation-adsorption method using clay-based materials was developed to solve this problem. The purpose of this study is to purify bioethanol and determine the physical characteristics of the bioethanol produced and to assess the % purity of bioethanol from adsorption distillation. Characterization of activated natural kaolin as adsorbent, determination of the optimum contact time in the distillation-adsorption process, determination of the optimum mass of kaolin used and determination of the physical properties of bioethanol have been carried out. The results showed that 1 hour adsorption distillation could increase the ethanol content from 7.9% to 29.33%. In the study of the effect of the mass of kaolin, the optimum result was 25.25% ethanol using a mass of 5 grams. Physical properties test of bioethanol obtained a density of 0.8211 gr/cm³ and a viscosity of 2.096 cps.

1. Introductions
Global warming is one of the major impacts contribute by fossil fuels. In 2010 the number of vehicles in the world reached more than 1 billion and increasing continuously. Global transportation sector contributes 19% of carbon dioxide (CO₂), and more than 70% of carbon monoxide (CO) [1]. This certainly raises CO₂ emissions level on the earth's surface. This strengthens the government's reason for developing alternative energy sources as a substitute for fossil fuels as outlined in the Presidential Regulation of the Republic of Indonesia Number 5 of 2006 [2].

Bioethanol has been known as an alternative energy source instead of petroleum [3]. Bioethanol is ethanol that can be produced from plant by fermentation process. Bioethanol can be produced from various raw materials, which contain starch and glucose. Bioethanol instead of petroleum fuel is important, due to the availability of dwindling fossil resources and the high level of environmental pollution resulting from burning fossil fuels. The advantage of using bioethanol as a fuel is a better combustion rate than fossil fuels (octane value reaches 110, has a smaller emission value, and is a renewable fuel.

The application of bioethanol has a dilemma because the material used to produce bioethanol may otherwise global food supply [4]. Various studies have been explored bioethanol production materials that do not interfere with the main food, including agricultural waste such as pineapple [2]; bakery
wastes, particularly waste cake,[5] bagasse [6]; durian seeds [7]; cassava and sweet potato peels [8] and others. Waste-based bioethanol which has the highest content is a mixture of pineapple peel and cherry fruit [9].

In addition to raw materials, the use of bioethanol as fuel has requirements that must meet Fuel Grade Ethanol (FGE). One of the FGE requirements is that the bioethanol purity must reach 96-99.5%. Therefore, further purification steps are needed to achieve these qualifications. The distillation method is the most commonly used conventional method in the purification of bioethanol. The distillation stage can produce high levels of ethanol, but has a weakness that the ethanol produced will be more volatile (ethanol loses), because ethanol steam distillation is generally carried out at 80°C. It’s necessary to find another method that is more effective in the purification of bioethanol.

Setyawati, [2] have increased bioethanol purity from pineapple peel using natural zeolite and limestone. The initial bioethanol purity was 3.9% then after increased to 27.22% by purification using natural zeolite, previous studies the bioethanol purity is still small. It is necessary to improve the method in the purification process so that the results obtained are more optimum.

An easy and economical method of purification of bioethanol is using clay-based adsorbent [10]. clay can absorb water in bioethanol mixture. The clay proposed in this study is kaolin. Kaolin is a clay mineral containing aluminum silicate and its very abundant in Bangka Island. Kaolin is used as an ingredient in several products manufacture in various industries, as a mixture or as the main ingredient [11]. Kaolin is used as an adsorbent because it is cheap, safe and its adsorption ability is easily increased through the activation process. The ability of clay material in the bioethanol distillation process needs to be studied so that it will produce bioethanol with a higher purity level with low production costs.

2. Material and methods
2.1. Materials
Cherries fruit and pineapple peels from Bangka, Indonesia, sulfuric acid (H₂SO₄, Merck, 99%), sodium hydroxide (NaOH, Merck), distilled water, Saccharomyces cerevisiae (Saf-Instant), standard ethanol (7,9%) and natural kaolin from Merawang District, Bangka, Indonesia.

2.2. Equiment and Instrumentation
The equipment used in this research are: digital scales, blender, glassware, magnetic stirrer, pH meter, furnace, pycnometer, a set of distillation apparatus, centrifuge, Oswald viscometer, alcohol refractometer. The instruments used for the analysis are: X-Ray Diffraction (XRD), Fourier Transform Infra Red Spectroscopy (FTIR), and Gas Chromatography (GC).

2.3. Method
Ethanol that use in this study was prepared by basic concept of ethanol production [12].

2.3.1. Bioethanol Productions
150 grams each cherries fruit and pineapple peels were cleaned then 600 mL of water was added and blended. The mixed slurry to 100 mL of 3% H₂SO₄ then heated at the temperature of 100°C and stirred. After that, the solution was cooled to room temperature. To condition the pH 4-5, NaOH was added. Add 10% yeast solution and sugar as nutrients, then put the solution in a closed container.

2.3.2. Preparation and Activation Natural Kaolin
Kaolin used in this study from Merawang District, Bangka, Indonesia. The kaolin is dried for 2 hours at 105 °C. Kaolin was ground and filtered through a 20mesh sieve. Activation is carried out chemically. 1 gram of natural kaolin is mixed in 10 mL of 3M H₂SO₄. The activation process was carried out by stirring the kaolin for 6 hours then the solution was allowed to stand for 24 hours. The kaolin was washed using distilled water until pH 6 (close to neutral). kaolin is filtered and then dried at 100°C for 18 hours [13].
2.3.3. Effect of Kaolin Mass on Bioethanol Purification Process

1, 2, 3, 4 and 5 grams of activated kaolin were added to a distillation flask and mixed with 30 mL of ethanol, respectively. The adsorption distillation process at 78-80 °C for 2 hours. The resulting distillate was collected in a distillate flask. The purified bioethanol then measured using gas chromatography.

3. Results and Discussion

Quality bioethanol product is majorly dependent on the production routes. Bioethanol production consists of several sequential procedures: pre-treatment, hydrolysis, fermentation and distillation, each of the stage is branched and each branch will give different results in ethanol quality as well as overall production cost [1].

3.1. Bioethanol productions

In this study, the production of bioethanol was initiated by pre-treatment by converting the material into a slurry. This stage is followed by a hydrolysis stage to break down carbohydrates with the help of water and a 3% (v/v) sulfuric acid catalyst. According to Sakar [14] chemical pre-treatment methods involve the use of dilute acids, alkalis, ammonia, organic solvents, SO₂, CO₂, or other chemicals. This method is easy to do and has good conversion results in a short time, so it is widely used. Glucose in the raw material was 5%, and after hydrolysis the glucose increased to 6% (measurement results using a refractometer). The hydrolysis step is important because hydrolysis determines the amount of glucose produced for fermentation by microorganisms [15].

Fermentation is carried out using the help of microbes called yeast in anaerobic conditions [16]. The microorganism in this study is Saccharomyces Cerevisiae, because its quickly grow and has tolerance to high ethanol concentrations. Factors that influence the fermentation process is pH. The pH used in the fermentation process is pH 4-5, because it is good for lactic acid in yeast growth [17]. In this study, the fermentation time was 3 days. The reactions that occur in the fermentation process are as follows [18]:

\[
\text{C}_12\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{inverter}} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6 \quad \text{(Reaction 1)}
\]

\[
\text{C}_6\text{H}_{12}\text{O}_6 \xrightarrow{\text{zymase}} \text{2C}_2\text{H}_5\text{OH} + 2\text{CO}_2 \quad \text{(Reaction 2)}
\]

Simple distillation carried out to separate the ethanol from the mixture. The working principle of distillation is the separation of a homogeneous liquid mixture consisting of two or more components with different boiling points between liquids. The distillation process is carried out by evaporating to produce distillate liquid. Distillation is carried out at 78-80°C which is the boiling point of ethanol. The ethanol produced after simple distillation was 7.9%.

Bioethanol was determined using gas chromatography method. The principle of assay by gas chromatography is that the sample is brought to a capillary tube to be separated based on the constituent components which are forwarded to the detector. The detector will produce a chromatogram which will then be analyzed using gas chromatography. Ethanol sample is injected first with pure ethanol standard as a comparison to calculate the ethanol content. Pure ethanol standard used is 15%. Qualitative analysis is carried out by comparing the sample retention time(tr) with the standard retention time(tr, std). Quantitative analysis was used to determine the peak area or peak height of the chromatogram.

3.2. Activation of Natural Kaolin as an Adsorbent

Kaolin activation using sulfuric acid aims to increase the surface area. Sulfuric acid has two H⁺ ions that can be exchanged for cations such as K⁺, Na⁺ and Mg⁺ in the space structure between the kaolin layers so that the metals dissolve [19]. The activation reaction using sulfuric acid (H₂SO₄) with kaolin is:

\[
\text{Al}_2\text{O}_3.2\text{SiO}_2.2\text{H}_2\text{O} + 2\text{H}_2\text{O} + 3 \text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 2\text{SiO}_2 + 5 \text{H}_2\text{O}
\]
Diffraetogram data (Figure 1) shows absorption peaks at natural kaolin $2\theta(\^) = 8.937; 12.371; 24.875; 38.463; 55.17; 62.365$. $2\theta(\^)$ for the mineral kaolinite is 12.371; 24.875; 55.17 and 62.365. The position of the peaks corresponds to JCPDS 29-1488, JCPDS 14-0164 and JCPDS 05-0143. Natural kaolin and activated kaolin have similar diffractograms, but differ in intensity. The intensity of acid-activated kaolin was higher than that of natural kaolin before activation. Data shows that kaolin activation increases crystallinity and mineral content.

FTIR characterization aims to determine the functional groups and types of vibrations in kaolin. Sunardi [20] stated that activated kaolin absorption has a slimmer and sharper shape. The Fourier Transform Infrared (FTIR) spectrum is shown in Figure 2. FTIR spectrum of activated kaolin shows O-H vibrations at 3662 cm$^{-1}$ and 3695 cm$^{-1}$. Al-OH vibrations are hydroxyl groups bound to octahedral Al atoms on the surface between silicate layers [20]. The wavenumbers of 1009 cm$^{-1}$ and 1114 cm$^{-1}$ show the stretching vibration of Si-O which is a typical absorption of kaolinite minerals. The absorption peak at 914 cm$^{-1}$ is the stretching vibration of Al-OH. The wave number of 757 cm$^{-1}$ on activated kaolin shows Si-O vibrations [21]. Wavenumber 699 cm$^{-1}$ is the stretching vibration of Si-O-Al [20].

3.3. Distillation-Adsorption by Kaolin Addition
The initial bioethanol used in the increasing process was 7.895%, the distillation-adsorption time is 1, 2, 3 and 4 hours. The distillate was analyzed using Gas Chromatography. The effect of contact time variation on the distillation-adsorption of activated kaolin on bioethanol is shown in Figure 3.
Increasing in distillation-adsorption time causing lower the ethanol content, and vice versa. This causes the longer the distillation-adsorption time, the lower ethanol produced. The highest ethanol content is in distillation-adsorption with 5 gram kaolin addition, it can be seen from the initial ethanol 7.895% which increased to 25.25%. The ethanol content in 2 gram to 3 gram kaolin addition increased from 17.47% to 21.32%, then decreased to 21.10% in the 4 gram kaolin additions (Figure 4). Ethanol content decreased due to several factors such as heating temperature, absorbent and pressure. During the distillation process, the temperature must be kept constant at 78-80ºC so that the heat generated is able to maintain the steam velocity of the mixture that takes place during distillation. Heat instability causes the rate of evaporation to be unstable.

Kaolin is proven to increase the ethanol content by the distillation-adsorption process [22]. The mechanism of increasing ethanol is the absorption of water molecules in the ethanol mixture by kaolin. Absorption cause by kaolin that has an interlayer able to absorb water molecules in the ethanol mixture. Water enter between kaolin layers, because the general nature of kaolin can expand when mixed with water. When kaolin expands it will absorb water molecules so that the water content in the mixture decreases and the ethanol content increases.

The absorption mechanism occurs because the framework structure contains vacant space and is occupied by cations and free water molecules, allowing ion exchange [23]. This adsorption usually occurs on solid surfaces that are rich in hydroxyl groups –OH (hydroxyl) [24]. Bioethanol purification occur physically because it is influenced by the porosity of kaolin, the greater the cross-sectional area of kaolin, and the absorption of kaolin to water molecules in ethanol solution [25]. After obtaining optimum purification, kaolin mass and optimum contact time, then ethanol with the highest content (29.33%), tested for its physical properties, the results are density 0.8171 gr/cm³ and viscosity 1.664 cps.

4. Conclusion
The contact time of kaolin-bioethanol in the distillation-adsorption process was optimum for 1 hour with a concentration of 29.33%. The optimum variation of kaolin mass in the adsorption distillation process was obtained at 5 grams with an ethanol content of 25.25%. Physical characteristics of bioethanol 29.33%, density 0.8171 gr/cm³ and viscosity 1.664 cps.

References
[1] Aditiya, H. B., Mahlia, T. M. I., Chong, W. T., Nur, H., & Sebayang, A. H. 2016 Renewable and sustainable energy reviews 66 631-653
[2] Setyawati, H, Rahman, N. A., & Solekah, S. 2012 Jurnal Teknologi Technoscientia 4 2
[3] Astuti, A., & Suwondo, T. 2012 Spektrum Industri 10 2
[4] Kiran, E. U., & Liu, Y. 2015 Fuel 159 463-469
[5] Uçkun Kiran E, Trzcinski AP, Liu Y. 2014 Biofuel Res J 3 98-105.
[6] Hermiati, E., Mangunwidjaja, D., Sunarti, T. C., Suparno, O., & Prasetya, B. 2010 Jurnal Litbang Pertanian 29 4
[7] Turnip, A., & Dahlan, M. H. 2012 Jurnal Teknik Kimia 18 2
[8] Oyeleke, S. B., Dauda, B. E. N., Oyewole, O. A., Okolie, I. N., & Ojebode, T. 2012 Advances in Environmental Biology 241-246
[9] Sari, F. I. P., Wibowo, B. S., & Irwanto, R. 2020. In Proceeding of National Colloquium Research and Community Service 4.
[10] Gozan, M., Setiawan, M. S., & Lischer, K. 2017 Makara Journal of Technology 21 1
[11] Utari, T. 1994. Doctoral dissertation, Tesis. Fakultas Pascasarjana, Universitas Indonesia, Depok.
[12] Binod, P., Sindhu, R., Singhania, R. R., Vikram, S., Devi, L., Nagalakshmi, S., & Pandey, A. 2010 Bioresource technology 101 13
[13] Bachmid, I. 2015 Hasanudin University Repository
[14] Sarkar, N., Ghosh, S. K., Bannerjee, S., & Aikat, K. 2012 Renewable energy 37 1
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