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Production and Characterization of Bioethanol from Acid Catalysed Hydrolysis of Cellulosic Biomass (*Maize Cob*)

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Abstract: The purpose of this finding is to produce ethanol using a second generation biomass (*maize cob*) and to investigate the potential of bioethanol production from cellulosic biomass (*maize cob*). Due to a great dependence on fossil resources, continuously rising of petroleum cost and increase in greenhouse emission have compelled policy makers toward attaining a renewable and sustainable source of energy such as bioethanol. In the cause of production of bioethanol using *maize cob*, the study of dilute H_2SO_4 hydrolysis (0.25 M to 2M) was first carried out at varying temperatures; (40 to 100°C) and reaction time (60 to 105 min) under a magnetic stirrer. The percentage yield of glucose was carried out to ascertain the yield from the substrate used, physicochemical characterization was also done to know both the physical and chemical component of the bioethanol produce also, fuel characterization was conducted on the bioethanol to ascertain if the produce is truly bioethanol and to know if it can be used as fuels in engines. From the result, a low glucose yield was observed at low acid concentration of 0.25 M and 0.5 M with gradual increase at 1 M and 2 M. A remarkable glucose yield was observed at high temperature 90°C with declining effect on glucose yield as the reaction time exceeded 90 min. The result further showed that yeast had effect on the glucose yield during fermentation. Bioethanol was later recovered through distillation at 78.9°C after fermentation. Physicochemical properties of the bioethanol under study such as; color, specific gravity (0.781 g/cm^3), pH (7.2) and refractive index (1.3477) indicated that both complied with ASTM Standard for E100 with exception of Refractive Index which is slightly low. The fuel properties such as; Flash Point (16.50°C) and Octane Rating (117) indicated that both are within ASTM E100 set limit with exception of Cloud Point (-11°C) which is lower than the Standard and Pour Point (-13°C) which is higher than the ASTM Limitations. From this findings, it is well discovered that *maize cob* has high cellulosic content and as such it is suitable for bioethanol production having passed the physicochemical and fuel properties characterization.

Keywords: Bioethanol, Fermentation, Distillation, *Maize Cob*, Glucose

1. Introduction

The availability of energy in an area determines the socio-economic development of such an area. While the socio-economic development of a nation depends largely on the availability and the consumption of energy [1]. One of the greatest challenges of the society in 21st century is meeting the growing demand of energy for transportation, heating, industrial processes, and to provide raw materials for industries in a sustainable way. More also, the energy crisis and climate warming have given rise to the search for alternative fuels. The main reason for the energy crisis is the limited amount of fossil fuels. Nowadays, biomass has been focused as an alternative energy source due to its environmental friendly nature since it maintains the level of carbon dioxide in the atmosphere constant through the process of photosynthesis. The carbon dioxide emitted during combustion of biomass is been absorbed during the process of photosynthesis [2]. Bio-fuels are one of such alternative fuels that could minimize greenhouse gas emission as well as complimenting the fossil fuels which may be due to the presence of oxygen molecules within the bio-fuel which leads to better and complete combustion [3].

Energy is the main driver of socio-economic growth of any nation. It plays a vital role in the overall frame work of development worldwide [4]. Two globally known bio renewable transport fuels are currently available which may replace petroleum-based petrol and diesel. These are bioethanol and biodiesel [5]. Ethanol is also known as ethyl alcohol; it is a volatile, flammable, colorless liquid with slight characteristic odor, it has a chemical formula C_2H_6O. It can be produced in one of the two ways; either by petrochemical process i.e. during refining of petroleum by hydrolysis of ethylene [6]. The second way in which ethanol can be obtained is through fermentation of sugars such as sugar cane juice, sugar beet, molasses, starch based materials such as maize, wheat, potato, cassava and many more or using cellulosic feedstock such as; paper, cardboard, wood, and other fibrous plant material sourced from agricultural feedstock [7]. Currently the most widely used bio renewable engine fuel in the world is bioethanol. Biofuels amount to 0.5% of primary energy used in the world. The production of biofuels increased by 13.8% in the year 2010. The main contributors to the growth of ethanol production were North America, South America and Central America (BP Statistical Review of World Energy June 2011). This came as a result of the expected environmental damages like global warming, acid rain and urban smog. These problems have tempted the public to reduce the carbon emissions and shift toward utilizing a variety of renewable energy resources such as; solar, wind, biofuel, etc. that are less environmentally harmful. The sustainability of bioethanol made it the most promising alternative biofuel that can play an important role in addressing such environmental problems caused by fossil fuels. Similarly, Ethanol has been used as an Otto engine fuel starting from the dawn of automotive industry. The first commercial vehicle which was capable of running on petrol, kerosene or ethanol was Ford T built in 1908. The decreasing prices of petrol and prohibition of alcohol consumption made ethanol an impractical fuel [8].

2. Materials and Method

2.1. Sample Collection and Treatment

Maize cods were obtained randomly around Asaba town, Oshimilli south Local Government Area in Delta State, Nigeria. The cods were crushed using a wooden pestle before subjecting to pretreatment using water to remove dust and other impurities. The sample was allowed to dry at room temperature. Finally, Mortar and Pestle was used to reduce the size of the *maize cob*s aimed at increasing the surface area of the material.

2.2. Methods

2.2.1. Acid Hydrolysis

Acid hydrolysis is the oldest technology for converting cellulose biomass to bioethanol [9]. There are two basic types of acid hydrolysis processes commonly used: dilute acid and concentrated acid hydrolysis. The dilute acid process is conducted under high temperature and pressure and has a reaction time at a scale of up to minutes, facilitating continuous processing. The concentrated acid process uses relatively mild conditions with a much longer reaction time [10-13]. In this finding, concentrated acid hydrolysis was employed. This method provides a complete and rapid hydrolysis of cellulose to glucose and hemicelluloses to 5-carbon sugars with little degradation. The critical factors needed to make this process economically viable are to optimize sugar recovery and cost effectively recovering the acid for recycling [14, 7]. 10 g of each dried pulverized plant sample was weight separately using electronic weighing balance and placed into a 250 cm^3 conical flask, 10% sulfuric acid was added and made up to 150 cm^3. The mixture was autoclaved at 121°C for 15 minutes and was then filtered using whatman filter paper to remove the unhydrolysed materials [15]. The primary advantage of the concentrated acid process is the potential for high sugar recovery efficiency [7].

2.2.2. Determination of Glucose Content

Glucose content of the samples was achieved by measuring 3 cm^3 of dinitrosalicylic assay (DNS) reagent and added to 3 cm^3 of hydrolysate sample in a lightly capped test tube (to avoid loss of liquid due to evaporation). The mixture was heated at 90°C for 5-15 minutes to develop the red brown color. 1 cm^3 of 40% Potassium Sodium Tartrate (Rochelle salt) solution was added to stabilize the color. This was then cooled to room temperature. Absorbance was recorded for the resultant solution using a spectrophotometer at 540nm [9].

2.2.3. Fermentation of the Hydrolyze Maize Cob

Fermentation of hydrolyzed *maize cob* was carried out using method reported by [16] with some modifications.

After the pH of the mixture is regulated between 4.5-6.0 using ammonium acetate buffer solutions, exactly 1.0 g of yeast and 2 ml of the mixture were added to 20 ml of warm water which was later shaken for 5 minute to activate the yeast. This was later added to the 150 ml mixture in the bottle and then closed tightly. The mixture was then left for 96 hours to ferment. The same procedure was repeated for 3.0 g, 5.0 g, and 7.0 g of yeast respectively [16].

2.2.4. Ethanol Recovery

After fermentation, the mixture was then removed and filtered. The filtrate contained ethanol and some other impurities. The filtrate was distilled at 78.9°C in order to recover the ethanol. The distilled ethanol was later reconditioned with Zeolite 4A and redistilled to obtain anhydrous bioethanol.

2.2.5. Confirmatory Test

Confirmatory test of certain physicochemical as well as fuel properties was carried out to ascertain whether the distillate is actually bioethanol or not.

2.3. Physicochemical Parameter

2.3.1. Physical/Visual Examination

The appearance of the bioethanol produced was observed by naked eyes.

2.3.2. pH

Exactly 100 ml of the sample were accurately measured and poured into 250 ml beaker. The pH meter was on and the testing electrode was introduced into the sample in a beaker. Digital readout of the pH meter displayed the digits and was recorded as the pH of the sample.

2.3.3. Specific Gravity

An empty bottle was placed on weighing balance and the reading was recorded, the bottle was removed and filled with 20 ml of the distillate which was later placed on a weighing balance, the reading was taken. The bottle was then removed and filled with 20ml distilled water. The reading was recorded and the specific gravity was calculated using the formula (ASTM D1298).

$$\text{Specific gravity} = \frac{\text{Wt of bottle+sample} - \text{Wt of empty bottle}}{\text{Wt of bottle+water} - \text{Wt of empty water}} \quad (1)$$

2.3.4. Refractive Index

Abbe's refractometer was used in the determination of refractive index. This instrument measures the index of refraction by measuring the critical angle of total reflection. In this case, a few drops of the sample were transferred into the glass slide of the refractometer. Water at 30°C was circulated round the glass slide to keep its temperature uniform. Through the eyepiece of the refractometer, the dark portion viewed was adjusted to be in line with the intersection of the cross. At no parallax error, the pointer on the scale pointed to the refractive index.

The refractometer was calibrated using distilled water where the refractive index of water at that temperature was obtained [17].

2.4. Fuel Properties of Bioethanol

2.4.1. Pour and Cloud Point

Exactly 10 ml of the sample was poured in a cylindrical tube, the machine was switched on and the temperature was allowed to drastically drop to -15°C (i.e. real time temperature) for one hour. The samples were placed in a testing compartment (Cold bath), the compartment contained a solvent basically ethanol which serves as the cooling solvent. Testing begins at -15°C. The tube was tightly fixed in the vertical position. Pour point determination was done according to ASTM D97-02 through cooling under specified temperature and intervals of 3°C to check for its liquidity. Record was observed as pour point, the lowest temperature can flow (ASTM D97-02). The sample was allowed to continue cooling for about 40 min where it forms cloudy; a thermometer was dipped into the tube to record the temperature (ASTM D2500-05).

2.4.2. Flash Point

Exactly 70 ml of the sample was poured into a test cup; the sample was stirred under a prescribed rate, and heated at constant rate. At specified temperature interval, a fire was ignited to test cup's opening which make steam sample momentarily ignited and spread to the liquid surface's minimum temperature. This was recorded as the flash point under normal atmospheric pressure (ASTM D92).

2.4.3. Octane Rating

Exactly 10 ml of the sample was introduced into 25 mm cylindrical cupboard to the mark and placed into cupboard knob where testing begins. The machine (Cadonhaicr KD-R3039) was turn on, a selection was made for ethanol, the testing begins and was recorded (ASTM D2700-18).

3. Result

Table 1. *Physicochemical Characterization of Bioethanol.*

Parameter	Unit	Bioethanol
Appearance		Colorless
pH		7.2 ± 0.4
Refractive index		1.3477 ± 0.05
Specific Gravity	g/cm^3	0.781 ± 0.03

Table 2. *Fuel Properties of Bioethanol from Maize Cob.*

Parameter	Unit	Bioethanol
Cloud Point	°C	-11 ± 0.03
Flash Point	°C	16.50 ± 0.04
Octane Rating	°C	117 ± 0.02
Pour Point	°C	-13 ± 0.03

4. Discussion

Bioethanol production from *maize cob* was assessed and the experimental bioethanol appears to be colorless and free from any particles, thus, indicates that it's within the minimum ASTM specification for bioethanol fuel hence, can be used as fuel for vehicles. The pH of the sample was measured in order to ascertain the acidity and alkalinity of the bioethanol produced. The result presented in table 1 indicates the pH of 7.2 for experimental bioethanol falls within ASTM E100 specification (6.5-9.0) for bioethanol fuel which is a clear indication that the bioethanol produced is neither acidic nor alkaline. The pH below the specification indicates a strong increase in the risk for developing reflux disease when consumed and also the risk of corrosion of engine is high2. Also, the refractive index was measured in order to identify as well as determine the purity of the bioethanol synthesized. The result 1.3477 from table 1 indicates that the experimental bioethanol is slightly lower than that of ASTM E100 Standard (Range 1.3568-1.444) and also slightly lower than the value of 1.46 obtained for *B. sapida* [18] and 1.45 obtained for *C. lanatus* by [19]. Thus; this is a clear indication of the presence of impurities and increases the risk of clogging the engine filters when used as a fuel.

Specific gravity is the ratio of the density of a substance compared to the density of a reference substance. The specific gravity of the experimental bioethanol was measured in order to indicate the density of it by comparing it to the density of water. The result 0.781 gcm-3 presented in table 2 indicated the specific gravity of the experimental bioethanol which is in total agreement with the standard obtained from ASTM E100 (range 0.789-0.801), and also in close proximity to the findings from [20] who reported a value of (0.88) for waste cooking oil, [21] who reported a value of (0.87) for waste cooking oil also [22] who reported (0.87) for *Haveabrasilliensis*oiland [23] who also reported (0.89) for *Haveabrasilliensis* oil. It is noted that the more the water content the higher the specific gravity of the liquid.

Flash point is one of the numbers of properties which must be considered in assessing the overall flammability of hazardous of a substance. Is a lowest temperature at which materials will ignite when given an ignition sources. The result 16.50°C presented in table 2 indicated that the flash point of the experimental bioethanol is within the ASTM E100 standard (range 16.50-16.70). Higher flash point indicates that a fuel is safe for handling, storage and transportation even under mild condition of temperature.

Pour point is a property of a liquid which at low temperature it becomes semi solid and loses its flow characteristics often referred as ''freezing point'' usually due to high paraffin content. The result presented in table 2 showed that the experimental bioethanol has a good pour point value -13°C which is above the limit set by ASTM for E100 (-5.0°C) thus is a clear indication that it is free from fatty acids and can be used in polar region where the atmospheric pressure is below -13°C. Just like pour point, cloud point was also measured in order to ascertain the lowest temperature below which cloud of wax crystal appears in the fuel when it is cool. Result from table 2 revealed that the cloud point of the experimental bioethanol -11°C which is however below the ASTM standard (-23°C). The lower the cloud point and pour point temperature obtained indicates the biodiesel can still flow in a very low temperature [21].

Octane rating is a number that is used to measure the antiknock properties of a liquid fuel. In other words is a measure of ignition quality of the fuel. The higher the octane number the more suitable it will be as fuel. The result of octane rating; 119 from table 2 was reported for experimental bioethanol which is in total agreement with ASTM E100 standard for bioethanol (96 above). The higher octane number reported was not surprising as global ethanol was believed to have high octane number thus making it suitable for blending with other petroleum products for vehicles engine efficiency and also reduces cost of fuel. [24] reported that ethanol with high octane number is believed to have high heat of evaporation and high flammability temperature that influences the engine performance positively and increases the compression ratio.

5. Conclusion

The main aim of the current study was to investigate the potential of *Maize Cob* for bioethanol production. Based on the research, the following conclusions were reached; it was found that *Maize Cob* could be a raw material for bioethanol production as 86% yield was realized. It was also found that the substrate can be hydrolyzed using sulfuric acid to yield glucose, based on the glucose yield attained;

This study discovered the use of *maize cob* as substrate for bioethanol production and serve as an alternative fuel. This study will help researchers uncover critical areas of bioethanol production that many researcher were unable to explore. Thus, a new theory on hydrolysis of biomass may be arrived for the bioethanol production.

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