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Analysis of the Calorific Value and Specific Gravity of Breadfruit Peel Bioalcohol (Artocarpus Altilis) as an Alternative Fuel at Various Distillation Temperatures

Hendry Sakke Tira[1*], Mirmanto[1], Iwanuddin[1], Salman[1], Sudirman[2]

[1] Mechanical Engineering Department, Faculty of Engineering, University of Mataram, Indonesia.

[2] Chemistry Department, Faculty of Mathematics and Natural Sciences, University of Mataram, Indonesia.

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Corresponding Author:
Hendry Sakke Tira
hendrytira@unram.ac.id

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Abstract: The objective of this study was to investigate how distillation temperature affected the specific gravity (SG) and calorific value of bioalcohol derived from breadfruit peels (Artocarpus altilis) as an alternative fuel. The process of producing bioethanol from breadfruit peels begins with pretreatment of the peels, followed by hydrolysis with hydrochloric acid, fermentation, and finally distillation. The hydrolysis process used 20% hydrochloric acid in a volume of 25 ml, and the fermentation took 6 days with a mass of 30 gr of yeast Saccharomyces cerevisiae. The distillation process lasted two hours, with temperatures varying between 70, 80, and 90°C. This study yielded the highest alcohol content of 72.80% at 70°C and the highest volume of bioalcohol of 35.67 ml at 90°C. Meanwhile, the best Specific Gravity (SG) at 70°C was 0.8393. Furthermore, the calorific value test results revealed that the calorific value increased with increasing alcohol content. The highest calorific value obtained was 23003.406 J/gr, which was close to the ethanol calorific value of 29700 J/gr, while the lowest calorific value obtained was 22339.008 J/gr at a distillation temperature of 90°C

Keywords: Bioalcohol; Breadfruit; Calorific Value; Distillation; Specific Gravity

Introduction

Today the energy crisis and limited fuel oil are becoming serious problems. This is because the quantity of fuel derived from fossils is decreasing. Energy consumption will also continue to increase along with the growth of the world population, as more countries have developed into industrialized countries. World crude oil will decrease from 25 billion barrels to 5 billion barrels in 2050 (Hu et al., 2019; Tira et al., 2023).

In Indonesia the use of fuel oil is increasing but the availability of fuel sources is decreasing resulting in the government having to cut fuel subsidies. In addition to cutting fuel subsidies, the government is also taking steps to save energy and look for new energy sources to replace petroleum.

Breadfruit or which has the Latin name Artocarpus altilis is a type that is very well known in Indonesia and many other countries. Breadfruit has a relatively high starch content. Breadfruit has a chemical composition of 72% starch, 8% fat water, 8.43% fiber, 4.70% total hydrogen, 4.20% ash, 0.44% calcium, and 0.13% phosphorus. The flesh of the breadfruit is widely used in processed foods, while the skin is underutilized and simply discarded, despite the fact that the breadfruit peel contains starch that can be converted into ethanol.

To turn it into ethanol, it needs a hydrolysis process. Hydrolysis is a chemical reaction that breaks a molecule into two parts by adding a water molecule (H_2O), with the aim of converting polysaccharides into simple monomers (Ayodele et al., 2020; Samsudin et al., 2020). One part of the molecule has hydrogen ions (H^+) and the other part has hydroxyl ions (OH^-). Generally, this hydrolysis occurs when salts of weak acids or weak bases (or both) are dissolved in water as shown in the chemical reaction equation 1 (Cuevas et al., 2021).

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$$(C_6H_{10}O_5)n + nH_2O \rightarrow n(C_6H_{12}O_6) \quad (1)$$

Similarly, the distillation process is critical for producing high-quality bioethanol. In theory, the greater the difference in boiling points between the components, the better the separation by distillation will take place, resulting in purer results. The application of this process is based on the theory that in a solution, each component will evaporate at its boiling point.

Several tests have been carried out to obtain bioethanol, including through the process of converting carbohydrates into sugar or glucose using several methods including acid hydrolysis and enzymatic (Dey et al., 2020; Zabed et al., 2017). Bioethanol can be produced from several materials such as lignocellulosic materials, starch-containing materials (sago, sweet potato, corn, and cassava), and sucrose-containing materials (sugar cane and palm sap) (Ansar et al., 2021; Huang et al., 2020).

Varying the conditions during the fermentation process has also been carried out. Fermentation results are influenced by many factors. Such as, food or substrate, types of microbes and surrounding conditions (Jayakody et al., 2017). Glucose produced from the hydrolysis process is then fermented by yeast (Saccharomyces cerevisiae) to produce ethyl alcohol (ethanol) and CO_2 through the following reaction, equation 2 (Bautista et al., 2019).

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \quad (2)$$

In this study the temperature of the distillation process will be varied. This is intended to observe the characteristics of the specific gravity and heating value of the bioethanol produced. It is hoped that through this research a clear picture of the optimal distillation temperature in producing bioethanol characteristics will be obtained in accordance with the acceptable standard of bioethanol fuel.

Method

In conducting the research, a procedure in this activity is needed to facilitate the course of the research. At this stage the breadfruit is washed, then sliced to take the skin. Cut into small pieces, after that it is dried in the sun for about 4 days so that the water content is reduced or dry. After drying, breadfruit peel is mashed with a blender and then sifted to become flour.

The next stage is the hydrolysis process. Enzymatic hydrolysis and chemical hydrolysis are the two most common methods for converting simple sugars from lignocellulosic materials prior to fermentation (Seifollahi & Amiri, 2019; Vasić et al., 2021; Yuan et al., 2021). Concentrated acid hydrolysis and diluted acid hydrolysis are two conventional techniques for converting simple sugars in which lignocellulosic materials are subjected to concentrated acid or diluted acid for a specific temperature and period of time. In this study the hydrolysis process applied was chemical hydrolysis. At this stage breadfruit peel flour is weighed with a ratio of 1:10, in 100 grams of breadfruit peel flour mixed with distilled water with a volume of 1000 ml and stir the mixture until it is mixed to the maximum. Breadfruit peel flour solution was put into a three-neck flask and added with 10 ml volume of HCl and 20% HCl concentration to go through the hydrolysis process. The hydrolysis process lasted for 120 minutes and the temperature was 100°C. The resulting hydrolysis solution is then cooled and filtered.

The next stage is the fermentation process. Depending on the composition of the lignocellulosic hydrolysate substances, the transformation of sugars to ethanol is mainly carried out via a biological pathway involving bacteria or yeast (Offei et al., 2018). A fermentation process will convert the hydrolyzed glucose solution into alcohol. The fermentation process was carried out under anaerobic conditions for 6 days, and 30 g of Saccharomyces cerevisiae yeast was added to one liter of solution. Before the fermentation process is carried out, the fermenter tools are sterilized using an autoclave to kill bacteria. After that, the acidity of the hydrolyzed glucose solution was adjusted to 5 by adding NaOH and measured with universal indicator paper. The solution whose pH has been adjusted is then put into the fermenter as much as 400 ml, then closed tightly until it is airtight for 6 days.

After all the above processes then proceed with the distillation stage. The distillation method employed in this study is simple distillation. The difference in boiling points of the volatile components of the test compound serves as the basis for separation in simple distillation. When the mixture is heated, the component with the lower boiling point evaporates first. Differences in volatility, or the tendency of a substance to become a gas, determine evaporation rates in addition to differences in boiling points. This distillation is done at atmospheric pressure. After experiencing the fermentation process for 6 days, 400 ml of the fermented glucose solution was distilled using a simple distillation apparatus. Distillation is carried out once. In the distillation process there are three variations of heating temperature, namely 70, 80, and 90°C. Samples 1, 2, and 3 were heated for 2 hours and the temperature was maintained. The distillation results of samples 1, 2 and 3 were collected for the volume of bioalcohol produced and the alcohol content was measured. The distillation apparatus used can be seen in Figure 1.

Figure 1. Simple distillation process

The next test is to measure the specific gravity and the calorific value of bioethanol. Specific gravity (SG) is the ratio between the density of fuel and the density of water at the same temperature. The relationship between specific gravity (SG) and density can be seen in the equation 3.

$$Specivic\ gravity\ (SG) = \frac{\rho_f}{\rho_{water}} \quad (3)$$

Where:
ρ_f = Density of fuel (Kg/m^3)
ρ_{water} = Density of water at room temperature (Kg/m^3)

The heating value is one of the important basic properties of fuel which is considered as energy in the form of heat transferred when the product of complete combustion of a fuel sample is cooled to the initial temperature of the fuel. PAAR 1241 EF bomb calorimeter is used to measure the calorific value of bioalcoholic fuels. Then equation 4 and 5 are used to calculate the final calorific value (Nguyen et al., 2022):

$$HCV = \frac{[(m_w+m_k)\times C_{pw}\times \Delta T]-[y\times HV_p]}{m_{bb}} \quad (4)$$

$$LCV = HCV - X_{H_2O} \, . \, L_{H_2O} \quad (5)$$

Where:
HCV : higher calorific value
LCV : lower calorific value
m_w : mass of water in vessel (g)
m_k : calorimeter water value (g)
m_f : sample mass (g)
C_{pw} : specific heat of water (J/gr °C)
ΔT : corrected temperature rise (°C)
y : length of wire burned (cm)
HVp : heating value of the lighter is 9.62 J/cm
$X_{(H2O)}$: mass of condensed water
$L_{(H2O)}$: latent heat constant H_2O at 25°C = 2442 J/g

This study also employs GCMS-QP2010 to analyze the alcohol content of bioalcohol fuel distillation. GC (Gas chromatography) and MS (Mass spectrometry) are used to separate and identify a mixture's volatile components.

Results and Discussion

The alcohol content of the distillation results shown in Figure 2 demonstrates that the distillation temperature has an effect on the alcohol content produced. From the tests that have been carried out with three temperature variations, it shows that the distillation results at a temperature of 70ºC produced the highest alcohol content with an average of 72.80% compared to the distillation temperatures of 80ºC and 90ºC, respectively 71.15 and 66.94%. This occurs because the distillation operating temperature has a temperature tolerance of ±5°C. As a consequence of this condition, the operating temperature approaches the boiling point of alcohol, which is 78°C. As a result, the volume of alcohol content at 70°C is greater than at other distillations' operating temperatures. A high alcohol content indicates that the alcohol contains little water. Furthermore, even though the operating temperature of the distillation is still lower than the boiling temperature of alcohol, the broth may evaporate due to the low vapor pressure above the liquid surface when the water is in aqueous fermentation. As a result, the water vapor condenses with the alcohol vapor and evaporates. Following the condensation process, the water vapor becomes a liquid phase and mixes with the resulting bioethanol.

In certain cases, the presence of water in the fuel is beneficial. The addition of water to the combustion chamber lowers the combustion temperature, resulting in lower NOx emissions, which are harmful and can cause cancer (Chybowski et al., 2015; Y. Zhu et al., 2019). However, water enters the combustion chamber from other sources or systems rather than from the fuel itself. Another issue is that water in the combustion chamber will impede the fuel combustion process, reducing engine power and increasing hydrocarbon emissions (S. Zhu et al., 2019). As a result, the yield of bioethanol obtained from this test requires further distillation to reduce the water content in bioethanol.

The alcohol content is inversely proportional to the volume of alcohol produced from the distillation process, where the volume of alcohol increases as the distillation temperature increases. At a temperature of 70ºC it produces the smallest volume of distillation with an average of 13.33 ml, while at a temperature of 90ºC it produces the highest volume of distillation products which is equal to 35.67 ml. This occurs because the distillation process, which occurs at high temperatures of 90°C, is closer to the boiling point of water at 100°C than the boiling point of alcohol at 78°C, resulting in more water evaporating and entering the condensation chamber than alcohol. The more steam that enters the condensation chamber, the more liquid that condenses.

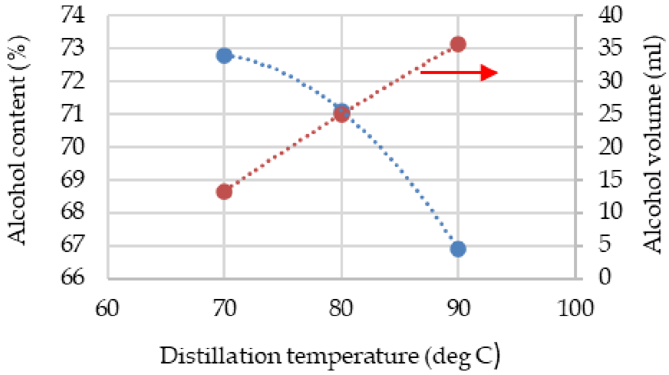

Figure 2. The content and volume of alcohol produced under variations in distillation temperature

Specific gravity (SG) is the ratio between the density of fuel and the density of water at the same temperature. In this study, the calculation of the density of fuel and water is calculated at a temperature of 30°C. For more details, the data results are shown in Figure 3.

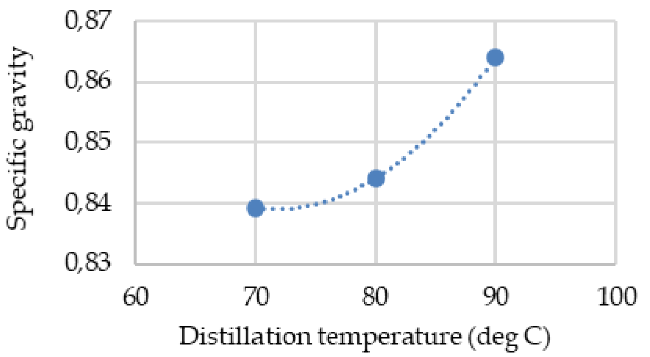

Figure 3. Specific gravity produced based on variations in distillation temperature

Figure 3 depicts the effect of distillation temperature on the specific gravity of the resulting alcohol. According to the results of the tests, the distillation temperature has an impact on the specific gravity produced. The highest alcohol content was obtained at 70°C, and the lowest specific gravity value was 0.8393. The lowest alcohol content and highest specific gravity value were obtained at 90°C. As a result, the relationship between distillation temperature and specific gravity can be concluded to be directly proportional. This means that when the distillation temperature is high, the specific gravity is also high, and vice versa when the distillation temperature is low. At a distillation temperature of 70°C with a tolerance of ±5°C the specific gravity of the bioethanol produced is close to the specific gravity of alcohol, namely 0.7983. This is because if the distillation is carried out at high temperatures, then the amount of water accompanying the alcohol will also be more and vice versa so that the density of the distillate will also be high. As is known, specific gravity is the ratio between the specific gravity of alcohol and the specific gravity of water at the same temperature (Alshameri, 2020).

The SG value in this study is still relatively far above the allowable threshold for all fuels in spark ignition engine vehicles. According to PT Pertamina data, the permitted SG value range is 715 – 745 (Tira et al., 2021). An excessively high SG value will hamper fuel injection through the injectors. As a result, the process of fogging the fuel will be hindered, resulting in higher emissions and lower engine power. If the SG value of the fuel does not match, the injector will be damaged in a short period of time.

Figure 4 shows the effect of the distillation temperature on the calorific value of the alcohol produced. The higher chlorine value is directly proportional to the lower calorific value. From the results of the tests that have been carried out, the highest average calorific value is 23,003.406 J/g at a temperature of 70°C. While the lowest calorific value was obtained at 22,339.008 J/g at a temperature of 90°C. Therefore, it can be concluded that the relationship between the distillation temperature and the higher calorific value and the lower calorific value is inversely proportional, meaning that the higher the distillation temperature, the lower the calorific value. This is because at a high temperature of 90°C it is closer to the boiling point of water by 100°C, so that the water also evaporates and mixes with the alcohol. This is confirmed by the theory which states that the calorific value is inversely proportional to the water content (Lu et al., 2019; Yang et al., 2022).

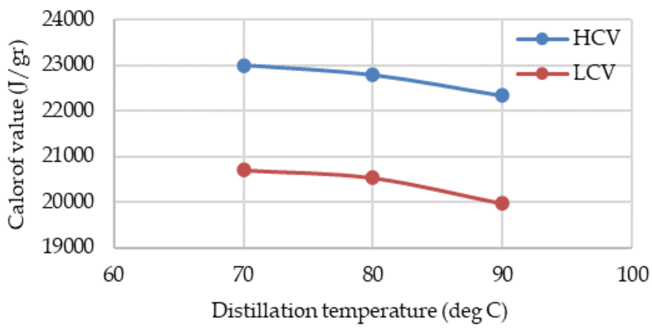

Figure 4. Calorific value produced based on variations in distillation temperature

The composition of the ethanol content in the samples tested influences the calorific value of the fuel. The highest ethanol content was obtained at a distillation temperature of 70°C when compared to other distillation temperature variations. Thus, the calorific value of bioethanol, both lower and higher calorific value, was found to be higher at the distillation temperature variation of 70°C than at the other variations. Ethanol has a lower heating value of 26,700 J/g and a higher heating value of 29,700 J/g (Rakopoulos et al., 2014). Because the bioethanol produced during the distillation process contains water, the calorific value obtained is clearly lower than the ethanol calorific value data. The lower the calorific value of bioethanol, the higher its water content. Because of its low calorific value, bioethanol is difficult to use as a fuel. When compared to the calorific values of pertamax and premium, which are commonly consumed, which are 43,616 and 42,098 calorie, respectively, the use of bioethanol as a result of this test will be less cost effective. A fuel with low calorific value necessitates a larger volume to produce the same power (Ilbas et al., 2019).

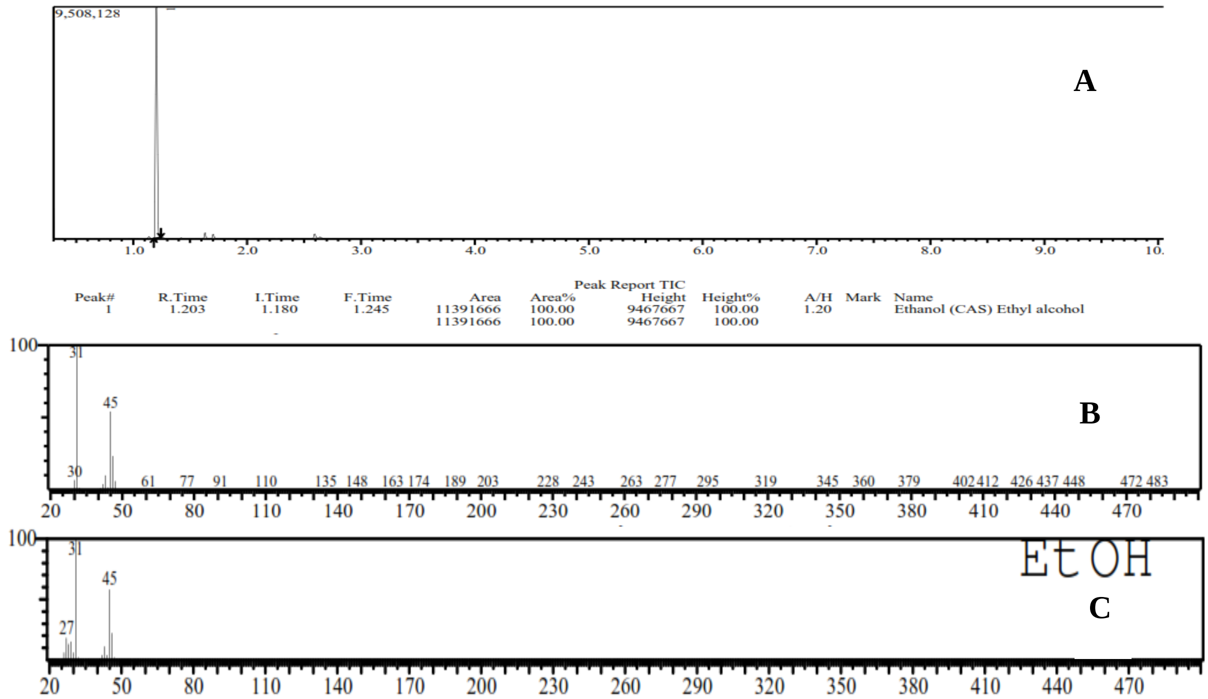

Figure 4. A) GCMS breadfruit peel chromatogram, B) alcohol spectrum of breadfruit peel, C) spectrum ethanol

Research was also conducted by analyzing the bioalcohol produced by GCMS. The results are shown in Figure 4. The chromatogram peaks were identified by comparing the MS spectra to the Wiley database to determine the type of compound (Figure 4B). The peak spectrum of the prepared bioalcohol is shown in Figure 4A, and the reference spectrum for the Wiley database, ethanol, is shown in Figure 4C. It is clear that the bioalcohol spectra produced from breadfruit peel agree well with the ethanol spectra from Wiley's reference data. Based on fragmentation, it appears that this similarity occurs at m/z 31 and 45. However, no compounds with m/z 26-29 were found in the test sample's bioalcohol spectrum. This indicates that the distillation process is not producing the purest alcohol possible. These findings are in line with those shown in Figures 2 and 3, where the properties of the resulting bioalcohol differ from those of pure ethanol. However, all processes carried out, from preparation to separation, have been satisfactory in terms of the resulting product being in the form of ethanol. This is demonstrated by comparing the results to WIley's ethanol spectrum. The only issue that must be carried out is to remove the remaining water content in the bioalcohol. This can be actually achieved in one of two ways: through repeated or multilevel distillation.

Conclusion

Some conclusions that can be drawn from this research are the distillation temperature greatly affects the production of bioalcohol from the breadfruit peels and the optimum distillation temperature in this study was 70°C with a tolerance of ±5°C because it is close to the boiling point of alcohol. The operating temperature of the distillation is directly proportional to the volume of distillation produced and inversely proportional to the alcohol content produced. This occurs because the amount of water that also evaporates is greater at high distillation temperatures. In this regard, the bioethanol produced by this research has a quality that is still fairly low than that of gasoline, particularly in terms of water content. Furthermore, the specific gravity value is inversely proportional to the alcohol content produced; this is because alcohol with a high concentration has a lower density value when compared to alcohol with a low concentration. The resulting bioalcohol has a specific gravity that is higher than the allowable threshold for a premium substitute fuel. The calorific value is directly proportional to the alcohol content, which means that as the alcohol content increases, so will the calorific value. The highest calorific value was obtained at 70°C and the lowest calorific value was obtained at 90°C in this study. However, the heating value of the bioethanol produced remains low. As a result, process improvement is still required to increase its calorific value.

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Author Contributions
Hendry: design a research concept then compose an introduction, method, results and discussion, and summary. Mirmanto and Salman aided in the preparation of the equipment and supplies used, as well as the substance of the articles. Iwanuddin was assigned responsibility for testing and data collection. Sudirman aided in the review of the results and discussion section, particularly in the discussion of chemical analysis.

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Conflicts of Interest
The author declares no conflict of interest.

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