Characterization of Cocoa Pulp (*Theobroma cacao* L) from South Halmahera as an Alternative Feedstock for Bioethanol Production

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Abstract. South Halmahera is one of the cocoa-producing centers in North Maluku, but the pulp of cocoa is less noticed and assumed to be not important in commercial purpose and is largely disposed as agroindustry residue. This study aimed to characterize the cocoa pulp from southern Halmahera for bioethanol production. Survey and observation methods were conducted to obtain bioethanol feedstock from cocoa pulp. Cocoa pulps mucilage is a waste that can be processed into bioethanol products with high economic value. The results of this study indicated that the average of 100 kg of cocoa beans produced 5-8 liters of mucilage juice residues. The results of this study indicated that cocoa pulp from southern Halmahera had the optimum time for the fermentation process for 12 days. The level of alcohol produced by fermentation was 4.85%, and this level was a low category.

Keywords: Cocoa, pulp, South Halmahera, feedstock, fermentation, bioethanol

1. Introduction

Cocoa is a crop cultivated largely by smallholder farmers in the tropical low land including the parts of Latin America, West Africa, and Indonesia [1]. North Maluku Province has a distinctive character with regional ecological conditions that are very suitable for cocoa production. Cocoa producing centers in North Maluku are in the South Halmahera, North Halmahera, and West Halmahera districts, the islands of Tidore. Cocoa is a plantation commodity that highly contributes to the economy of the people in North Maluku. In 2008, cocoa provided opportunity of employment and became a source of income for 24,707 farmers in an area of 41,498 ha [2]. Due to these considerations, it is very reasonable that North Maluku was used as one of the provinces implementing the Cocoa National Movement (Gernas Cocoa) program in 2009 aiming to make the North Maluku as one of the centers for national cocoa production. Cocoa fruit has not been used optimally by cocoa farmers [3].

One of the factors causing the low quality of Indonesian fermented cocoa beans is a high level of acidity. The high level of acidity in cocoa fruits creates a low quality of produced chocolate [4]. Cocoa
beans with the high acidity levels are influenced by the entry of acetic acid from excessive pulp fermentation [5]. Cocoa beans should not be too acidic, or the pH must be above 5.0 to bring out the best flavor. Seed acidity is a critical aspect in the formation of chocolate flavor because it is not only related to the sour taste, but the important thing is to determine the course of the flavor formation compound. Flavor formation is more likely to occur on seeds pH of 5.0-5.5 than pH of 4.0-4.5 [6]. An excessive amount of pulp, in addition to causing excessive acid formation, can also inhibit the flow of oxygen into the mass of cocoa beans in the chest so that the fermentation process runs less perfectly [5,6]. Therefore, the amount of pulp in the process of the seed fermentation must be reduced so that the fermentation time can be shorter and the acidity of dry seeds can be reduced. During the process of mechanical extraction of cocoa seeds, a predominance of pulp and mucilage residues is generated [7], and 50% of this is considered to be waste with no further commercial application; but it is now recognized that its components have potential as inputs and energy for second-generation biofuel [8].

Nowadays, the energy sector faces two principle problems worldwide, a decline in oil reserves and pollution caused by burning fossil fuels [9]. Couple with this, thermoelectric plants (coal, natural gas, oil, and nuclear) are responsible for about 80% of world electricity production, a process which generates large amounts of CO₂ contributing to global warming [10]. As a result, there is a need to find new sources of renewable energy with the capacity to generate environmentally-friendly electrical energy [11]. The use of bioethanol as fuel is increasing due to depleting petroleum reserves, rising oil prices, the enactment of greenhouse gas emission reduction regulations, and the elimination of methyl tertiarybutyl ether (MTBE) policies, as well as the tendency to shift consumption to environmentally-friendly renewable energy sources [12–14]. Bioethanol fermentation can be described as the biochemical process which converts sugar into cellular energy, thereby producing ethanol and metabolic waste production [15,16]. Bioethanol is generally made of sugary plants such as sugar cane, sweet sorghum, and beets. Though these plants have other useable values as foodstuffs, the price of these foodstuffs on the market continues to rise as the interest of factories and producers of Biofuels (BBN) to enhance the material to bioethanol [17].

The use of renewable resources, particularly agricultural and forest residues, the major component of cellulose starch, lignin, xylanase and pectin, is providing some alternatives to using oil and fossil fuels [12]. In this case, cocoa bean is rich in sugars (17-20%), salts (8-10%), peptones (2-3% pectin), organic acids (1-2%) and 0.6% proteins [18]. After initial fermentation, cocoa pulp juice is obtained and it can be fermented to produce bioethanol. This study aimed to characterize cocoa fruit pulp from southern Halmahera for bioethanol production.

2. Methods

The liquid cocoa pulp (Theobroma cacao L.) was collected by means of harvested cocoa pods which were peeled and separated from the peel with its contents (fruit flesh). The fruit flesh in the form of seeds, placenta, and cocoa pulp was put into a clean nylon sack and then pressed for a while. The mucilage juice that came out during the ripening process was stored in a jerry can container with a temperature of 5 °C for 6 hours.

The starter was made as a growth medium for Saccharomyces cerevisiae. A total of 1.5 grams of yeast tape was added with 50 mL of cocoa pulp liquid for each container; then it was homogenized first with a magnetic stirrer while being heated on a bath at 70 °C for 15 minutes. After that, the starter was allowed to stand for 24 hours in aerobic conditions. After 24 hours, the starter was ready to be inoculated on the fermentation media. The starter that had been made was added with 500 mL of cocoa pulp liquid in an aseptic state and the next process was fermentation for 3-7 days. After the fermentation, the ethanol content with alcohol vinometer was tested, the non-reducing sugar levels and pH level were measured.
3. Results and Discussion
The characterization of cocoa pulp was carried out through the measurement of alcohol levels, non-reducing sugar levels, and pH levels (Table 1).

Table 1. The characterization of pulp cocoa

| Pulp sample | Volume of sample (ml) | % Sugar non-reduction | % Alcohol in sample | pH |
|-------------|-----------------------|-----------------------|---------------------|----|
| A           | 1500                  | 8                     | 4.1                 | 3  |
| B           | 1500                  | 7.8                   | 3.8                 | 4  |
| C           | 1500                  | 8.3                   | 4.3                 | 4  |

The results showed that the average percentage of alcohol produced was 4%, while the percentage of non-reduced sugar content was about 8%. The pH of the pulp after the cocoa was fermented had an acidic pH of 3-4. Based on this study, the data showed that 20 kg of cacao pulp could produce 1.2-1.5 fermented alcohols. The processes and alcoholic fermentation products from cocoa pulp waste can be seen in Figure 1.

![Figure 1](image-url)

**Figure 1.** The processes of alcohol fermentation and the product of alcohol fermentation from the waste of cocoa pulp

Alcohol fermentation is a reaction to the conversion of glucose to ethanol (ethyl alcohol) and fermentation of carbon dioxide which takes place under anaerobic conditions [19]. The organisms that play a role are Saccharomyces cerevisiae (yeast) for making tape, $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 + 2ATP$ (The released energy: 118 kJ per mole). The energy produced is 5 times greater than the energy produced by anaerobic alcohol fermentation [20]. There are so many factors that directly or indirectly affect the fermentation process. There are many factors that influence fermentation including substrate, temperature, pH, oxygen, microbes used, and the time of fermentation. However, this study focused on substrate and pH [21].

Cocoa pulp contained 2-3% pectin. In bioethanol production, pectin was changed into alcohol through enzymatic process. Pectinases produced by various microorganisms such as bacteria and fungi, constitute a group of enzymes that catalyze pectin substance degradation by means of depolymerization (hydrolyses and lyases) and de-esterification (esterase) reaction [19]. For example, some pectinolytic yeasts degrade cocoa pulp, reducing it to monosaccharide [18]. Saccharomyces cerevisiae is the most commonly detected and abundant species of all types of yeast extracted during cocoa bean fermentations, possibly due to its rapid growth, pectinolytic activity, and ethanol tolerance, followed by *Pichia kudriavzevii* and *Pichia membranifaciens* [22–24]. The more substrate is used, the more pectin can be converted to alcohol by saccharomyces.

In this study, the fermentation was carried out for 7 days. Alcoholic fermentation resulted in a by-product in the form of acetic acid. The more longer the fermentation time, the more higher pH and the percentage of alcohol will be produced [25]. The alcohol content produced in this study was still very...
low compared to the composition of non-reduced sugar found in the liquid cocoa pulp [26]. These results indicated that there was still sugar that could be processed into alcohol. The addition of fermentation time would produce more alcohol. This case showed that fermentation was influenced by fermentations time. This research is the initial research for the development of the second generation Bioethanol from cocoa waste, so that further research is needed with more complex variables.

4. Conclusion
This study provided information on bioethanol processing models from cocoa waste, namely cocoa pulp with the optimum time for the fermentation process for 12 days. The level of alcohol produced by fermentation was 4.85%. This level was a low category.

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