

Production And Characterization Of Bioethanol From Cassava Peels

Irene Akinyi Odongo¹, Elly Tetty Osewe¹, Sylvia Opiyo¹.

¹(Department Of Physical And Biological Sciences, Murang'a University Of Technology, Kenya)

Abstract

Majority of rural Africans use inefficient energy sources like wood and fossil fuels, which are not environmentally friendly and hazardous to human health. Bioethanol is an alternative clean source of energy that can be obtained from biomass and other agricultural wastes. Producing bioethanol from agricultural wastes cleans up the environment as it prevents the cutting of trees for wood fuel, thus solve the problem of de-forestation. It also gives farmers an additional source of income from otherwise wasted agricultural materials, reduces indoor pollution, and is more cost-effective due to its higher calorific value. This research focused on characterization of cassava (*Manihot esculenta* Crantz) peel bioethanol. Bulk fermentation of bioethanol was conducted under optimum fermentation conditions, which were determined through Taguchi optimization. The experimentation involved the utilization of cassava (*Manihot esculenta* Crantz) peel pretreated with 0.5 M sulphuric acid. *Saccharomyces cerevisiae* were employed as the yeast source to ferment the acid-pretreated cassava peels. Bulk production was conducted to ensure a sufficient quantity of bioethanol was generated for characterization. The volume of the substrate was raised to 500 ml, and 45 g of yeast was added to the substrate media to start the scaled-up production. In addition, the fermentation period was 18 hours, precise temperature of 40 °C and a pH of 4.5. After the production the produced bioethanol was characterized to establish the following parameters i.e. the density, specific gravity, ethanol concentration, ash content sulphur content, calorific value, pH and the electrical conductivity. The bioethanol produced was characterized and the following parameters registered; The bioethanol yield was 200 L/ton of cassava peels bioethanol, density of 0.8763 g/cm³, specific gravity of 0.8779 g/cm³, ethanol concentration of 73.63 %v/v, ash content of 0.005, sulphur content of 0.0788, flash point of 17 °C, kinematic viscosity of 3.677 centistrokes (cst), the calorific value of 21.89 MJ/kg, pH of 4.286, and conductivity of 8.81 µs/m.

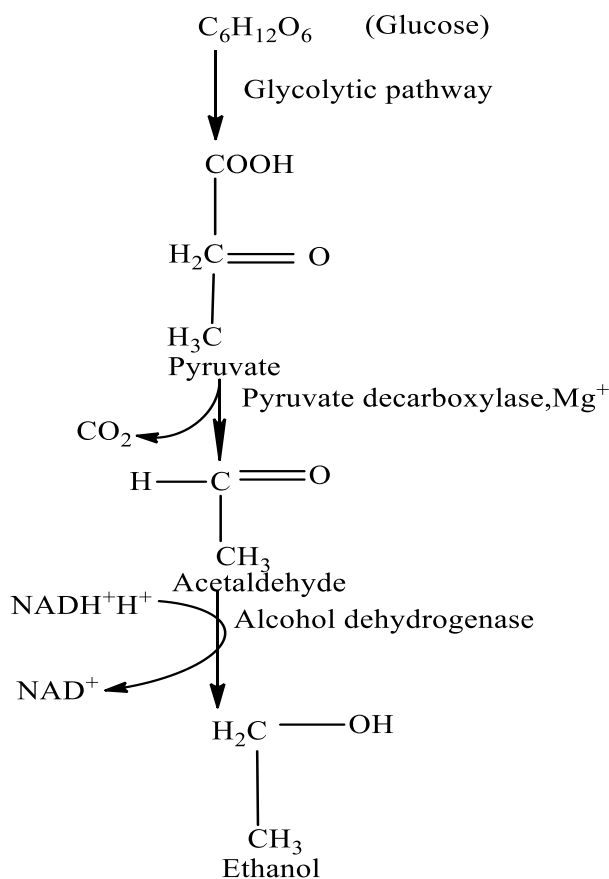
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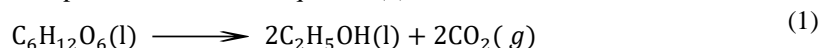
I. Introduction

The reliance on fossil fuels as the dominant source of energy has resulted in many detrimental environmental consequences¹. Emissions of hazardous particles and gases play a significant role in climate change. Pollutant gases cause a variety of health and developmental defects in children². Nowadays, bioethanol is the most utilized liquid biofuel on the market.³ Therefore, biofuels are alternative sources of clean and affordable energy⁴. The manufacture of bioethanol uses many biomass sources⁵. Many countries have set lofty goals for replacing petroleum-based fuels with them⁶. Before fermentation, lignocellulose must undergo pretreatment. Various methods are available such as using physical, chemical, and physicochemical methods and biological agents like *Aspergillus niger*, *A. oryzae*, *Humicola insolens* and *Trichoderma reesei*, which deconstruct the lignocellulose structure^{7,8}. Although fermentation is a natural process, microorganisms are still needed for the conversion of C₆H₁₂O₆ into C₂H₅OH or lactic acid, or many other products, where numerous industrial yeasts, including, *Saccharomyces cerevisiae* are employed for these purposes⁹. It is the primary fermentative strain employed in industries producing sugar-based biofuels. Pretreatment transforms the cellulosic material or slurry into fermentable sugars, making it suitable for either enzymatic or acidic hydrolysis. *Saccharomyces cerevisiae* is used in fermentation to convert C₆H₁₂O₆ into C₂H₅OH under anaerobic conditions and at a specific temperature⁹. The yeast cells directly metabolize a sugar like glucose through the glycolysis pathway in order to produce energy for biosynthesis. For every mole of glucose consumed, the fermentation process' total reactions provide two moles of ethanol and carbon dioxide^{10,11}



Scheme 1: Yeast fermentation of glucose into ethanol ^{12, 11}

The summary of the fermentation process is shown in equation (1) below;



Factors that affect bioethanol yield include; pHs, fermentation time, yeast: substrate ratio, and temperature. Based on the results, the greatest bio-ethanol yield was 45.50 % at the same time the fermentation temperature was 35 °C, the yeast concentration was 10 %, the C₆H₁₂O₆ concentration was 100 g/L, and the fermentation time was 6 days ¹³. Eighty three percent of C₂H₅OH was obtained from cassava peel using *Zymonas mobilis*¹⁴. Egboosiuba ¹³ characterized the obtained bioethanol and obtained that the water (H₂O) content of the bioethanol produced was 0.0021 ppm, sulphur content was 0.0003 %, which was lower than the ASTM maximum standard fuel sulphur value of 0.05 %. The flash point of the bioethanol produced was 14.2 °C. Bioethanol generated had a specific gravity of 0.785 kg/L at room and at standard temperature was 0.750 kg/L.

II. Material And Methods

Yeast (*Saccharomyces cerevisiae*) was purchased from a local supermarket. Pearl millet was obtained from a local market, Buffer tablets pH 4 and 7, NaOH 99.9%, and H₂SO₄ 98% of analytical grades were obtained from Sigma Aldrich Chemical distributors, Nairobi Kenya.

Sample collection and preparation

The cassava used in this study was obtained from a farmer in Kodiaga and its geographical coordinates is 0°05'55.7" North and 34°26'14.8" East situated in North Gem, Siaya County, Kenya. The cyanic cassava was washed with water to remove soil pollutants, fertilizers and other foreign substances associated with biomass waste and then peeled off. The peels were sun-dried for one week to remove the moisture and finally milled to obtain cassava peel powder.

Sulphuric acid pretreatment

Using Yussouff ¹⁵ method with some modifications, acid hydrolysis was carried out by adding 200 g of cassava peels powder to 1000 ml of 0.5 M sulphuric acid in a 1000 ml beaker. The samples were heated for 2 hours in a water bath at 98 °C, sterilized in an autoclave for 15 minutes at 121°C, allowed to cool, and then filtered

through No. 1 whatman filter paper using vacuum filtration method. The sample was stored in the refrigerator at 4 °C and later used for bioethanol production.

Determination of the percentage sugar content

After cassava was hydrolyzed, the quantity of total sugar in the hydrolysate was established using refractive index. To do this, a drop of cassava hydrolysate was applied to the glass slide a graduated hand refractometer model REF107 and the brix reading was expressed as a percentage. Following AOAC (2000), a hand refractometer model REF107 was used to calculate the brix (%) ¹⁶.

Production of bioethanol

For the scaled production, 1200 ml of sulphuric pretreated cassava filtrate was poured into a 2000 ml beaker. The sample was then placed on a magnetic stirrer and the filtrate pH was adjusted to 4.5 using 825 ml of sodium hydroxide. Subsequently, 500 ml of the adjusted filtrate was poured into four 500 ml Erlenmeyer flasks with 45 g of yeast added to each flask. These flasks were then placed in a water bath set at 40 °C for six hours. Overnight, the samples were placed in an incubator set at 40 °C to continue fermenting for the next 12 hours, totaling the fermentation time to 18 hours. Following this, the samples were immediately distilled off for further processing. The fermented liquid was poured into a round-bottomed flask, placed on a heating mantle connected to a distillation column, and immersed in running water. The distillate was collected in a vial placed to the opposite end of the distillation column at 78 °C. This was done for each fermented broth using the method indicated by Oyeleke ¹⁷.

Estimation of bioethanol yield

The yield of bioethanol can be stated in a variety of ways, such as mL/g of substrate, g/g of substrate, mL/L of solution, g/L of solution, etc. In order to improve comparability, the bioethanol yield unit was changed to the same unit. The unit was changed in this study into L bioethanol/ton for cassava peel substrate based on the following assumptions in the equation(2) and (3) ¹⁸.

$$\frac{g \text{ bioethanol}}{1 \text{ litre final solution}} = \frac{g \text{ substrate}}{1 \text{ litre initialsolution}} \quad (2)$$

$$= \frac{L \text{ bioethanol}}{\text{ton substrate}} \quad (3)$$

Determination of density, specific gravity and ethanol concentration

The density meter model DMATM 4100 Instrument was calibrated using water as calibration standards. Using a syringe the sample was slowly injected into the glass oscillator until it was completely filled and care was taken to ensure that no air bubbles was present. The readings were taken once constant temperature of 20.0 ±0.3°C was reached.

Determination of ash content

The ASTM D1998 method was used to establish the amount of ash in the biomass samples 1g of each sample was placed in a pre-weighed crucible, which was then placed into a desiccator to dry after being burned at 550 °C for 1 hour in a muffle furnace for ashing process.

Ash content was calculated using Equation (4):

$$\text{Ash content (\%)} = \frac{W_2 - W_0}{W_1 - W_0} \times 100\% \quad (4)$$

Where: W_1 = weight of the container + biomass sample before burning

W_0 = Weight of the container

W_2 = weight of the container + biomass sample after burning

Determination of sulphur content

Using Ismail ¹⁹ methods with some modifications 20 ml of 1:1 hydrochloric acid was added to 20 ml of bioethanol in a beaker, and the mixture was stirred. This step converted the sulfur in the bioethanol to sulphuric acid. The beaker was then placed on a sand bath and heated for 30 minutes, evaporating the excess water and ethanol and concentrating the sulphuric acid. The solution was filtered using a filter paper, and the filtrate was collected in another beaker, while the residue on the filter paper was discarded. 20 ml of barium chloride solution

was added to the filtrate, and the mixture was stirred well, precipitating the sulphuric acid as barium sulfate. The mixture was allowed to stand until the precipitate settled at the bottom of the beaker. If no precipitate formed, it indicated that the sulfur content was very low or negligible. The mixture was filtered again using a filter paper, and the precipitate was collected on the filter paper. The precipitate was washed with distilled water to remove any impurities. The filter paper with the precipitate was transferred to a pre-weighed crucible or beaker. Additionally, an empty filter paper was weighed to use as a blank. The filter paper with the precipitate and the blank were ashed until they turned white, removing the organic matter and leaving only the barium sulfate. The ashed samples and the blank were weighed, and the weight of the blank was subtracted from the weight of the sample to determine the weight of the barium sulfate. The weight of sulfur in the sample was calculated using equation (5):

$$\text{Weight of sulphur} = \text{weight of barium sulphate} \times 233.3906 \quad (5)$$

Where,

32.06 is the atomic weight of sulphur in g/mol

233.39 is the molecular weight of barium sulphate in g/mol

The percentage of sulfur in the sample was calculated using equation (6)

$$\text{Percentage of sulphur} = \frac{\text{weight of sulphur}}{\text{weight of bioethanol sample}} \times 100\% \quad (6)$$

Determination of flash point

The flash point of bioethanol was determined using the Pensky Martens (ASTMD93) method. The test sample was placed in a metal cup in such a way that it just touched the prescribed mark on the inside of the cup. The cover was then be positioned on the cup. The Bunsen burner was used to deliver heat to the apparatus's lower side. The heating was set to provide a 7 °F per minute temperature rise, and the sample was constantly agitated. As the temperature of the flash approaches, the injector burner lights up and then injected in the sample at approximately 12-second intervals until a distinct flash is visible within the container and the injector burner is turned off. A thermometer was used to determine the close flash point at this moment ²⁰.

Determination of viscosity

The Ostwald viscometer was first taken and thoroughly rinsed with water. Subsequently, the apparatus was dried in the oven. It was filled with the test then partially sample (bioethanol) from the lower end of the tube. The liquid was introduced into the viscometer and drawn up to the upper bulb of the tube. The level was maintained stationary by holding it with a finger. The time taken by the sample to descend from the upper marked level to the lower marked level was carefully observed. This process was repeated twice more, and readings were recorded each time ²¹.

Determination of calorific value

Calorimeter model BCY-1A was used to measure the calorific value of the fuel. A crucible was inserted into the bomb after adding of 1g of the fuel. The bomb was filled with oxygen and placed inside the jacket before the fuse was connected with a nichrome wire. The jacket was filled with 2000 ml of water and the calorimeter was put together. A thermometer was used to check the temperature once every minute until it reached a steady value ²².

Determination of pH

The bioethanol was tested using a pH meter biobase model 930 by dipping the pH meter electrode into the sample until it showed a stable scale reading on the pH meter ²³.

Determination of electrical conductivity

The instrument utilized was a digital electrical conductivity meter model 950. 30 ml of bioethanol was transferred into a 100 ml beaker. The electrode was submerged up to the point of censorship. After a stable reading was acquired, the meter was turned on to the necessary calibrated units, and readings was done in triplicate ²⁴.

III. Results And Discussion

Characterization of cassava peel bioethanol

In this study, instead of the typical expression of bioethanol yield as grams of bioethanol per gram of substrate, the yield was measured as liters of bioethanol per fresh cassava, to facilitate comparison with previous research findings. In this study, the yield of bioethanol was established using equation 2 and 3 above. The yield of bioethanol was 200L/ton of cassava peels bioethanol was close to 160 L/ton reported by Dinata and Kartawiria ¹⁸. Density is a crucial characteristic of fuel that plays a significant role in determining its energy content and

practical utility. Ethanol combustion efficiency is crucial for optimizing the quantity of energy converted from the fuel to heat. Incomplete combustion reduces cooking efficiency and results to energy loss. The key to burning ethanol efficiently is to achieve full combustion, which reduces the amount of unwanted byproducts like carbon monoxide produced and instead converts the fuel to CO₂ and H₂O. The density of the produced bioethanol was 0.8763g/cm³ with a specific gravity of was found to be 0.8779g/cm³ (Table 1), which was lower than 0.9970 g/cm³ and 0.955 g/cm³ specific gravities reported by Omoruyi²⁵ and Ogunsuyi²⁶ respectively.

Table 1: Properties of bioethanol produced from sulphuric acid pretreated cassava peels

S/N	parameter	Units	Experimental results	ASTM Standards for Bioethanol
1	Density @ 20 °C	g/cm ³	0.8763	0.750-850
2	Specific gravity	g/cm ³	0.8779	0.87
3	Concentration of EtOH	% v/v	73.63	-
4	Ash		0.005	-
5	Kinematic Viscosity @ 20 °C	Cts/sec	3.6765	5.0 max
7	Sulphur content	% wt	0.0788	0.05
8	Flash point (closed cup)	°C	17	18.60
9	pH	a.u	4.286	-
10	Calorific value	MJ/kg	26.89-29.70	21.89 MJ/kg
11	Electrical conductivity	µS/m	8.81	500max

The concentration of ethanol refers to the amount or proportion of ethanol present in a solution. The concentration of ethanol in the produced bioethanol was 73.63 % v/v, which was higher than 45.50 % reported by Egboosiuba¹³. The ash content of the produced bioethanol was 0.005, which can be considered very negligible. The ash content value was comparable to that previously reported²⁷. Ash buildup can decrease airflow and impair efficient combustion. Ash and other byproducts may be produced when ethanol is not completely burned. A portion of these byproducts might contain contaminants that worsen indoor air quality, which has an impact on the environment and public health

Viscosity is a measure of a fluid's resistance to progressive deformation brought on by shear or tensile stress. When adjacent particles in a fluid collide while moving at different speeds, viscosity is produce²¹. The atomization of the fuel during combustion is impacted by the fuel's viscosity. Increased viscosity can lead to inefficient combustion and poor atomization, which would reduce the burning efficiency and increase emissions. Low kinematic viscosity of ethanol produces less emission during combustion, especially when it comes to particle matter. Reduced production of smoke and other pollutants as well as more thorough combustion can result from the fuel's fine atomization. The produced bioethanol had a kinematic viscosity of 3.6765 cst (Table 1) which was lower but within the ASTM standards than the kinematic viscosity of 1.21×10³ cst previously reported¹³, but was within the ASTM standards.

The amount of sulphur in the produced bioethanol was 0.0788012 % which was close to the one reported by Umezuegbu²⁸ of 0.06 % but lower than the sulphur content of 1.58 reported by Suleiman²⁰. The amount of sulphur in bioethanol can affect how well it burns. Incomplete combustion of sulphur can produce sulphur dioxide (SO₂). The sulphur level of bioethanol is typically a cause for worry. A high sulphur level may cause partial combustion by interfering with the burning process. In addition to producing less energy, incomplete combustion releases hazardous byproducts such carbon monoxide (CO) and particulate particles.

The flash point of the produced bioethanol was 17 °C which falls closely within the range of ASTM standards for combustible and flammable liquids but lower than the flash point of 46 °C reported by Ogunsuyi²⁶. Flame and combustible-grade liquids are fuels with a flash point below 37.8 °C (ASTM, 2011). Due to its volatile nature, bioethanol vapor and oxygen may combine to create a combustible mixture. Because of this, bioethanol evaporation into the air occurs more quickly at higher concentrations, leading to increased combustibility. Higher burning efficiency is preferred to minimize fuel use, guarantee lower emissions, and enhance fuel's efficiency. The low flash point of 17 °C of ethanol implies that ethanol can quickly combine to create a combustible mixture, which can ignite spontaneously.

The pH of the produced bioethanol was 4.286, which was higher and thus less acidic than a pH of 2.85 reported previously²⁹. In terms of acidity, ethanol is rather a weak acid. When contaminants are present in the ethanol, they may behave as bases or acids, changing the solution's overall acidity. Pollutants or impurities can significantly impact the suitability of fuel for various applications. Extremely low pH levels can corrode fuel storage tanks and transportation infrastructure, potentially rendering them unfit for use in certain environment.

The calorific value of fuel bioethanol was 21.89 MJ/kg, which was a bit lower than the 29.78 MJ/kg calorific value of ethanol reported Nwifo³⁰. However, the calorific value can be increase by adding the number of Carboxy Methyl Cellulose (CMC)³¹. The presence of carbon and hydrogen content elements in CMC has the potential to enhance the fuel's calorific value. This is due to the combustion process, where carbon interacts with

oxygen, resulting in the generation of heat ³¹. The calorific value of fuel bioethanol reveals the amount of energy one can obtain by burning a specific mass of bioethanol. A higher calorific value implies that the fuel can release more energy when combusted, making it more efficient for use as a source of heat.

The produced bioethanol had an electrical conductivity of 8.81 $\mu\text{s}/\text{m}$ which was within the ASTM standards (Table 1). The electrical conductivity was lower than the electrical conductivity of 329 $\mu\text{s}/\text{m}$, 330 $\mu\text{s}/\text{m}$, 230 $\mu\text{s}/\text{m}$, 300 $\mu\text{s}/\text{m}$, 150 $\mu\text{s}/\text{m}$ obtained from the following varieties of cassava TMS 92B/00068, TMS 91/02324, TMS 92B/0061, TMS 98/0505, TMS 98/058 respectively reported by Ademiluyi ²⁴. Fuel ethanol's electrical conductivity is a crucial factor to consider when assessing the quality of the fuel. Electrochemical or galvanic corrosion is more likely to occur in high-conductive fluids due to the correlation between conductivity and the presence of corrosive ions like chlorine ³². Higher purity bioethanol typically has lower electrical conductivity. Bioethanol boasts a commendably low electrical conductivity, attributed to its pure composition resulting from fermentation, where the absence of ionic components prevents an increase in its conductivity.

IV. Conclusion

The cassava peels not only satisfies the ASTM legal requirements but also provide advantages for the environment. Cassava peel bioethanol can therefore be suggested as a practical alternative fuel source for a range of applications, supporting sustainable energy practices and lowering reliance on fossil fuels, based on the empirical evidence provided in this work. The 200 litres per tonne of bioethanol was obtained at the optimum pH of 4.5, temperature of 40 °C, 45 g of yeast, glucose concentration of 14.5 %, fermentation period of 18 hours. The properties of the cassava peels bioethanol had the following characteristics density of 0.8763 g/cm³, specific gravity of 0.8779 g/cm³, ethanol concentration of 73.63 %v/v, ash content of 0.005, sulphur content of 0.0788, flash point of 17 °C, kinematic viscosity of 3.677 centistokes (cst), calorific value of 21.89 MJ/kg, pH of 4.286, and conductivity of 8.81 $\mu\text{s}/\text{m}$.

V. Recommendation

In order to enhance the production of bioethanol under the specified conditions of pH 4.5, yeast quantity of 45 g, temperature of 40 °C, and fermentation duration of 18 hours, it is very important to maintain pH of the fermentation media throughout the process this will ensure optimal activity of the yeast. Quality yeast strains should be utilized, with careful attention to the viability of the yeast strain that used during fermentation. Fermentation temperature to be strictly maintained at 40 °C for optimal activity of the yeast, and process of fermentation to be monitored closely to adjust parameters as needed.

Future works

Bioethanol, while meeting biofuel requirements, there is needs to improve its calorific value. Carboxymethyl Cellulose (CMC) can increase ethanol's calorific value by adding more flammable material and increasing the carbon-to-hydrogen ratio. CMC also improves fuel atomization and combustion efficiency, allowing for more thorough mixing of fuel with air.

Declaration of conflict of interest

The authors hereby declare no conflict of interest in publishing this paper.

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