Utilization of Waste Banana for Bioethanol Production to Replace Methanol in Biodiesel Process

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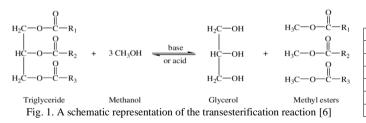
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Abstract— The current study investigates the possibility of substituting bioethanol for short-chain alcohols in the production of biodiesel via a fermentation process using waste bananas. For one week, waste bananas from a local market were fermented with S.cerevisiae (Baker's yeast) to generate ethanol that contained 8% bioethanol. A triple distillation process resulted in a product that was 95% pure bioethanol. Molecular sieves were used to absorb the remaining water in bioethanol as a dehydration step. Pure bioethanol was added to create potassium ethoxide, which is used to make biodiesel. After washing, 81.17% of biodiesel was produced. The viscosity, flash point, density, and acid value of the biodiesel were compared to those of biodiesel made with potassium methoxide and potassium ethoxide, respectively. All parameters are within ASTM specifications, demonstrating that bioethanol produced from waste banana fermentation is an excellent short-chain alcohol substitute for biodiesel production.

Keywords—Banana waste, Biodiesel, Bioethanol, Fermentation, Transesterification.

I. INTRODUCTION

The depletion of fossil fuel resources and the growing discussion of environmental pollution has gained renewable energy sources attention. Biodiesel is a promising alternative energy with properties that comply with fossil diesel [1]. Biodiesel has various advantages over fossil diesel, including a comparable energy potential, minimal sulfur emissions, and abundant raw materials, such as edible and non-edible oil sources, which contribute to sustainable development [2]. The transesterification process is the most prevalent method for biodiesel production, and the reaction parameters have been optimized by numerous researchers worldwide [3-4]. Biodiesel is produced by the reaction of triglyceride sources with alcohols of short chain in the presence of a catalyst. [5] Both homogeneous and heterogeneous catalysts can be utilized for transesterification. During the stoichiometric reaction, 3 mol of methanol and 1 mol of triglycerides react at approximately 60°C to form biodiesel and glycerol, as shown in Figure 1 [6].



Upon completion of the reaction, the products were transferred to a separation funnel and allowed to settle overnight to form two layers. Most of the time, leftover glycerol generates an environmental problem due to its low purity and treatment [7]. Residual glycerol comprises unreacted raw components like triglycerides, methanol, and soap [8]. Methanol is a substance that is produced through chemical processes, whereas other compounds have biological origins. Therefore, substituting methanol with bioethanol is a crucial and timely concern for a sustainable product to move forward. Biodiesel production costs primarily comprise raw materials, which account for between 60% and 95% of total production costs [9-10]. Therefore, minimizing the cost of raw materials to replace fossil fuels in the transportation industry is essential. The necessity for alcohol accounts for almost 20% of the cost of raw materials. Methanol is the typical alcohol used for transesterification. However, methanol must be replaced by inexpensive organic bioethanol to reach the true benefit of biodiesel. Figure 2 depicts the chemical structures of methanol and ethanol, and Table 1 lists their salient properties.

Fig. 2. Methanol structure at the left and ethanol structure at the right side

TABLE 1. physiochemical properties of methanol and ethanol [11].						
Physiochemical property	Methanol	Ethanol				
Molecular weight (g/mol)	32.04	46.07				
Oxygen content (wt.%)	49.93	34.73				
Carbon content (wt.%)	37.5	52.2				
Hydrogen content (wt.%)	12.5	13.1				
Destiny (g/cm ³)	0.792	0.785				
Boiling point at 1 atm (°C)	64	78				

Previous research has been undertaken to study the effect of ethanol and bioethanol on biodiesel production [12]. The study examined the output and properties of biodiesel produced from bioethanol. However, the primary objective of this study was to examine the lack of research on the use of fermented bioethanol in biodiesel synthesis and the relative impacts of methanol, ethanol, and bioethanol on the fuel.



II. METHODOLOGY

Production of bioethanol from fermentation:

A sample of fully ripened and damaged bananas were collected from a local market in Colombo, ready to be discarded in the municipal waste. The samples were then sterilized by washing them in a 5% KMnO₄ solution and rinsing them twice with distilled water. Then, 7.6kg of the banana sample was ground in a kitchen blender to reduce the particle size and increase the rate of downstream reactions. After adding water to dissolve the banana sample in a solid: liquid ratio of 1: 4, the entire sample was transferred into the tank, which had excess air space. The medium's specific gravity was determined. Following that, the pH of the medium was determined and adjusted to 5. The sample was then introduced into the fermentation process. Alcoholic fermentation of reducing sugars is a biological process in which a microorganism converts simple sugar to ethanol, releasing CO₂ and other byproducts in the process. The baker's yeast (Saccharomyces cerevisiae) inoculum was prepared by dissolving it in 500 mL of warm water containing dissolved 100 g of sugar. The yeast was added at a 25: 1 weight ratio of banana sample to yeast. The prepared banana sample was then inoculated with yeast inoculum. The fermentation tank was covered with a lid, and an air trap was installed to extract CO₂ from the medium by creating an anaerobic environment. Fermentation took place at room temperature (on average, 30°C). Temperature is critical in fermentation because it increases the rate of fermentation when the medium temperature rises. When temperatures exceed 40°C, most enzymes in microorganisms denature or unfold, resulting in a decrease in the rate of fermentation. After seven days of fermentation, the fermented medium was filtered to remove solid particles. The specific gravity of prepared bioethanol was determined. Specific gravity reduction was revealed the presence of ethanol in the medium, and a specific gravity method was used to approximate the ethanol yield. To separate the bioethanol, a distillation series was performed. After the distillation process, the bioethanol sample reached 95% purity. Bioethanol from the distillation process was dehydrated using 3A molecular sieves to reduce the remaining water content which is less than 1% by volume.

Bioethanol characterization:

The physical properties of bioethanol, such as flash point, density, kinematic viscosity, and cetane index, were determined in the laboratory. The ASTM analytical technique was used to ensure that all samples were subjected to the same conditions.

The purity of the ethanol produced from waste banana fermentation was analyzed by gas chromatography equipped with a flame ionization detector, GC-FID, at the industrial technology institute, Sri Lanka.

Production of biodiesel from transesterification:

A sample of waste cooking oil (WCO) was collected from a local market in Colombo, ready to be discarded in the municipal waste. To remove suspended matter and moisture content from WCO, filtration followed by preheating at 110°C

were carried out. According to ASTM D664-07, the acid value of WCO was 1.86 mg KOH/g. Due to the acid value being less than 2 mg KOH/g, direct transesterification was performed in a closed container. Transesterification was carried out in the manner described by Miyuranga et al. [13]. Alcohol such as methanol, ethanol, and bioethanol (6: 1 alcohol molar ratio by molar of oil) and potassium hydroxide (1 wt.% by oil weight) were combined to promote the formation of potassium methoxide or potassium ethoxide, depending on the type of alcohol used. When the alkoxide (methoxide or ethoxide) was introduced to the WCO, the transesterification reaction was commenced. The reaction was carried out at 600 rpm for 30 minutes at a temperature of 60°C. After 30 minutes, the solution was transferred to a separatory funnel and kept at room temperature for four hours to separate the glycerin and biodiesel layers. The upper layer, comprised of biodiesel, was removed and rinsed with hot water to remove any remaining catalyst from the biodiesel. Any remaining water and alcohol were removed by heating it for 20 minutes at a temperature of 110°C. Washing and drying were carried out until the pH of the biodiesel reached approximately 7. The percentage of biodiesel produced was calculated as shown in (1). В

$$Biodiesl yield \% = \frac{Biodiesel \ dry \ weight}{WCO \ dry \ weight} \times 100\%$$
(1)

Biodiesel characterization:

The physical properties of biodiesel derived from methanol, ethanol, and bioethanol were determined in the laboratory, including flash point, density, kinematic viscosity, and chemical characteristics of acid value. The ASTM analytical technique ensured that identical conditions were maintained for all samples.

III. RESULTS AND DISCUSSION

Fermentative ethanol or bioethanol refers to the ethanol that is created organically. Due to its capacity to function as an oxygenating component for gasoline, ethanol has gained a significant presence in the fuel sector as a replacement for existing fuels and as a fuel additive. The process of ethanol production is based on the raw materials employed. Since the commencement of ethanol production, first-generation feedstocks consisting of starchy or sugar-containing materials have been used as feedstocks. The widespread use of firstgeneration feedstocks to create ethanol has led to a food crisis and ethical problems. Fermentation was followed by S. cerevisiae activity for one week to make bioethanol, resulting in an 8 wt.% bioethanol production from 7.6 kg of waste banana. To determine the level of purity of the produced bioethanol, the specific gravity of the bioethanol after the first distillation was determined to be 0.9576. Its confirmed purity was 25% (v/v). To achieve the requisite level of purity, which was determined to be 95% (v/v), a number of distillations were necessary (triple distillation). Due to the use of molecular sieves of type 3A, the concentration of water molecules in the final bioethanol solution was decreased to less than 1%, enabling the completion of the process of enhancing the bioethanol's purity to 98%. The results of the



analysis of the physicochemical properties of final bioethanol are presented in Table 2.

TABLE 2. physiochemical properties of bioethanol			
Physiochemical property	Bioethanol		
Density at 15°C (g/cm ³)	0.790		
Kinematic viscosity at 40°C (cSt)	1.1325		
Flash point (°C)	13		
Cetane index	5-8		
Ethanol content (vol.%)	98		

This study was conducted utilizing a lower alcohol-to-oil molar ratio, such as 6: 1, to assess the impact of alcohol type on biodiesel production. This experiment examined several distinct types of alcohol, including commercially available methanol, ethanol, and generated bioethanol. Figure 3 depicts the yield of biodiesel that may be produced from the various Table 3 depicts the biodiesel's alcohols, while physicochemical characteristics. According to Fig. 3, the most outstanding results for the generation of biodiesel were obtained by transesterifying WCO with methanol. This generated a yield of 94.23%. This was followed by ethanol, which resulted in an 83.5% biodiesel yield. Bioethanol produced a yield that was substantially identical to that of ethanol (81.17%), demonstrating that the substitution of bioethanol for ethanol had no adverse effect on biodiesel production.

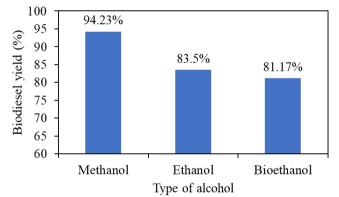


Fig. 3. Effect of type of alcohol on biodiesel yield (reaction condition: catalyst amount 1 wt.%; alcohol-to-oil molar ratio of 6: 1; reaction temperature 60°C reaction time 30 min, reaction stirring speed 600 rpm

Although the yield of biodiesel produced by the conversion of ethanol and bioethanol over methanol was relatively low. this could be explained because ethanol/bioethanol is less reactive than methanol [14], which results in lower yields. Although ethoxide ions have a higher nucleophilicity (1.0) than methoxide ions (0.82), they have lower mobility than methoxide ions due to their longer carbon chain [15]. Also, Alkaline metal hydroxides are precursors to transesterification catalysts because they react with ethanol to form the active species CH₃CH₂O⁻, whereas alkaline metal alkoxides are already catalysts. Water is formed concurrently with the synthesis of the active species CH₃CH₂O⁻, which results in hydrolysis and saponification processes, lowering ethyl ester yields. As a result, the overall water content of the reaction medium was higher in bioethanol than in commercially available ethanol or methanol. Due to the highwater content of bioethanol, the yield of biodiesel produced from bioethanol was slightly lower than that produced from ethanol. Water content must be kept to a minimum in the reaction medium to prevent hydrolysis, which reduces transesterification yield. Triglycerides are hydrolyzed by water to form FFA, which are then converted to soaps in an alkaline reaction medium [16].

According to the observation of this study, more soap was formed from ethanol and bioethanol. This is attributed to the fact that the water content in ethanol is higher than that of methanol, according to Mendow, Veizaga and Querini [17], which promotes the side reaction saponification with the homogeneous base catalyst in this study. Ethanol's more excellent solvency implies the creation of emulsions (and soaps) due to the properties of ethanol, which may inhibit mass transfers [17]. Bioethanol produced from waste banana fermentation had a lower purity (98%) than ethanol (99.5%). Thus, bioethanol theoretically contributes more water to the reaction medium, increasing soap production. To substantiate the theory, biodiesel from WCO and bioethanol were produced at a high alcohol-to-oil molar ratio of 24: 1 to observe the precise observation. Increased soap formation resulted in a higher alcohol-to-oil molar ratio for bioethanol over ethanol. Increased soap creation results in the formation of gels, as shown in Fig. 4a, which could trap a significant number of esters within the glycerin layer, resulting in the loss of biodiesel. As a result, complications arise during the glycerol separation process. Previous studies have also observed this situation [18-20]. This can be expressed as excess ethanol/bioethanol in the reaction medium, posing phase separation problems. Excess ethanol/bioethanol, which is soluble in the glycerol-rich phase, results in a decrease in the latter's density, resulting in phase inversion. Moreover, ethyl esters were more challenging to synthesize with basic catalysts than methyl esters, owing to the production of stable emulsions during ethanolysis. According to Zhou, Konar, and Boocock [21], these emulsions are far more stable in ethanolysis, and important separation and purification difficulties are addressed. Emulsions are formed in part by producing polar hydroxyl groups and nonpolar hydrocarbon chains in mono and diglyceride intermediates that have a high surface activity and are utilized as emulsifiers in the food sector.

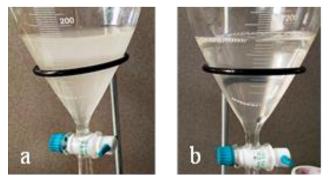


Fig. 4. transesterification product with alcohol-to-oil molar ratio of 24: 1. a: bioethanol; b: ethanol (reaction condition: catalyst amount 1 wt.%; alcohol-tooil molar ratio of 24: 1; reaction temperature 60°C reaction time 30 min, reaction stirring speed 600 rpm



The physical and chemical properties of WCO-derived biodiesel derived from methanol, ethanol, and bioethanol were investigated. The measured properties were compared to ASTM specifications, and the results are presented in Table 3. Due to the higher molecular weight of ethyl esters derived from ethanol and bioethanol, their kinematic viscosity was slightly more significant than methyl esters. However, the density, kinematic viscosity, acid value, and flash point of biodiesel produced from methanol, ethanol, and bioethanol were determined to be within the ASTM limit. Thus, the physicochemical properties of biodiesel derived from bioethanol were consistent with ASTM standard values, indicating that bioethanol could be used in the production of biodiesel.

This study suggests a more environmentally-friendly method of manufacturing biodiesel from bioethanol by substituting chemically manufactured alcohol since bioethanol is significantly less toxic than methanol; thereby, biodiesel could be produced with minimal impact on the environment.

TABLE 3. physiochemical properties of biodiesel derived from methanol,
athenal and bioathenal

		ASTM	WCO	WCO	WCO
Physicochemical	Test	D6751	Biodiesel	Biodiesel	Biodiesel
property	method	standard	with	with	with
		values	Methanol	Ethanol	Bioethanol
Density at 15°C	ASTM	0.860-	0.882	0.893	0.898
(g/cm^3)	D4052	0.900			
Kinematic	ASTM				
viscosity at 40°C	D445 -	1.9-6.0	4.2	5.4	5.8
(cSt)	19a				
Acid value (mg	ASTM	< 0.5	1.85	1.75	1.72
KOH/g)	D664	<0.5	1.65	1.75	1.72
	ASTM				
Flash point (°C)	D93 -	>130	138	140	139
	20				

IV. CONCLUSION

The present study examines methanolysis and ethanolysis of waste cooking oil using methanol, ethanol, and bioethanol. A yield of 8 wt.% bioethanol was obtained from 7.6 kg of waste banana. After triple distillation, 95% pure bioethanol was obtained. As a dehydration step, molecular sieves were used to absorb the remaining water content in bioethanol and increase the purity by 98%. Pure bioethanol was introduced to produce potassium ethoxide for the production of biodiesel. A yield of 81.17% was obtained by maintaining a molar ratio of 6: 1 for bioethanol and using 1 wt.% KOH as the catalyst for 30 minutes at a temperature of 60°C for ethanolysis by bioethanol, whereas a yield of 83.5% was obtained by ethanol, indicating nearly the exact biodiesel yield under the same reaction conditions. The biodiesel's viscosity, flash point, density, and acid value were compared to those of biodiesel produced using potassium methoxide and potassium ethoxide (ethanol from a chemical supplier). All parameters meet ASTM standards, demonstrating that bioethanol produced from waste banana fermentation is an excellent short-chain alcohol substitute for biodiesel production.

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REFERENCES

- U. Lawan Muhammad, "Biofuels as the Starring Substitute to Fossil Fuels", *Petroleum Science and Engineering*, vol. 2, no. 1, p. 44, 2018. http://dx.doi.org/10.11648/j.pse.20180201.17
- C. Brunschwig, W. Moussavou and J. Blin, "Use of bioethanol for biodiesel production", *Progress in Energy and Combustion Science*, vol. 38, no. 2, pp. 283-301, 2012. https://doi.org/10.1016/j.pecs.2011.11.001
- F. Ma and M. Hanna, "Biodiesel production: a review1Journal Series #12109, Agricultural Research Division, Institute of Agriculture and Natural Resources, University of Nebraska–Lincoln.1", *Bioresource Technology*, vol. 70, no. 1, pp. 1-15, 1999. https://doi.org/10.1016/S0960-8524(99)00025-5
- K.A. Viraj Miyuranga, U.S.P.R. Arachchige, D. Thilakarathne, R.A. Jayasinghe and N.A. Weerasekara, "Effects of Physico-Chemical Properties of the Blended Diesel and Waste Cooking Oil Biodiesel", *Asian Journal of Chemistry*, vol. 34, no. 2, pp. 319-323, 2022.https://doi.org/10.14233/ajchem.2022.23502
- K.A.V. Miyuranga, D. Thilakarathne, Udara S.P.R. Arachchige, R.A. Jayasinghe and N.A. Weerasekara, "Catalysts for Biodiesel Production: A Review", Asian Journal of Chemistry, vol. 33, no. 9, pp. 1985-1999, 2021. https://doi.org/10.14233/ajchem.2021.23332
- D. Thilakarathne, K.A.V. Miyuranga, U.S.P.R. Arachchige, N.A. Weerasekara, R.A. Jayasinghe, "Production of Biodiesel from Waste Cooking Oil in Laboratory Scale: A Review", International Journal of Scientific Engineering and Science, vol. 5, no. 6, pp. 28-34, 2021.
- K.A.V. Miyuranga, U.S.P.R. Arachchige, R.A. Jayasinghe, and G. Samarakoon, "Purification of Residual Glycerol from Biodiesel Production as a Value-Added Raw Material for Glycerolysis of Free Fatty Acids in Waste Cooking Oil," Energies, vol. 15, no. 23, p. 8856, Nov. 2022, https://doi.org/10.3390/en15238856
- F. Pitt, A. Domingos and A. Barros, "Purification of residual glycerol recovered from biodiesel production", South African Journal of Chemical Engineering, vol. 29, pp. 42-51, 2019. https://doi.org/10.1016/j.sajce.2019.06.001
- U.S.P.R. Arachchige, K.A.V. Miyuranga, D. Thilakarathne, N.A. Weerasekara, R.A. Jayasinghe, "Potential Utilization of Waste Cooking Oil in Sri Lanka: Policy Implementation", *International Journal of Scientific Engineering and Science*, vol. 5, no. 11, pp. 1-5, 2021
- D. Thilakarathne, U. Arachchige, R. Jayasinghe, N. Weerasekara and K. Miyuranga, "Impact of the Quality of Waste Cooking Oil on Biodiesel Production", in *ITUM Research Symposium 2021*, ITUM, University of Moratuwa, Sri Lanka, 2021, pp. 97-100.
- S. Iliev, "Comparison of Ethanol and Methanol Blending with Gasoline Using Engine Simulation", in Biofuels - Challenges and opportunities. London, United Kingdom: IntechOpen, 2018 [Online]. http://dx.doi.org/10.5772/intechopen.81776
- A. Hassan, H. Alhameedi and J. Smith, "Using ethanol for continuous biodiesel production with trace catalyst and CO2 co-solvent", Fuel Processing Technology, vol. 203, p. 106377, 2020. https://doi.org/10.1016/j.fuproc.2020.106377
- K.A.V. Miyuranga, Balasuriya B.M.C.M, D. Thilakarathne, U.S.P.R. Arachchige, N.A. Weerasekara, R.A. Jayasinghe, "Production of Biodiesel Using Acetone as a Co-Solvent", International Journal of Scientific Engineering and Science, vol. 6, no. 2, pp. 52-56, 2022.
- M. Kulkarni, A. Dalai and N. Bakhshi, "Transesterification of canola oil in mixed methanol/ethanol system and use of esters as lubricity additive", Bioresource Technology, vol. 98, no. 10, pp. 2027-2033, 2007. https://doi.org/10.1016/j.biortech.2006.08.025
- M. Kim, C. DiMaggio, S. Yan, S. Salley and K. Ng, "The synergistic effect of alcohol mixtures on transesterification of soybean oil using homogeneous and heterogeneous catalysts", Applied Catalysis A: General, vol. 378, no. 2, pp. 134-143, 2010. http://dx.doi.org/10.1016/j.apcata.2010.02.009
- M. Lam, K. Lee and A. Mohamed, "Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review", Biotechnology Advances, vol. 28,



Volume 6, Issue 12, pp. 9-13, 2022.

500-518, no. 4. pp. https://doi.org/10.1016/j.biotechadv.2010.03.002

2010.

- 17. G. Mendow, N. Veizaga and C. Querini, "Ethyl ester production by homogeneous alkaline transesterification: Influence of the catalyst", Bioresource Technology, vol. 102, no. 11, pp. 6385-6391, 2011. https://doi.org/10.1016/j.biortech.2011.01.072
- 18. D. de Oliveira, M. D. Luccio, C. Faccio, C. D. Rosa, J. P. Bender, N. Lipke, C. Amroginski, C. Dariva, J. V. de Oliveira, "Optimization of Alkaline Transesterification of Soybean Oil and Castor Oil for Biodiesel Production", Applied Biochemistry and Biotechnology, vol. 122, no. 1-3, pp. 0553-0560, 2005. https://doi.org/10.1385/abab:122:1-3:0553
- 19. A. Domingos, E. Saad, H. Wilhelm and L. Ramos, "Optimization of the

ethanolysis of Raphanus sativus (L. Var.) crude oil applying the response surface methodology", Bioresource Technology, vol. 99, no. 6, pp. 1837-1845, 2008. https://doi.org/10.1016/j.biortech.2007.03.063

- 20. M. Černoch, M. Hájek and F. Skopal, "Ethanolysis of rapeseed oil -Distribution of ethyl esters, glycerides and glycerol between ester and glycerol phases", Bioresource Technology, vol. 101, no. 7, pp. 2071-2075, 2010. https://doi.org/10.1016/j.biortech.2009.11.035
- 21. W. Zhou, S. Konar and D. Boocock, "Ethyl esters from the single-phase base-catalyzed ethanolysis of vegetable oils", Journal of the American Oil Chemists' Society, vol. 80, no. 4, pp. 367-371, 2003. http://dx.doi.org/10.1007%2Fs11746-003-0705-1