Alcohol dehydration of palm sugar (*Arrenga pinnata*) from Lalolae Village, East Kolaka, Southeast Sulawesi

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**Abstract.** This research aimed to obtain ethanol from fermented palm sugar with high purity. There are two main techniques used in this study to increase the purity of alcohol, namely modified multilevel distillation and the use of molecular sieve as the principal dehydrator agent. The process carried out to produce ethanol uses a distillation and dehydration process, with raw materials fermented using *Saccharomyces cerevisiae* and traditional technology. At first, prepare two column reflux distillation apparatus had been designed and constructed successfully to prepare bio ethanol. The sugar content of palm sugar used was 12.4%. Bioethanol is produced from 10% inoculum concentration and variations in fermentation time of 12 hours, 24 hours 36 hours, and 48 hours at pH 5. The results of measurement using alcoholmeter, the highest alcohol concentration was obtained at the condition of 36 hours fermentation time by 9%. The distillation and dehydration process is carried out continuously at a distillation temperature of 79 °C with a mass of 20 gram molecular sieves. The results of measurement of alcoholmeter obtained bioethanol levels of 54%.

**1. Introduction**

Palm or palm trees (*Arenga pinnata* Merr.) are plants that produce industrial materials for a long time. Unfortunately, this plant lacks attention to be developed or cultivated in earnest by various parties. So many varieties of products are marketed every day that come from palm trees, and the demand for these products both for export needs and domestic needs are increasing. Almost all parts of palm trees are useful and can be used for a variety of needs, starting from the physical part (roots, stems, leaves, fibers, etc.) and their products (sap and fruit). In the Southeast Sulawesi community, especially the people of the East Kolaka Regency, *Sonneratia* sp. Bark. (locally called: Buli wood) is used as a mixing material for palm juice in the fermentation process of palm sap into alcoholic beverages, to obtain good quality alcoholic drinks with a distinctive aroma. In addition, the presence of the bark in the fermentation of palm sugar in alcoholic beverages produces a more durable fermentation product [1].

The sugar content of palm sap, which ranges from 6-16% [2] makes this plant has great potential to be used as a source of raw materials in ethanol production. The raw material containing sugar in the form of a solution can make the ethanol production stage shorter, which is directly started with fermented palm sugar. Starch in the middle part of the palm tree can be converted by the tree itself into sugar, which is then tapped by humans and is known as sap. The sap which is tapped from male flower cob can produce 4 to 6 litters per day in two tappings. Each male flower can be tapped for 3-4 months or until the cob dries.
Palm sugar has a glucose content that is quite high when compared with several other plants. In a fresh condition, the sap tastes sweet, smells of sap and is colorless. Palm sugar contains several nutrients, including carbohydrates, proteins, fats, and minerals. Sweet taste for sap due to its carbohydrate content reaching 11.28%. The newly dripping sap from flower bunches has a pH of about 7 (neutral pH), but the influence of the surrounding conditions causes palm sugar to be easily contaminated and undergo fermentation so that the sweet taste of palm sap quickly turns to acid (pH decreases) [3].

High water content is one of the obstacles to processing palm sugar into high purity alcohol (> 95%). Based on the research conducted [4], the percentage of alcohol concentration obtained after fermentation reached 11.1-15.6% and after the distillation process only produced alcohol with a purity of 45%. Basically, Ethanol produced in two forms, namely hydrated and anhydrous. Hydrated ethanol has a purity of 95% while anhydrous ethanol is ethanol with purity > 99% [5]. Ethanol from fermented palm sugar by dehydration method can be used as absolute ethanol with a purity level of > 95% [6].

The problems faced in alcohol purification include the diversity of ethanol levels produced by farmers and small-scale processing units, temperature control and its relation to the conditions of ethanol to be provided and the mass of ethanol products. For this reason, it is necessary to study bioethanol purification techniques with the right and efficient method [7].

As Mathewson reports in [8] that to obtain absolute ethanol, it can use a pellet-shaped synthetic absorbent that can selectively bind water molecules. This method has advantages; besides being cheap, this method does not leave any residue in the ethanol obtained. In addition, the used molecular sieve can be reused after drying at a certain temperature.

There are two main techniques used in this study to increase the purity of alcohol, 1) modified multilevel distillation, and 2) the use of molecular sieve as the primary dehydrator agent with pellet-shaped. With this method, it is expected to obtain ethanol from fermented palm sap with absolute purity.

2. Methods

2.1 Sampling
The results of tapping palm sugar were obtained from local residents of East Kolaka Regency. Samples of palm sap that has been tapped from the bunches of male palm trees then filtered to separate the insects that are in the sap. Then cooled in the freezer to prevent contamination of other microorganisms.

2.2 Fermentation Optimization
The yeast used in the fermentation process is S. cerevisiae A12, an ethanol-tolerant yeast strain commonly used in bread making. The sap that has been tapped from 100 mL sugar palm trees is put in mL into Erlenmeyer (pyrex), added 2 g of KH₂PO₄ (Merck), 2 g of urea (Merck) and 20 mL of distilled water and NaOH solution (Merck) 1% (1-2 drops) to pH = 6. Then 10 mL of Saccharomyces cerevisiae inoculum is added. Fermentation is carried out by anaerobic conditions by regulating so that air does not enter. Fermentation is carried out at room temperature by shaking using a shaker platform for 72 hours (± three days). Next filtered to remove biomass, pH was measured after fermentation and centrifuged for 5 minutes fermented.

2.3 Dehydration Process
After the fermentation process, it is continued with purification through a two-stage distillation process. In the first stage, the alcohol (ethanol) produced by the fermentation process is distilled at a temperature of 70-80 °C accompanied by the addition of CaO (Pudak scientific). In the second stage, the distillation residue is dehydrated by adding molecular sieve 4a powder.

2.4 Determination of Alcohol Content
Pure ethanol obtained was analyzed for its characteristics using alcoholmeter (China OEM) and Gas Chromatography (Techcomp GC 7900).

3. Result and Discussion
This research was conducted to understand the efficient and effective process of palm sugar tapping; Design and construct of multilevel distillation with two column reflux distillation apparatus, and obtain the high bioethanol purity of bioethanol by using palm sugar feedstock.

3.1 Optimization of fermentation
This research was conducted to determine the optimum condition of the fermentation process from palm sap to bioethanol using yeast with variable changes, namely and fermentation time at optimum pH 5 [9]. The optimum condition of palm sugar fermentation was measured after going through the separation process using a rotary evaporator to separate the fermented liquid from the impurities in the form of residual nutrients, biomass, and others. The bioethanol produced was measured using alcoholmeter. The bioethanol concentration obtained in the research variables is presented in Figure 1. The level of alcohol at optimum pH 5 produced the highest alcohol content of 12.4% (v/v) at 72 hours. In Figure 2, it can be seen that the best time in the fermentation process is 72 hours, that suggests the optimum time of yeast performance is 72 hours. This explains that yeast is at an exponential phase at that time. The exponential phase is the phase where cells will grow and divide to the maximum amount. When the fermentation time exceeds 72 hours, there is a decrease in the concentration of alcohol produced, suggests that at 84 hours the yeast has undergone a stationary phase where the nutrient element has begun to run out.

At the beginning of fermentation, the alcohol content produced is still low, with increasing fermentation time, the alcohol content produced increases. The fermentation time affects the results of alcohol because the longer the fermentation time will improve the alcohol content. But if the fermentation is too long, the nutrients in the substrate will run out and the yeast does not work optimally to convert sugar because the yeast lacks food, and results in reduced performance so that the alcohol content produced does not increase [10]. In addition, decreased alcohol concentration can be caused by the alcohol produced being converted to acetic acid due to the presence of an alcohol oxidation reaction [11].

3.2 Distillation Process
The distillation process is the processing of bioethanol which is associated with an increase in ethanol levels with the use of temperature in the evaporation tank and controlling the temperature of the...
distillation column. While dehydration is related to a rise in ethanol levels through the use of hydrate (3Å synthetic zeolite) which absorb bioethanol-containing water in a closed process system.

The ethanol content obtained from fermentation consists of a mixture of ethanol-water and impurity compounds so that it is purified to increase the levels of fermented bioethanol. The ethanol content of fermentation is 13%. In this study, to increase ethanol levels up to 96%, repeated distillation was carried out, bioethanol levels could not be raised again when they reached 96%. Although purified by continuous distillation, the ethanol content obtained will not exceed 96% of the volume. Therefore, to refine ethanol, adsorption is necessary using adsorbents which act as a molecular sieve [12].

| Table 1. Alcohol levels of the distillation process |
|---------------------------------------------------|
| No | Distillation Temperature (°C) | Levels of Alcohol Distillation 1 | 2 |
|----|-------------------------------|---------------------------------|---|
| 1  | 79                           | 28%                             | 46% |

The level of alcohol in the observation of the distillation process increased from 28% to 46% at the second distillation stage. This is happening because in the process of re-distillation the water content in alcohol decreases. Subsequently, the 46% content is used as raw material for the dehydration process using a molecular sieve.

### 3.3 Dehydration Process

Dehydration of alcohol is a purification process to get alcohol at levels above the azeotropic point. Dehydration via distillation of adsorption using Zeolite adsorbent (Poskal Mic water adsorbent) with a ratio of Zeolite: bioethanol ratio; 1: 1; 1: 2, 1: 3 and 1: 4. Bioethanol purification results exhibit in Table 2 below.

| Table 2. Levels of alcohol after the dehydration process |
|----------------------------------------------------------|
| No | The ratio of Zeolite: bioethanol | Alcohol level (%) |
|----|---------------------------------|-------------------|
| 1  | 1:1                             | 48                |
| 2  | 1:2                             | 54                |
| 3  | 1:3                             | 51                |
| 4  | 1:4                             | 52                |

The highest bioethanol level occurred in the ratio of zeolite: bioethanol 1: 2 by 54%. This purity has not been categorized as Fuel Grade Ethanol (FGE), so it cannot be used as a fuel mixture for vehicle engines. These results indicate that the more zeolite used as an adsorbent, the higher the bioethanol content produced. It is following the theory that the more the number of adsorbents used the smaller the adsorption load of the adsorbent so that more adsorbates will be absorbed [13].

### 3.4 Bioethanol Validation with Gas Chromatography

The time used by certain compounds to move through the column to the detector is known as retention time. This time is measured by time from when the sample is injected at the point where the display shows the maximum peak height for the compound. This retention time is one indicator of the bioethanol content of palm sap. Based on the measurement of Gas Chromatography (Figure 2) with the condition of a column temperature of 180 °C, bioethanol from the sapper has a retention time of 1,195 minutes.
3.5 Bioethanol Physical Properties Test from Palm Sugar

The physical properties of bioethanol are highly dependent on the hydroxyl group in ethanol. This group causes the polarity of the molecule and produce intermolecular hydrogen bonds. This property causes differences in the physical properties of bioethanol, including the degree of equality and density. The testing of bioethanol physical characteristics such as the density carried out on bioethanol obtained from the dehydration process. Table 3 shows that the lowest density is obtained at the highest bioethanol level of 0.873 mg/ml. The bioethanol density value obtained decreases with increasing alcohol content in bioethanol. The density value obtained in this study exceeds absolute bioethanol density which is equal to 0.789 g / ml [14]. It is caused by the distillation that is carried out only by simple distillation instead of azeotropic distillation and less carefulness in maintaining temperature stability in the distillation process so that the steam that comes out is not only bioethanol but mixed with water.

| No | Ratio Zeolite: Bioethanol | Bioethanol grade (%) | pH of Fermentation Process | Density (mg/ml) |
|----|--------------------------|----------------------|---------------------------|-----------------|
| 1  | 1:1                      | 48                   | 5                         | 0.902           |
| 2  | 1:2                      | 54                   | 5                         | 0.873           |
| 3  | 1:3                      | 51                   | 5                         | 0.889           |
| 4  | 1:4                      | 52                   | 5                         | 0.884           |

4. Conclusion

The process carried out to produce ethanol uses a distillation and dehydration process, with raw materials which are first fermented using yeast. Bioethanol yielded from 10% inoculum concentration and variation of fermentation time 12 hours, 24 hours, 36 hours, 48 hours, 72 hours and 82 hours at pH 5, respectively. The alcoholmeter result suggests that the highest alcohol concentration about 12.4% at 36 hours of fermentation. The distillation and dehydration process is carried out continuously at a distillation temperature of 79 °C with a mass of 20 gram molecular sieves. From the results of measurements of alcoholmeter obtained bioethanol levels of 54%.
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