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Glycerol-Assisted Batch Extractive Distillation for Upgrading Cassava Bioethanol beyond the Azeotrope: Response Surface Optimization of Purity and Yield

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A B S T R A C T

Simple batch distillation, the most accessible separation equipment for small- and medium-scale bioethanol producers, cannot enrich ethanol beyond the ethanol–water azeotrope (≈97.2% v/v), whereas fuel-grade ethanol requires at least 99.5% (v/v). This study evaluated glycerol, an abundant biodiesel by-product, as a green entrainer for the laboratory-scale batch extractive distillation of cassava bioethanol and optimized the process by response surface methodology. Bioethanol pre-concentrated to 95% (v/v) (baseline) was distilled at five glycerol-to-ethanol ratios (0.2–1.0 v/v; 500 mL charge per batch), and the cumulative distillate was sampled at five collection times (20–60 min), giving n = 25 observations. Relative to the baseline, ethanol purity increased to 97.0–99.2% (v/v), a 40–84% reduction in the non-ethanol fraction, with diminishing returns above 0.6:1; collection time did not affect purity. Reduced quadratic models described purity (adjusted $R^2 = 0.993$) and distillate yield (adjusted $R^2 = 0.865$). Desirability-based optimization located the optimum at a glycerol ratio of 0.86:1 and 60 min, with a predicted purity of 99.16% (v/v) and a yield of 61.1% of the feed (D = 0.961). Gas chromatography–mass spectrometry showed that ethanol accounted for 99.64–99.81% of the detected organic compounds, so the remaining impurity was mainly water. Glycerol-assisted batch distillation therefore breaks the azeotrope with simple equipment, but a final polishing step is still required to reach fuel grade. By valorizing a biodiesel by-product for decentralized bioethanol upgrading, the approach contributes to SDG 7 and SDG 9.

Contribution to Sustainable Development Goals (SDGs):
SDG 7: Affordable and Clean Energy
SDG 9: Industry, Innovation and Infrastructure
SDG 12: Responsible Consumption and Production
SDG 13: Climate Action

1. INTRODUCTION

Fuel-grade ethanol can reduce dependence on fossil fuels while lowering greenhouse gas emissions, owing to its high octane number and cleaner combustion compared with gasoline. For fuel use, however, ethanol must be nearly anhydrous: the Indonesian standard for denatured bioethanol for gasohol requires a minimum ethanol content of 99.5% (v/v) [1], because residual water lowers the calorific value, promotes corrosion in fuel distribution systems, causes phase separation in gasoline blends, and impairs engine performance [2]. Reaching this purity is

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difficult because ethanol and water form a minimum-boiling azeotrope at about 95.6 wt% (≈97.2% v/v) and 78.2 °C at atmospheric pressure [3]; at this composition the vapor and liquid have the same composition, so conventional distillation cannot enrich the ethanol further. Azeotropic distillation, pressure-swing distillation, membrane pervaporation, molecular-sieve adsorption, and extractive distillation have all been developed to overcome this limit. Extractive distillation is among the most widely adopted options: a high-boiling solvent is added that interacts selectively with one component, raising the relative volatility of ethanol to water without forming a new azeotrope [4], [5]. Its performance depends strongly on the solvent. Glycerol is an attractive green solvent because of its high boiling point, negligible vapor pressure, low toxicity, biodegradability, and abundant supply as a by-product of the biodiesel industry, and its three hydroxyl groups give it a strong affinity for water [6].

Fermentation broths are normally concentrated by simple distillation to technical-grade ethanol of about 95% (v/v) [7], [8]. This product is widely used in the chemical, pharmaceutical, and cosmetic industries, but it cannot be used directly as fuel, so an additional dehydration step is required to meet the fuel-grade specification [7], [9].

Among the available dehydration options, extractive distillation is attractive because the added high-boiling solvent interacts selectively with water, lowering its volatility and increasing the relative volatility of ethanol, so the separation becomes more efficient than conventional distillation without forming a new azeotrope [10]–[12].

The use of green solvents in extractive distillation processes is increasingly being developed as an alternative to conventional solvents that pose potential environmental risks. Glycerol is a suitable solvent: as a major by-product of the biodiesel industry, it is abundantly available, has low toxicity, is biodegradable, and possesses a high boiling point (290°C), making it an ideal eco-friendly solvent for extractive distillation [13], [14]. In extractive distillation, a solvent's effectiveness is determined by its ability to alter the mixture's vapor-liquid equilibrium, thereby increasing the relative volatility of the component to be separated. Glycerol features three hydroxyl (-OH) groups capable of forming strong hydrogen bonds with water molecules. This interaction reduces the volatility of water while increasing the relative volatility of ethanol, resulting in more effective ethanol-water separation compared to conventional distillation. Furthermore, compared to other solvents such as ethylene glycol and diethylene glycol, glycerol offers several advantages: lower vapor pressure, a higher boiling point, and origin from a renewable source as a by-product of the biodiesel industry. Beyond enhancing separation efficiency, the use of glycerol supports the implementation of green chemistry and circular economy concepts by transforming an industrial by-product into a value-added solvent [15]–[17].

Glycerol-based extractive distillation for ethanol dehydration has been studied mostly through steady-state simulation and optimization of continuous columns, in which the solvent is fed near the top of the column and recovered in a second column [15], [18], and through process-design and sustainability assessments that compare alternative solvents [10]. Experimental studies of glycerol-assisted batch extractive distillation are fewer [19], and statistical optimization of the glycerol dose and operating time with fermentation-derived bioethanol, including the trade-off between product purity and yield, has received little attention [20]. Such information is needed to judge whether glycerol alone can bring bioethanol to fuel grade in simple batch equipment, of the kind available to small and medium-scale producers, or whether an additional dehydration step is required. For such producers, the practical bottleneck is that a single-stage still delivers ethanol close to the azeotrope, whereas multi-column extractive systems and molecular-sieve units add equipment and operating complexity. The research question addressed here was therefore: to what extent can glycerol, added directly to the still of a simple batch apparatus, raise the purity of cassava bioethanol above the azeotrope, and which glycerol dose and collection time give the best compromise between purity and yield? It was hypothesized that ethanol purity would increase with the glycerol-to-ethanol ratio, with diminishing returns once most of the water is bound by glycerol, whereas distillate yield would be governed mainly by the collection time. This study used bioethanol obtained by fermentation of cassava, a widely available bioethanol feedstock in Indonesia, and (i) quantified the effects of the glycerol-to-ethanol ratio and the distillate collection time on ethanol purity and distillate yield in batch extractive distillation, (ii) developed and statistically evaluated response surface models for both responses, (iii) characterized the organic purity of the product by gas chromatography–mass spectrometry (GC-MS), (iv) identified the operating conditions that best balance purity and yield using the desirability approach, and (v) quantified the improvement relative to the pre-concentrated feed and compared it with recent experimental benchmarks.

2. MATERIALS AND METHODS

2.1. Materials

Bioethanol produced by the fermentation of cassava, with an ethanol content of 10% (v/v) as measured by an alcoholmeter, was used as the raw material. Glycerol (>99%) was obtained from PT Jayamas Medika Industri (Indonesia) and used as received.

2.2. Pre-concentration by simple distillation

The fermented broth was first concentrated by simple distillation in the apparatus shown in Fig. 1: 500 mL of broth was heated at 78 °C and 1 atm for 90 min [8]. The distillate contained 95% (v/v) ethanol, close to the azeotropic composition, and was used as the feed for extractive distillation.

2.3. Extractive distillation

Extractive distillation was carried out in the laboratory-scale batch apparatus shown in Fig. 1, which consisted of a three-neck flask heated by a heating mantle and stirred magnetically, a distillation column, a water-cooled condenser, and a distillate

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receiver. The still was a 1000 mL three-neck round-bottom flask heated by a Electrothermal EM 1000, 450 W heating mantle; the column was a Vigreux column of 30 cm length and 25 mm internal diameter, and the still temperature was monitored with a K type thermocouple. Glycerol was premixed with the 95% (v/v) bioethanol in the still at glycerol-to-ethanol volume ratios (A) of 0.2:1, 0.4:1, 0.6:1, 0.8:1, and 1:1, giving a total charge of 500 mL (bioethanol feed volumes in Table 1). The mixture was stirred at 300 rpm to homogenize the viscous glycerol phase, and the still temperature was maintained at 78 °C. Each batch was operated for 90 min; the distillate was collected cumulatively, and its volume and ethanol content were recorded at collection times (B) of 20, 30, 40, 50, and 60 min. The distillate yield was calculated relative to the bioethanol feed as

$$\text{Yield (\%)} = \frac{V_{D,t}}{V_F} \times 100 \quad (1)$$

where $V_{D,t}$ is the cumulative volume of distillate collected up to time t (mL) and V_F is the volume of 95% (v/v) bioethanol charged to the still (250.0–416.7 mL).

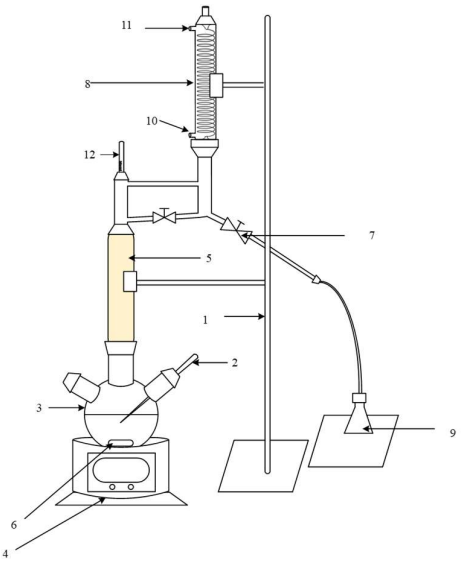


Fig. 1. Experimental setup: (1) stand and clamp; (2) thermocouple; (3) three-neck flask; (4) heating mantle; (5) distillation column; (6) magnetic stir bar; (7) valve; (8) condenser; (9) Erlenmeyer flask; (10) cold water inlet; (11) cold water outlet; (12) thermometer

2.4. Analytical methods

The ethanol content of the distillate (% v/v) was measured by immersing an alcoholmeter in 100 mL of distillate in a graduated cylinder. The alcoholmeter Gay-Lussac (Tralles; range 0-100% v/v; scale resolution 1% v/v) was read at 25-30 °C, and readings were corrected to 20 °C. The distillates collected at 60 min at ratios of 0.6:1, 0.8:1, and 1:1 were also analyzed by GC-MS to identify the organic compounds present. Analyses were performed on a Shimadzu QP2010 equipped with a HP-5MS/Rtx-5MS 30 m × 0,25 mm × 0,25 µm; helium 1,0 mL/min; injektor 250–280 °C; oven 40 °C column, with Helium as the carrier gas at 1.0 mL/min, an injector temperature of 250-280°C, and an oven program of 40°C; mass spectra were matched against the NIST 14/17 library. Compounds were identified by mass-spectral library matching and quantified as relative peak areas (area normalization) [9], [21].

2.4 Analytical methods

Isian	Cara mencari	Yang umum dipakai
Merek/tipe alkoholmeter	Tulisan pada batang alat	Alkoholmeter Gay-Lussac (Tralles)
Rentang	Skala pada alat	0–100% v/v
Resolusi	Jarak antar garis skala	1% v/v (ada juga 0,1% untuk rentang sempit)
Suhu saat dibaca	Catatan suhu waktu pengukuran	Suhu ruang, sekitar 25–30 °C
Metode koreksi suhu	Tabel apa yang dipakai untuk koreksi	Misalnya "OIML International Alcoholometric Tables". **Kalau sebenarnya tidak dikoreksi, hapus klausa koreksinya** dan tulis suhu pembacaannya saja.
Model GC-MS, kolom, gas pembawa, laju alir, suhu injektor, program oven, library	Semuanya tercantum di **header laporan/hasil cetak GC-MS** dari lab penguji (misalnya LPPT UGM, Lab Kimia UNAIR, Puslabfor)	Contoh yang umum: Agilent 7890B/5977B atau Shimadzu QP2010; kolom HP-5MS/Rtx-5MS 30 m × 0,25 mm × 0,25 µm; helium 1,0 mL/min; injektor 250–280 °C; oven 40 °C (tahan 2 menit) → 10 °C/min → 280 °C; NIST 14/17

2.5. Experimental design and statistical analysis

The two factors, the glycerol-to-ethanol ratio (A, 0.2–1.0 v/v) and the distillate collection time (B, 20–60 min), were studied at five levels each in a full 5 × 5 factorial arrangement, giving 25 observations (Table 1). Five batches were run, one for each glycerol ratio, and each batch was sampled at the five collection times; the batch is therefore the experimental unit and the cumulative distillate at a given time is the observation (n = 25). All 25 purity values were analyzed. Three yield observations at 0.2:1 (40, 50, and 60 min) were excluded because of an inconsistency in the recorded distillate volumes, leaving 22 observations for the yield analysis. The data were analyzed as a historical-data response surface design in Design-Expert® (Stat-Ease Inc., USA). Each response was first fitted to the full second-order polynomial

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_{12} AB + \beta_{11} A^2 + \beta_{22} B^2 \quad (2)$$

where Y is the predicted response (purity or yield) and β are the regression coefficients. Model significance was assessed by analysis of variance (ANOVA) on coded factors at $\alpha = 0.05$, and non-significant terms were removed by backward elimination while preserving model hierarchy [22]. Because the design contains no replicated batches, a lack-of-fit test could not be performed; model adequacy was therefore judged from the coefficient of determination (R^2), the adjusted R^2, the predicted R^2 (based on the PRESS statistic), the adequate precision, and residual diagnostics [23], [24]. Multi-response optimization used the desirability function of Derringer and Suich [25], in which each response is converted into an individual desirability

$$d_i = \frac{y_i - L_i}{U_i - L_i} \quad (3)$$

where L_i and U_i are the lowest and highest observed values of response i (97.0–99.2% for purity and 25.2–63.3% for yield),

with $d_i = 0$ for $y_i \le L_i$ and $d_i = 1$ for $y_i \ge U_i$. Both responses were maximized with equal weights and importance, and the overall desirability

$$D = (d_1 \times d_2)^{1/2} \quad (4)$$

was maximized within the experimental region. The uncertainty of the predicted optimum was expressed as 95% confidence and prediction intervals.

2.6. Performance indicators

The 95% (v/v) pre-concentrated feed was taken as the baseline (P_0) against which the upgrading step was evaluated. For each glycerol ratio, four indicators were calculated from the 60-min data: the purity gain, $\Delta P = P - P_0$ (percentage points, pp); the reduction in the non-ethanol fraction, $R = (P - P_0)/(100 - P_0) \times 100\%$; the remaining gap to the fuel-grade specification, $99.5 - P$ (pp); and the specific glycerol demand, defined as the volume of glycerol charged per volume of distillate collected (mL/mL). Because glycerol is not consumed in the separation, the last indicator represents the glycerol inventory that must be circulated and regenerated rather than a consumption rate.

3. RESULTS AND DISCUSSION

3.1. Feed pre-concentration and experimental results

Simple distillation raised the ethanol content of the fermented cassava broth from 10% to 95% (v/v), close to the azeotropic composition, confirming that further enrichment requires an entrainer. Table 1 summarizes the results of extractive distillation. Ethanol purity ranged from 97.0% to 99.2% (v/v) and was determined entirely by the glycerol ratio: at each ratio, the same purity was obtained at all five collection times. The yield increased with collection time at every glycerol ratio, from 25.2–42.5% of the feed at 20 min to 55.4–63.3% at 60 min. The two responses therefore depend on different factors, a pattern confirmed by the statistical analysis below.

Table 1. Feed volumes, ethanol purity, and distillate yield in batch extractive distillation of 95% (v/v) cassava bioethanol

A (v/v)	V_F (mL)	Purity[a] (% v/v)	Yield (% of feed) at B (min)				
			20	30	40	50	60
0.2	416.7	97.0	25.2	32.9	–[b]	–[b]	–[b]
0.4	357.1	98.1	39.2	41.7	43.7	53.2	63.3
0.6	312.5	98.8	41.6	43.2	44.8	46.4	55.4
0.8	277.8	99.0	42.5	43.9	51.5	52.2	61.2
1.0	250.0	99.2	40.0	42.4	44.4	52.0	60.0

[a] Identical at all five collection times. [b] Excluded from the yield analysis because of an inconsistency in the recorded distillate volumes.

3.2. Model fitting and statistical adequacy

For purity, the terms involving collection time (B, AB, and B^2) contributed nothing to the full quadratic model (sum of squares = 0; p = 1.000), because purity did not change with time at any ratio. The reduced model containing only A and A^2 (Table 2) was highly significant ($p < 0.0001$), with $R^2 = 0.9934$, adjusted $R^2 = 0.9928$, predicted $R^2 = 0.9919$, an adequate precision of 88.3, and a coefficient of variation of 0.07%. These statistics must be interpreted with care: because the five purity values at each ratio are identical and come from one batch, the data contain only five independent purity levels, and the very large F-value overstates the statistical precision. The model is best regarded as an accurate smooth description of the effect of the glycerol ratio rather than as evidence of extreme significance.

For yield, the full quadratic model gave an adjusted R^2 of 0.872 and a predicted R^2 of 0.780, but the AB interaction was not significant (p = 0.189) and was removed. The reduced model with A, B, A^2, and B^2 (Table 2) was significant ($F = 34.66$, $p < 0.0001$), and all of its terms were significant at $\alpha = 0.05$. Its adjusted and predicted R^2 (0.865 and 0.798) differ by less than 0.2, and its adequate precision (19.3) is well above the usual threshold of 4, indicating adequate predictive ability within the design space. No observation had a Cook's distance above 1 (maximum 0.73, at 0.2:1 and 20 min). In terms of the actual factors, the reduced models are

$$Y_{\text{purity}} = 95.680 + 7.579A - 4.107A^2 \quad (5)$$

$$Y_{\text{yield}} = 22.308 + 55.033A - 0.246B - 36.495A^2 + 0.00922B^2 \quad (6)$$

where A is the glycerol-to-ethanol ratio (v/v) and B is the collection time (min).

Table 2. ANOVA of the reduced quadratic models (coded factors)

Source	SS	df	MS	F-value	p-value
Ethanol purity, Eq. (5); n = 25					
Model	15.934	2	7.967	1658.03	< 0.0001
A	14.045	1	14.045	2922.88	< 0.0001
A^2	1.889	1	1.889	393.18	< 0.0001
Residual	0.106	22	0.0048		
Cor. total	16.040	24			
$R^2 = 0.9934$; adj. $R^2 = 0.9928$; pred. $R^2 = 0.9919$; Adeq. precision = 88.3; CV = 0.07%					
Yield, Eq. (6); n = 22					
Model	1549.09	4	387.27	34.66	< 0.0001
A	158.33	1	158.33	14.17	0.0016
B	1002.43	1	1002.43	89.72	< 0.0001
A^2	104.65	1	104.65	9.37	0.0071
B^2	51.46	1	51.46	4.61	0.0466
Residual	189.94	17	11.17		
Cor. total	1739.03	21			
$R^2 = 0.8908$; adj. $R^2 = 0.8651$; pred. $R^2 = 0.7983$; Adeq. precision = 19.3; CV = 7.20%					

SS: sum of squares; df: degrees of freedom; MS: mean square. Terms B, AB, and B^2 (purity) and AB (yield) were removed as non-significant.

3.3. Effect of glycerol ratio and collection time on ethanol purity

The contour plots in Fig. 2 summarize the two fitted response surfaces. For purity (Fig. 2(a)), the contour lines are parallel to the time axis, confirming that purity depends on the glycerol ratio alone. Purity rose steeply, from 97.0% to 98.8%, as the ratio increased from 0.2:1 to 0.6:1, but by only a further 0.4 percentage

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points between 0.6:1 and 1:1. According to Eq. (5), purity reaches a maximum of 99.18% at a ratio of 0.92:1, so raising the glycerol dose beyond this point brings no further benefit.

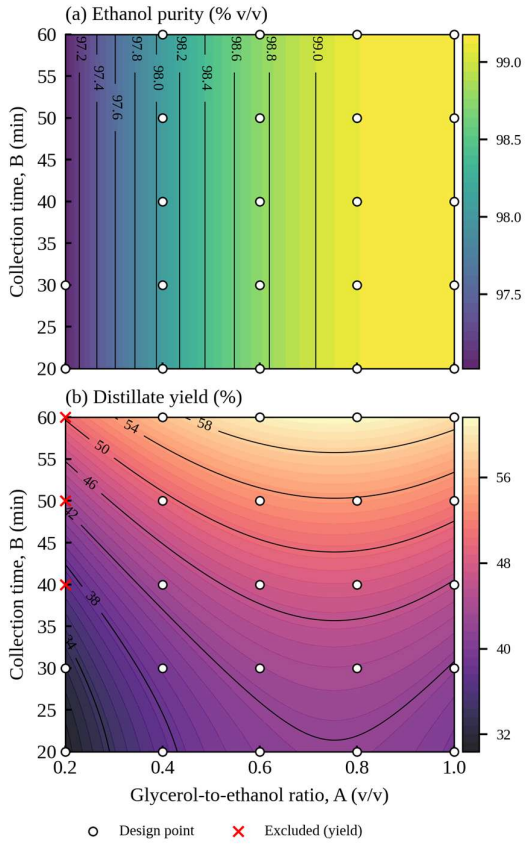


Fig. 2. Contour plots of (a) ethanol purity and (b) distillate yield (% of bioethanol feed) as functions of the glycerol-to-ethanol ratio and the distillate collection time, based on Eqs. (5) and (6). Circles: design points; crosses: yield observations excluded from the analysis

As Fig. 3(a) shows, the feed obtained by simple distillation (95% v/v) lies below the azeotrope, and the purity obtained at 0.2:1 (97.0% v/v) lies at the azeotropic composition (≈97.2% v/v). Every ratio of 0.4:1 or higher produced a distillate richer in ethanol than the azeotrope (98.1–99.2% v/v), which conventional distillation cannot achieve; this is direct evidence that a sufficient amount of glycerol breaks the azeotrope. The underlying mechanism is the strong and selective interaction of glycerol with water: its three hydroxyl groups form multiple hydrogen bonds with water molecules, lowering the activity coefficient and therefore the volatility of water in the liquid phase, while ethanol is affected much less [26]. The relative volatility of ethanol to water increases, and the vapor leaving the still is enriched in ethanol [11], [15], [27]. For the 95% (v/v) feed, ratios of 0.2:1 to 1:1 correspond to approximately 0.8 to 4.0 mol of glycerol per mol of water. At the lowest dose there is evidently too little glycerol per water molecule to shift the vapor–liquid equilibrium past the azeotrope, whereas above about 2.4 mol of glycerol per mol of water (0.6:1) most of the water is already strongly bound, so additional glycerol mainly dilutes the still contents. This explains the diminishing returns observed above 0.6:1.

The plateau at about 99.2% also reflects the configuration of the apparatus. In this batch set-up, glycerol is present only in the still, so the separation is enhanced mainly in the still and in the few equilibrium stages above it [28], [29]. In continuous extractive distillation, by contrast, the solvent is fed near the top of the column and flows down through all stages, so that every stage benefits from it; design and simulation studies of such columns report fuel-grade purities with glycerol and other glycols [15], [30]–[32]. The absence of a time effect within 60 min is consistent with batch operation: the distillate composition would be expected to fall only once the still becomes depleted of ethanol, whereas at most about 63% of the feed volume had been collected after 60 min. Changes smaller than the resolution of the alcoholmeter, however, cannot be excluded.

GC-MS analysis of the 60-min distillates (Table 3) showed that ethanol accounted for 99.64–99.81% of the total chromatographic peak area, the remainder consisting of trace C16–C18 fatty acids and their ethyl, glyceryl, and glycidyl esters. These values express purity on an organic basis: water is not recorded under typical GC-MS acquisition conditions and is therefore excluded from the area normalization [21], so they cannot be compared directly with the 99.5% (v/v) fuel-grade specification, which is defined largely by water content. The two methods are complementary. The alcoholmeter, which responds mainly to water, shows that 0.8–1.2% (v/v) of non-ethanol components remained at these ratios, whereas GC-MS shows that organic impurities made up only 0.19–0.36% of the detected compounds; the remaining gap to fuel grade is therefore mainly water. Notably, the organic purity decreased slightly as the glycerol ratio increased, opposite to the alcoholmeter trend. The glyceride-type impurities identified suggest a small carry-over of trace lipids from the glycerol or from the fermentation-derived feed that grows with the glycerol dose. The effect is small, but it indicates that an excessive glycerol dose offers no advantage and that glycerol quality should be specified, particularly if crude glycerol is to be used.

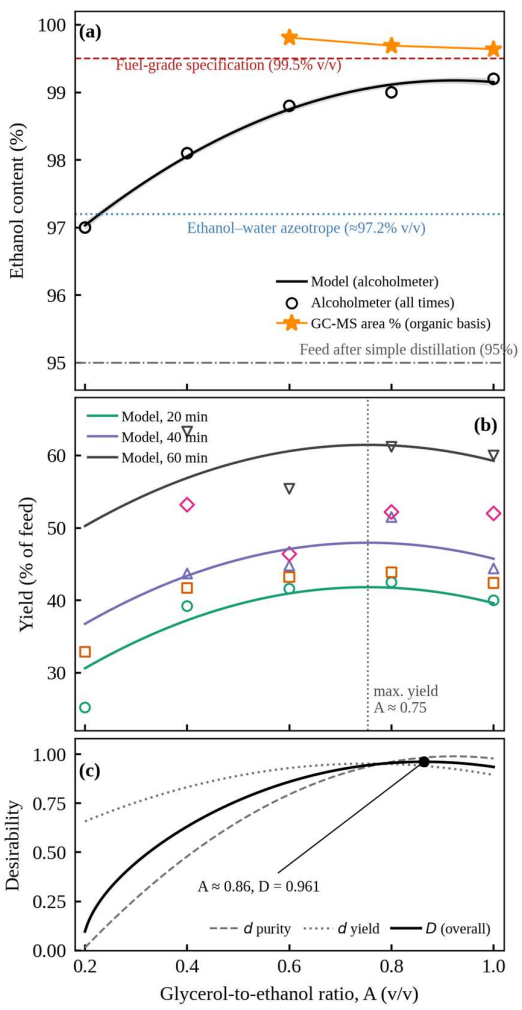


Fig. 3. Effect of the glycerol-to-ethanol ratio on (a) ethanol content measured by alcoholmeter (open circles, all collection times) and by GC-MS (stars, organic basis, 60 min), (b) distillate yield, and (c) individual and overall desirability at 60 min. Lines: reduced models (Eqs. 5–6); shaded band: 95% confidence interval

Table 3. GC-MS composition of the distillates collected at 60 min (relative peak area)

Ratio (v/v)	Sample code	Ethanol (area %)	Other organics (area %)	Minor compounds identified
0.6:1	INS 112.1	99.81	0.19	C16–C18 fatty acids; triolein
0.8:1	INS 112.2	99.69	0.31	Ethyl hexadecenoate; vaccenic acid; glycidyl oleate
1:1	INS 112.3	99.64	0.36	C16–C18 fatty acids; glycidyl oleate; 2-monoolein

3.4. *Distillate yield and the purity–yield trade-off*

Unlike purity, yield depended mainly on collection time (Table 2; F = 89.7). The increase was not linear: the cumulative volume grew slowly between 20 and 40 min and faster between 40 and 60 min, as reflected by the significant positive B^2 term. The distillation rate was therefore not constant during the run, which probably reflects the heating and column hold-up dynamics of the batch apparatus; these were not monitored here and should be recorded in future work. Because purity did not change over this period, extending the collection to 60 min increases the amount of product without a purity penalty. The absence of a significant AB interaction means that the effects of the two factors are additive: the glycerol ratio sets the purity, and the collection time sets most of the yield, which simplifies process control.

The glycerol ratio had a smaller but significant effect on yield, with a shallow maximum at about 0.75:1 (Fig. 3(b)). Between 0.4:1 and 1:1, the yield at a given time varied by only a few percentage points, and the curvature is driven mainly by the lower yields at 0.2:1 (25.2% and 32.9% at 20 and 30 min). A plausible explanation is that the glycerol dose influences the boil-up rate at the fixed still temperature by changing the bubble point and viscosity of the still contents; because the 0.2:1 level is represented by only two yield observations, this effect needs confirmation. The basis on which yield is expressed also matters. When yield is calculated relative to the total 500 mL charge, including glycerol, it falls at high glycerol ratios simply because less ethanol is charged; expressing yield relative to the bioethanol feed, as done here, avoids this artifact. Taken together, purity is maximal at about 0.92:1 and yield at about 0.75:1. Because both responses are nearly flat around their maxima, the trade-off between them is mild in the range 0.75:1–0.92:1.

3.5. *Multi-response optimization*

Fig. 3(c) shows the individual and overall desirability at 60 min, the collection time that maximizes yield without affecting purity. The overall desirability reached its maximum (D = 0.961) at a glycerol ratio of 0.86:1, where the predicted purity is 99.16% (95% prediction interval: 99.01–99.31%) and the predicted yield is 61.1% of the feed (53.2–68.9%) (Table 4). Although no separate confirmation run was carried out, the optimum lies between two tested conditions whose measured values bracket the predictions: 99.0% (v/v) purity and 61.2% yield at 0.8:1, and 99.2% (v/v) purity and 60.0% yield at 1:1, both at 60 min. The high desirability reflects the mild trade-off noted above. At 0.6:1, the predicted yield is practically the same (60.6%) and the predicted purity only 0.4 percentage points lower (98.75%), while GC-MS indicated the lowest organic impurity content at this ratio. A ratio between 0.6:1 and 0.86:1 therefore constitutes a robust operating window, with the higher end preferred when water removal is the priority.

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Table 4. Predicted responses at the optimum (A = 0.86 v/v, B = 60 min) and measured values at the nearest tested conditions

Response	Predicted at optimum			Measured, 60 min	
	Mean	95% CI	95% PI	0.8:1	1:1
Purity (% v/v)	99.16	99.12–99.20	99.01–99.31	99.0	99.2
Yield (% of feed)	61.1	57.6–64.5	53.2–68.9	61.2	60.0
Desirability, D	0.961	–	–	–	–

3.6. Upgrading performance relative to the baseline and comparison with previous studies

Table 5 expresses the results relative to the 95% (v/v) baseline. Every glycerol ratio improved on the feed, but only ratios of 0.4:1 or higher moved the product beyond the azeotrope. At the optimum, the purity gain was 4.16 pp, which corresponds to an 83.2% reduction in the non-ethanol fraction and leaves a gap of only 0.34 pp to the fuel-grade specification. Most of the improvement was obtained at low glycerol doses: raising the ratio from 0.2:1 to 0.6:1 removed a further 36% of the non-ethanol fraction, whereas raising it from 0.6:1 to 1:1 removed only 8%, while the specific glycerol demand rose from 1.08 to 1.67 mL per mL of distillate.

Table 5. Upgrading performance of glycerol-assisted batch extractive distillation relative to the 95% (v/v) feed (60-min data)

A (v/v)	Purity (% v/v)	ΔP (pp)	R (%)	Gap to 99.5% (pp)	Yield (%)	Glycerol demand (mL/mL)
Feed (baseline)	95.0	–	–	4.5	–	–
0.2	97.0	2.0	40.0	2.5	n.d.[a]	–
0.4	98.1	3.1	62.0	1.4	63.3	0.63
0.6	98.8	3.8	76.0	0.7	55.4	1.08
0.8	99.0	4.0	80.0	0.5	61.2	1.31
1.0	99.2	4.2	84.0	0.3	60.0	1.67
0.86 (optimum)[b]	99.16	4.16	83.2	0.34	61.1	1.41

ΔP: purity gain; R: reduction in the non-ethanol fraction; glycerol demand: mL of glycerol charged per mL of distillate. [a] Excluded from the yield analysis (Table 1). [b] Model predictions (Table 4).

Table 6 places these results alongside recent experimental benchmarks. Dakwa et al. [33] added glycerol directly to a fermented glutinous-rice broth and reported an optimum at about 50 mL of glycerol per 200 mL of broth, beyond which additional glycerol lowered the separation efficiency, an effect they attributed to the increased viscosity of the still contents. This agrees with the diminishing returns and the shallow yield maximum observed here, although their feed was far more dilute and their distillate remained well below the azeotrope. Starting from a comparable 95.64% (v/v) cassava distillate, Hargono et al. [34] reached 99.62% (v/v) with a zeolite 4A adsorption column, which indicates that the residual 0.3–0.5 pp left after glycerol-assisted distillation could be removed by a comparatively simple fixed-bed polishing step. Continuous extractive columns that use glycerol or glycerol–glycol mixtures reach fuel grade in simulation studies [15], [31], and a recent cost analysis showed that the cost of purifying bioethanol by extractive distillation falls as the ethanol concentration of the feed increases [35]. Response surface methodology has so far been applied mainly to the upstream fermentation stages of bioethanol production [36]; applying it to the downstream dehydration step, as done here, provides operating guidance at the point where the purity–yield trade-off is decided.

Table 6. Comparison with recent experimental studies on upgrading fermentation-derived bioethanol

Study	Feedstock	Upgrading method	Initial → final ethanol
Dakwa et al. [33]	White glutinous rice broth	Glycerol added to the still (50 mL per 200 mL broth); pycnometer	5.47% → 50.41%
Hargono et al. [34]	Bitter cassava	Distillation followed by zeolite 4A adsorption column	95.64% → 99.62% (v/v)
This study	Cassava	Glycerol-assisted batch extractive distillation (0.86:1, 60 min); alcoholmeter and GC-MS	95.0% → 99.16% (v/v, predicted); 99.2% measured at 1:1

Concentration units as reported by the original authors.

3.7. Practical implications for small-scale producers

The present unit is a laboratory-scale demonstration, and its performance should be read within these limits: one 90-min batch was run per condition, and heating energy, boil-up rate, and glycerol losses were not metered, so the energy consumption and operating cost per litre of product cannot yet be reported. The measured data nevertheless allow a first estimate of the material requirements of a scaled-up batch still. At the optimum, each litre of 95% (v/v) feed requires 0.86 L of glycerol and gives about 0.61 L of distillate at ≈99.2% (v/v), i.e., about 1.4 L of glycerol per litre of upgraded ethanol (Table 5). Because glycerol is not consumed but only takes up the water of the feed (about 0.05 L per litre) together with the ethanol left in the still, the viability of the process depends on regenerating the glycerol, for example by evaporating the absorbed water under vacuum, and on returning the ethanol-rich still residue to the next batch. Operating at 0.6:1 instead of 0.86:1 would reduce the glycerol inventory by about 30% at a cost of about 0.4 pp in purity.

For transfer to small-scale producers, the operating window identified here can be translated into a simple procedure with three control points that can be checked with low-cost instruments: the glycerol dose (measured by volume), the still temperature (78 °C), and the distillate collection time, with product acceptance verified by a temperature-corrected alcoholmeter reading. Routine upkeep would comprise inspection of the column joints and seals, the heating element, and the condenser water supply, together with monitoring of glycerol quality between regeneration cycles, because the GC-MS results show that glyceride-type impurities can be carried over into the product. Pilot-scale trials with replicated batches, metered energy input, and repeated glycerol recycling are needed to establish the operating cost, the glycerol make-up rate, and long-term reliability before field deployment.

3.8. Implications and limitations

Within the studied range, the alcoholmeter measurements and the purity model did not reach the fuel-grade specification of 99.5% (v/v): the highest measured purity was 99.2%, and even the upper 95% prediction limit at the model maximum (99.33%) remains below 99.5%. The GC-MS results show that organic impurities are minor, so the remaining gap is mainly water. Glycerol-assisted batch distillation is therefore best regarded as an effective dehydration step that brings cassava bioethanol well past the azeotrope; reaching fuel grade will require more separation stages with the solvent fed at the top of the column, or a polishing step such as molecular-sieve or zeolite adsorption [7], [11], [34].

Several limitations should also be noted. Each glycerol ratio was run as a single batch from which the five time samples were taken, so the observations are not fully independent and randomization was restricted; replicate batches, or a split-plot analysis, would give more reliable error estimates [24] and would allow a lack-of-fit test. Three yield observations at 0.2:1 were excluded, so the yield response at the lowest ratio rests on two points, and no separate confirmation run was performed at the predicted optimum. The water content of the distillate was not determined directly, so the composition of the non-ethanol fraction is inferred from the combination of alcoholmeter and GC-MS results. Alcoholmeter readings above 99% (v/v) depend strongly on temperature correction and scale resolution and cannot distinguish water from other components. Finally, future work should address the recovery and reuse of glycerol, for example by vacuum evaporation of the absorbed water, and the use of crude glycerol from biodiesel plants, whose methanol, salt, soap, and glyceride content may affect both separation performance and product quality.

4. CONCLUSION

Glycerol proved to be an effective green entrainer for upgrading cassava bioethanol by batch extractive distillation. After pre-concentration to 95% (v/v) by simple distillation, ethanol purity was controlled solely by the glycerol-to-ethanol ratio, increasing from 97.0% (v/v) at 0.2:1, essentially the azeotropic composition, to 99.2% (v/v) at 1:1, with diminishing returns above 0.6:1; collection time had no effect on purity. Relative to the 95% (v/v) feed, this corresponds to a 40–84% reduction in the non-ethanol fraction. Yield, expressed relative to the bioethanol feed, was controlled mainly by collection time and showed a shallow maximum at a ratio of about 0.75:1. Reduced quadratic models described purity (adjusted $R^2 = 0.993$) and yield (adjusted $R^2 = 0.865$; predicted $R^2 = 0.798$), and desirability-based optimization identified a glycerol ratio of 0.86:1 and a collection time of 60 min as the best compromise, with a predicted purity of 99.16% (v/v) and a yield of 61.1% ($D = 0.961$). GC-MS showed that ethanol made up 99.64–99.81% of the detected organic compounds, indicating that the remaining gap to the 99.5% (v/v) fuel-grade specification is mainly water. Future work should determine the water content of the product directly, replicate the batches, and combine glycerol-assisted distillation with additional separation stages or a final dehydration step, together with glycerol recovery and reuse. By turning a biodiesel by-product into a reusable entrainer for simple batch equipment, the process offers a low-complexity route for decentralized bioethanol upgrading in line with SDG 7 and SDG 9, which should be confirmed by pilot-scale trials with metered energy use and glycerol recycling.

DATA AVAILABILITY

The data supporting the findings of this study are available from the corresponding authors upon reasonable request.

DECLARATIONS

Author contribution: Conceptualization, K.N.S., A.F.K.N., A.F.N., and N.K.S.; methodology, K.N.S., A.F.K.N., A.F.N., and N.K.S.; data collection, A.N. and N.K.S.; data analysis, K.N.S. and N.K.S.; writing, K.N.S., A.F.K.N., A.F.N., and N.K.S.; supervision, N.K.S.; funding acquisition, N.K.S.

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During the preparation of this manuscript, the authors used Claude Opus 5.5 (Anthropic) to convert the manuscript into the AJARCDE template format (page layout, heading and paragraph styles, table, figure and equation formatting, and arrangement of the article information section). The tool was not used to write the scientific content, to collect or analyse data, to produce figures, or to generate references. All content was reviewed and validated by the authors, who take full responsibility for the content of this article.

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