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The Effect of Glycerol Addition as an Entrainer in Extractive Distillation for Bioethanol Purification from Fermented White Glutinous Rice

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Abstract
Bioethanol is a renewable liquid fuel that can be produced from carbohydrate-rich biomass, including white glutinous rice (*Oryza sativa glutinosa*). However, bioethanol produced from fermentation usually contains a large amount of water, and additional purification is required before it can meet higher fuel or industrial specifications. This study evaluated the effect of adding glycerol as a high-boiling hygroscopic binder during the extractive distillation of bioethanol produced from fermented white glutinous rice. Quantitative laboratory experiments were conducted using 200 mL bioethanol samples with glycerol additions at 0, 10, 30, 40, 50, 60, and 70 mL. The ethanol concentration in the distillate was determined from density measurements using a pycnometer and a calibration curve developed from ethanol standards. The calibration curve showed a strong linear relationship between ethanol concentration and density, expressed as $\varrho = -0.0017x + 1.0057$ with $R^2 = 0.9931$. The results showed that the addition of glycerol increased the apparent ethanol concentration compared to the initial/control sample. The highest ethanol concentration was obtained at 50 mL of glycerol per 200 mL of sample, with a density of 0.9200 g/mL and an ethanol concentration of 50.41%, which equates to a 44.94 percentage point increase from the baseline of 5.47%. Higher glycerol volumes reduced the separation performance, likely because excess glycerol increases viscosity and hinders heat and mass transfer during distillation. These findings suggest that glycerol can improve bioethanol purification at the optimum volume ratio, although the final product still requires further dehydration and analytical validation before it can be classified as fuel-grade ethanol.

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INTRODUCTION

The transition from fossil fuels to renewable energy has driven the focus on the development of bioethanol as a liquid fuel and chemical intermediate. Bioethanol is considered promising because it is produced from the biological conversion of biomass, can be blended with gasoline, and reduces dependence on non-renewable energy sources through a sustainable supply chain. Previous literature indicates that bioethanol offers superior combustion performance and a better environmental impact than fossil fuels, although its sustainability still depends heavily on the type of feedstock, conversion efficiency, and energy consumption during the production and refining stages (Göransson et al., 2021; Musa et al., 2023; Jain & Kumar, 2024).

The bioethanol production process generally involves raw material preparation, hydrolysis or saccharification, fermentation, and purification. Carbohydrate-rich materials such as sugarcane, starchy crops, and lignocellulosic residues can be used as feedstock, with different pretreatment requirements depending on their composition

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(Bhatia et al., 2020; Rajan et al., 2022). For starchy materials, hydrolysis is required to convert the starch into fermentable sugars before yeast fermentation. White glutinous rice is a starch-rich material with a high amylopectin content, making it a suitable substrate for ethanol fermentation when the starch is sufficiently converted to glucose (Anwar et al., 2020; Subroto et al., 2022; Wijayanti et al., 2023).

One of the main limitations of bioethanol produced through fermentation is the low ethanol concentration. Fermentation fluids generally contain water, residual sugars, yeast cells, organic acids, and other byproducts. Therefore, purification is not only the final step but also determines product quality, economic feasibility, and its application range. Distillation is the most common method for concentrating ethanol because ethanol is more volatile than water. However, conventional distillation becomes increasingly inefficient as ethanol concentration increases and is ultimately limited by the azeotropic behavior of ethanol and water (Baskaya et al., 2020; Iftikhar et al., 2020; Rachman et al., 2022).

Extractive distillation is a technique used to improve the separation of mixtures with components that have close boiling points or azeotropic tendencies. This method introduces a third component, called a solvent or entrainer, which selectively interacts with one of the components in the mixture and changes the relative volatility between the target components. The entrainer must have low volatility, a high boiling point, good selectivity, thermal stability, low toxicity, and be easily recovered (Rafiee et al., 2020; Utami et al., 2021). In an ethanol-water system, the desired entrainer is expected to interact more strongly with water so that the ethanol is more likely to evaporate and leave the distillation flask as distillate.

Glycerol is a promising binder for bioethanol purification because it contains three hydroxyl groups, is highly polar, has strong hydrogen bonding capacity, and has a boiling point much higher than ethanol and water. These properties allow glycerol to remain primarily in the liquid phase while interacting with water during heating. As a result, water volatility can be suppressed and ethanol enrichment in the distillate can be increased. Glycerol is also relatively readily accessible and is widely associated with biodiesel production as a byproduct, making it attractive for integrated renewable fuel processing schemes.

However, the addition of entrainer is not always good; a small amount of glycerol may not be enough to effectively bind water, while excessive glycerol can increase the viscosity of the liquid mixture, reduce mixing quality, inhibit heat transfer, and decrease mass transfer efficiency. Therefore, the optimal entrainer-to-feed ratio must be evaluated experimentally for each equipment scale and feed composition. This issue is particularly important for small-scale bioethanol production in the laboratory or for educational purposes, where simple equipment and density-based analysis are commonly used.

This study revises and strengthens a journal manuscript originating from an undergraduate thesis on the effect of glycerol addition in extractive distillation for bioethanol purification. This study uses experimental data obtained from white glutinous rice fermentation, pycnometric density measurements, and ethanol standard calibration. The research question is: how does the volume of glycerol affect the ethanol concentration of the distillate during extractive distillation of bioethanol produced from fermentation?

This article aims to provide a clearer, data-driven analysis of the purification process, identify the most effective glycerol volume within the tested range, and address the practical limitations of the results. This study does not claim to produce fuel-grade ethanol; rather, it demonstrates that glycerol can increase ethanol concentration under the tested conditions and that the addition of 50 mL of glycerol to a 200 mL bioethanol sample resulted in the highest purity observed. This distinction is important because fuel-grade ethanol requires much higher purity and validation with more selective analytical methods.

METHOD

This study used a quantitative laboratory experiment with a descriptive analytical design. The experiment was conducted at the Chemistry Laboratory of Mandalika University of Education (UNDIKMA) on June 25, 2025. The independent variable was the volume of glycerol added to a 200 mL bioethanol sample, while the dependent variable was the concentration of distillate

ethanol calculated from density measurements. Since the thesis data did not report repeated measurements for each treatment, the results were interpreted descriptively and not with inferential statistical testing.



Figure 1. Experimental Workflow used To Evaluate The Extractive Distillation of Bioethanol Through Glycerol Addition.

The main material used is crude bioethanol obtained from the fermentation of white glutinous rice. Glycerol is used as a binding agent, and distilled water is used for standard preparation and cleaning. The equipment used includes a set of standard distillation equipment consisting of a distillation flask, condenser, adapter, thermometer, heating mantle or heater, clamp, support, Erlenmeyer flask, measuring cylinder, volumetric pipette, volumetric flask, analytical balance, alcoholmeter, and pycnometer. Density measurements are carried out with pycnometers with a capacity of 10 mL and 25 mL according to the available measurement scheme.

The ethanol concentration in the distillate was estimated from the density using an ethanol standard calibration curve. Standard ethanol solutions with concentrations of 0.5%, 10%, 20%, 25%, 30%, 40%, 50%, and 70% were measured using a 25 mL pycnometer. The pycnometer was weighed empty, then reweighed after being filled with each standard solution. Density was calculated by dividing the mass of the liquid by the volume of the pycnometer. Linear regression was then applied with ethanol concentration as the independent variable and density as the dependent variable.

Table 1. Calibration Data for Ethanol Standard Solution.

Ethanol volume (mL)	25	25	25	25	25	25	25	25	25
Ethanol standard (%)	0	5%	10%	20%	25%	30%	40%	50%	70%
Ethanol mass (g)	25.06	24.88	24.68	24.3	24.12	24	23.5	22.95	22.03
Density (g/mL)	1.0024	0.9952	0.9872	0.9720	0.9648	0.9600	0.9400	0.9180	0.8812

Note. Linear regression of these data gives ϱ = -0.0017x + 1.0057, with $R^2 = 0.9931$. x represents the ethanol concentration (%), and ϱ represents the density (g/mL).

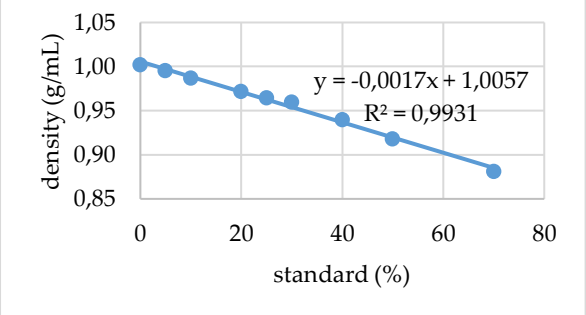


Figure 2. Calibration Curve Relating Ethanol Concentration to Density

For the purification experiments, each treatment used 200 mL of bioethanol sample. Glycerol was added at 0 mL, 10 mL, 30 mL, 40 mL, 50 mL, 60 mL, and 70 mL. The sample and glycerol were mixed until visually homogeneous, then transferred to a distillation flask. The apparatus was securely assembled, and the mixture was heated gradually. The distillate was collected after condensation through a condenser. The target operating temperature was maintained around the range of ethanol-rich distillation reported in the thesis procedure, approximately 79–85 °C at atmospheric pressure, while avoiding excessive heating that could introduce non-target components.

The density of each distillate was measured using a pycnometer. The measured densities were substituted into the calibration equation to estimate the ethanol concentration. Since the relationship between density and ethanol concentration is negative, a lower density indicates a higher ethanol concentration in the ethanol-water system. The increase in

concentration was calculated as the difference between the ethanol concentration of each treated distillate and the 0 mL baseline sample. Therefore, the values are reported as percentage points, not as a relative percentage increase..

RESULTS

Calibration Curve Performance

The calibration data yielded a strong negative linear relationship between ethanol concentration and density. The regression equation is $\varrho = -0.0017x + 1.0057$, with $R^2 = 0.9931$. This means that approximately 99.31% of the variation in measured density among the standard solutions is explained by ethanol concentration.

The trend makes chemical sense because ethanol has a lower density than water; therefore, increasing the ethanol fraction reduces the density of the solution. The high R^2 value supports the use of the calibration equation to estimate the ethanol concentration in the distillate, while recognizing that density is a bulk property and can be affected by dissolved impurities if present.

Table 2. Results of Bioethanol Distillation with Different Glycerol Volumes.

Glycerol volume (mL/200 mL)	Pycnometer volume (mL)	Empty pycnometer (g)	Filled pycnometer (g)	Density of distillate (g/mL)	Ethanol concentration (%)
0	25	16.01	40.91	0.9960	5.47
10	10	17.80	27.52	0.9712	20.29
30	25	16.01	39.90	0.9500	29.24
40	10	17.80	27.24	0.9430	36.35
50	25	16.01	39.01	0.9200	50.41
60	25	16.01	40.01	0.9590	26.94
70	25	16.01	40.01	0.9590	27.12

Note. The second treatment is labeled 10 mL in this revised table to align the experimental sequence with the journal draft and the intended order of glycerol variation. The increase in concentration is expressed as percentage points relative to the baseline concentration of 0 mL of 5.47%.

Bioethanol Purification Results

Distillation results showed that the addition of glycerol increased the apparent ethanol concentration of the distillate to a clear optimum. The base sample without glycerol contained 5.47% ethanol according to the calibration equation. The addition of 10 mL of glycerol increased the predicted concentration to 20.29%, and larger additions of 30 and 40 mL resulted in concentrations of 29.24% and 36.35%, respectively. The highest concentration was observed at 50 mL of glycerol, with 50.41% ethanol and a concentration increase of 44.94 percentage points.

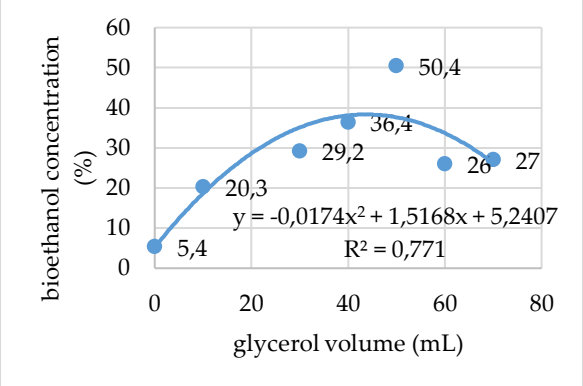


Figure 3. Effect of Glycerol Volume on Ethanol Concentration

Optimal Glycerol Volume

The data indicate that the optimum glycerol volume within the tested range was 50 mL per 200 mL bioethanol sample. This corresponds to an entrainer volume equal to 25% of the bioethanol sample volume. At this point, the density of the distillate reached its lowest value, 0.9200 g/mL, which corresponds to the highest predicted ethanol concentration. Increasing the glycerol to 60 and 70 mL caused the concentrations to drop to 26.94% and 27.12%, respectively. The decrease after the optimum point indicates that glycerol only improves separation when used at the correct ratio.

DISCUSSION

The increase in ethanol concentration after glycerol addition can be explained by the physicochemical characteristics of glycerol. Glycerol is a polar triol with three hydroxyl groups capable of forming strong hydrogen bonds with water. In the ethanol-water system, glycerol can associate preferentially with water molecules, thereby reducing the effective volatility of water in the liquid phase and increasing the relative tendency of ethanol to evaporate. This is consistent with the general

principle of extractive distillation, where high-boiling carriers alter component interactions and improve the separation of mixtures that are difficult to purify by simple distillation (Rafiee et al., 2020; Utami et al., 2021).

The experimental pattern is not linear over the entire range. The ethanol concentration increases from 5.47% at 0 mL glycerol to 50.41% at 50 mL glycerol, but then decreases sharply as glycerol is increased to 60 and 70 mL. This behavior indicates an optimal balance between water binding and process operability. At low to moderate glycerol volumes, hydrogen bonding interactions between glycerol and water likely increase ethanol enrichment. At excessive glycerol volumes, the liquid phase may become thicker, less evenly mixed, and more difficult to heat efficiently. High viscosity can reduce mass transfer between the liquid and vapor phases and can also cause uneven boiling, which reduces the practical efficiency of the distillation.

Therefore, the 50 mL optimum value should be interpreted as an empirical optimum for the specific feed composition, equipment, heating conditions, and analytical method used in this experiment. This value should not be directly generalized to industrial-scale bioethanol purification without further testing. In larger or continuous extractive distillation processes, entrainer flow rate, reflux ratio, column design, heat load, residence time, and entrainer regeneration will all influence the optimum operating conditions (Handayani & Pratiwi, 2023; Suprayitno et al., 2021).

The primary improvement in this revised manuscript is the interpretation of the reported concentration increases. The value reported as "increase (%)" in the source data is more accurately described as a percentage point increase because it is calculated by subtracting the baseline ethanol concentration from the treatment concentration. For example, a 50 mL treatment increased the ethanol concentration from 5.47% to 50.41%, representing an increase of 44.94 percentage points. Calling this a relative increase of 44.94% would underestimate the proportional change and introduce ambiguity. Correct terminology is crucial for factual and reproducible scientific articles.

The final ethanol concentration of 50.41% also requires careful interpretation. While this value represents the best performance in the experiment, it is still well below the specifications for fuel-grade ethanol, which typically requires very high ethanol purity and low residual moisture content. Therefore, this study should be viewed as a laboratory-scale demonstration of entrainer-assisted concentration enhancement, rather than as a complete fuel-grade bioethanol production process. Additional dehydration steps, such as repeated distillation, molecular sieves, pervaporation, or optimized extractive distillation with entrainer recovery, would be necessary to produce higher-purity ethanol (Bhatia et al., 2020; Rachman et al., 2022).

This analytical method also has limitations. Density measurements using a pycnometer are simple, inexpensive, and suitable for educational laboratories, but they are not fully selective for ethanol. The presence of residual glycerol, organic acids, dissolved solids, or other volatile byproducts can alter the density and bias the ethanol concentration estimate. Therefore, future studies should validate pycnometer-based results using more selective analytical methods such as gas chromatography, refractive index measurements, Karl Fischer water analysis, or near-infrared spectroscopy. Repeated measurements are also necessary to calculate standard deviations, confidence intervals, and statistical significance.

Despite these limitations, this experiment provides useful evidence that glycerol volume is a critical parameter in the extractive distillation of low-concentration bioethanol. The use of glycerol is particularly relevant in the context of renewable fuels because it is relatively safe, non-volatile under the conditions studied, and potentially available as a byproduct of biodiesel production. The finding that excess glycerol reduces performance is equally important because it suggests that process optimization must consider both chemical selectivity and physical transport properties.

CONCLUSION

The addition of glycerol as a binding agent increased the concentration of bioethanol distillate obtained from fermented white glutinous rice under the tested laboratory conditions. The calibration curve for density-based ethanol estimation was quite robust, with $\varrho = 13x - 13$ and $R^2 = 0.9826$. Among the tested glycerol volumes, 50 mL of glycerol per 200 mL of

bioethanol sample yielded the best results, giving a distillate density of 0.9200 g/mL and an estimated ethanol concentration of 50.41%. This represents a concentration increase of 44.94 percentage points compared to the 0 mL baseline of 5.47%. However, increasing the glycerol to 60 and 70 mL decreased the ethanol concentration, likely because the excess glycerol increases viscosity and reduces heat and mass transfer efficiency. This study indicates that glycerol can serve as an effective entrainer at the optimum ratio, but the achieved purity is not sufficient for fuel-quality ethanol. Future studies should test a narrower glycerol interval of approximately 50 mL, include experimental replication, validate ethanol concentration with selective methods such as gas chromatography or refractive index analysis, and evaluate entrainer recovery to improve process feasibility.

SUGGESTION

Based on the results and discussion, the following recommendations are proposed for further research: Refinement of Glycerol Concentration: Future studies should use a narrower concentration interval around the 50 mL optimum point (e.g., 45–60 mL) to more accurately identify the appropriate maximum volume ratio; Comprehensive Distillate Analysis: In addition to density, further characterization is recommended, including refractive index or Gas Chromatography (GC) for independent validation of ethanol concentration; analysis of residual water and glycerol content to verify purity and assess potential contamination at higher glycerol volumes.

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