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Comparative Study on Bioethanol Potentials of Guinea Corn Husk and Groundnut Shell

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Abstract:

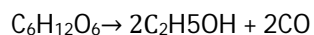
*The possibility of producing ethanol from such as guinea corn husk and groundnut shell was investigated. The guinea corn husk and groundnut shell were obtained at jega market. The method used includes acid hydrolysis with concentrated H₂SO₄, enzyme development, fermentation with *saccharomyces cerevisae*. Followed by distillation of fermented broth. The yield of the ethanol produced was 200ml for groundnut shell and 220ml for guinea corn husk within 3days of fermentation. Confirmatory tests was carried out which ascertained that the distillate was actually ethanol with respect to the standard from WHO and ASTM.*

Keywords: Bioethanol, potentials, guinea corn husk, groundnut shell, hydrolysis, fermentation

1. Introduction

Renewable energy is energy that is collected from renewable resources, which are naturally replenished on a human timescale, such as sunlight, wind, rain, tides, waves, and geothermal heat (Ellabban, *et al.*, 2014). Renewable energy often provides energy in four important areas: electricity generation, air and water heating/cooling, transportation, and rural (off-grid) energy services.

Ethanol is currently produced from sugar crops (sugarcane, sugar beet, sweet sorghum) or starchy crops (corn, wheat, cassava) through a process of fermentation and then distillation, employing first generation technology. The basic production process of ethanol from both types of crop is similar. However, the energy requirement for starch based ethanol is significantly more than that of sugar-based ethanol due to the additional process involved in converting starches into sugar. Energy and greenhouse gas balances are, therefore, more favourable for ethanol production from sugar crops than from starch crops (Mandil and Shihab-Eldin, 2010). Bioethanol production processes from sugar or starch crops are the most traditional and developed pathways. According to Chiaramonti (2007) as cited by Fink (2010), fermentation is performed by microorganisms in the absence of oxygen according to the following main reaction:



Ethanol (ethyl alcohol) has long been recognized as a fuel suitable for a variety of applications, including transportation and cooking. Ethanol can be used in stoves adapted for its use for cooking. It can be further processed to add a thickening agent, water and colouring to create a combustible ethanol gel that is safe, non-toxic, non-spill and potable. This gel has been successfully tried as cooking fuel with private sector plants in various Southern African countries (Utria, 2004) as cited by Zuzarte (2007). Ethanol (either straight or jellified) can also be used in households for cooking as a substitute for wood, charcoal or kerosene and for lighting as a substitute for kerosene. Gelfuel is currently being distributed in several countries in Africa as a fuel for cooking. Gelfuel has several advantages compared to straight ethanol: one cannot drink it, it is easier and less dangerous to store and transport, and it is less likely to have fire in the household because if the stove falls the

burning gel does not spread (Legoupil and Ruf (n.d). Ethanol can be used in blends of up to 10% in conventional spark ignition engines or in blends of up to 100% in modified engines (Mandil and Shihab-Eldin, 2010).

In recent years, the negative impacts of fossil fuels such as global warming, Greenhouse gases emissions and the fast depletion of fossil resources have resulted in an increased interest in the research of alternate power or sustainable energy such as biofuel (Palma *et al.*, 2012). Bioethanol has been considered a better choice than conventional fuels, as it reduces the dependence on reserves of crude oil. Bioethanol also promises cleaner combustion, lower emissions of air pollutants, high octane rating and more resistant to engine knock, which may overall lead to a healthier environment because it is carbon neutral and essentially free from sulfur and aromatics (Bailey, 1996; Prasad *et al.*, 2007; Gupta *et al.*, 2009). Today, bioethanol is one of the most dominant biofuel and its global production has increased sharply since year 2000. Generally, current production of bioethanol comes from sugar and starch-based materials such as sugarcane and grains (Dermirbas, 2009). However, considering the growing demand for human food, lignocellulosic biomass has arisen as a more suitable feedstock for bioethanol production and a viable long-term option for bioethanol production as compared to the other two groups of raw material (Hamelinck *et al.*, 2005). Lignocellulosic material is the most abundant plant biomass resources that can be used in bioethanol production industry. Examples of lignocelluloses are woody biomass, logging residues, energy crops (i.e. switch grass and poplar), agricultural residues (i.e. wheat straw, rice straw and corn stove), agricultural by-products (i.e. rice hull, sugarcane bagasse) and municipal solid waste (Tan *et al.*, 2008; Duku *et al.*, 2011). The lignocellulosic feedstock used in the current study for bioethanol production was the coconut husk. Coconuts are abundantly growing in coastal areas of all tropical countries. In Malaysia, about 115,000 ha of land were being used for coconut plantation in Year 2010 (Sulaiman *et al.*, 2013). It was estimated that approximately 5.3 tons of coconut husk will become available per hectare of coconut. Some of the coconut husk was used as fibre source for rope and mats but most of the coconut husks are routinely disposed of after the coconut water is sold (Tan *et al.*, 2008). This makes coconut husk a cheap and potential substrate that could be used for bioethanol production due to the presence of relatively high levels of cellulose and hemicelluloses in it (van Dam *et al.*, 2004).

2. Materials and Methods

2.1. Collection and Preparation of Samples

The guinea corn husk used for the production was collected from jega local market, jega local government Kebbi state Nigeria and.

The groundnut husk used for the productions was also collected from jega local market, jega local government Kebbi state Nigeria.

After collecting the guinea corn husk from the market, it was allowed to dry (i.e. sun drying) for days, and then it was grounded with mortar and pestle so as to increase the surface area. So as the ground nut shell.

2.2. Yeast Propagation

The source of the micro-organism *saccharomyces cerevisiae*, used was active dried yeast.

Active dried yeast was added to lukewarm water and allowed to stand for 5 hours, the yeast was observed from time to time for growth.

2.3. Bioethanol Production

The methods used in production bioethanol includes; acid hydrolysis with 100ml concentrated H_2SO_4 , enzyme development, fermentation, filtration of fermented broth and distillation.

2.4. Hydrolysis

100ml of concentrated H_2SO_4 was added to (1kg) of guinea corn husk and placed on regulated heating mantle at 40°C for 6 hours. Sample was tested for starch using iodine solution every 340mins. Until it is no more turning blue-black. When Glucose level was reached, the acid neutralize with sodium Hydroxide solution yeast was added and the temperature is reduced to 40°C for two hours. Mixture of ethanol, glucose and sodium chloride was obtained. The same procedure was repeated for groundnut husk.

2.5. Enzyme Development

The synthetic enzyme (zymase) was mixed inside the cooking vessel with water to facilitate agitation in high viscous stage at gelatination. Boiling water was quickly added to the mixture, Gelatination occurred and a marsh was formed, the marsh was allowed to cool to 75°C and the second addition of remaining synthetic enzyme was made.

Liquefaction and saccharification took place over a holding period of 4hours. The marsh was checked at 30minutes interval with iodine solution to be sure of obtaining maltose and P^H is Equally checked (PH 4.8)

2.6. Fermentation

The mixtures were transferred into the fermenter and covered for 24 hours, then the propagated yeast was added and allowed to ferment for 3 days. Conversion of glucose to ethanol took place by the enzyme called Zymase.

2.7. Filtration of Fermented Broth and Distillation

After fermenting, the broth was filtered with mesh of 63 microns. The liquid obtained (filtrate) was distilled using simple distilling apparatus to obtain ethanol of 90% concentrate. The distilled ethanol was reconditioned with 50g of zeolite 4A and redistilled to obtain ethanol of 99.9% pure. Absolute ethanol.

2.8. Confirmatory Test

Confirmatory test was carried out to ascertain that the distillate was actually alcohol.

2.9. Physical Parameters

2.9.1. Determination of Specific Gravity

2.9.1.1. Procedure

An empty density bottle was weighed on a weighing balance and recorded as (W_1)g. and both the density bottle and the guinea corn husk distillate was weighed (W_2)g. also the density bottle and distilled water was weighed and also recorded as (W_3)g. The same procedure was also repeated for groundnut husk distillate.

$$\text{Specific Gravity} = \frac{W_2 - W_1}{W_3 - W_1}$$

2.9.1.2. Refractive Index

A small drop of acetone was placed on the center of the prism, to clean up the lens and view finder of the refractometer, then the groundnut husk distillate was placed on the prism. The light source, index arm, and compensator drum were adjusted to align the sample through the eye piece. The refractometer then provides a digital read-out of the refractive index which was 1.410. The same procedure was also repeated for guinea corn husk distillate and the same result was also obtained. The physical parameter such as, the pH was measured using pH meter and the colour was also observed.

2.9.1.3. Boiling Point

Measure 10ml of the sample into 50ml platinum dish. Increase the temperature gradually until it starts boiling.

2.9.1.4. Determination Of Heavy Metals

Heavy metals are the heavy dense metallic elements that occur in trace levels, but are very toxic and tend to accumulate, hence commonly referred to as trace metals. (Radojovic and Vladimir, 1992). The heavy metals comprising of Cl, Al, Cr, Mn, Pb, Hg, Zn, Ni, Fe, Cu, Mg, K, Ca and Co were determined according to the method of Shahidi *et al*, (1999). 10g of the samples was weighed into a beaker, the mixture of HNO_3 , water and perchloric acid was added at the ratio of 1:3:0.5, and digested for 24 hours. Then the digested samples were analyzed for Fe^{2+} , Zn^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Cr^{3+} , Cu^{2+} , Hg^{2+} . By means of Atomic Absorption spectrophotometry.

2.10. Fuel Characteristics.

2.10.1. Determination of Cloud Point

2.10.1.1. Procedure

0cm³ of the produced bioethanol was poured into cloud point jack, thermometer was inserted into cloud point jack, and the cloud point jack was inserted into the Stanhope seta at -35^oc for about 5 minute till the cloud occurs or appears.

2.10.2. Determination of Pour Point

2.10.2.1. Procedure

50cm³ of the produced bioethanol was poured into pour point jack, thermometer was inserted into pour point jack, and the pour point jack was inserted into the Stanhope seta at -35^oc for about 10 minutes till the bioethanol sticks and forms ice in the pour point jack.

2.10.3. Determination of Flash Point

2.10.3.1. Procedure

66cm³ of bioethanol produced was poured into the flash point jack, thermometer was inserted inside flash point jack, the jack was inserted into flash point tester, after setting of the tester the reading at temperature of 32°C, the checking of flash point observations occur at the interval of every minutes, until the flash point of produced bioethanol occur.

2.10.4. Octane Number

Is a measure of ignition quality of fuel. The higher the octane number, the easier the fuel will ignite when it is injected into the engine the better the fuel.

3. Results and Discussions

3.1. Results

The results of the fuel (Bioethanol) produced from guinea corn husk and groundnut shell through fermentation process are shown in table 1, 2 and 3 below.

Parameters	Groundnut Shell	Guinea Corn Husk
Color	Colorless	Colorless
Physical state at room temperature	Liquid	Liquid
Fuel yield (%)	22.0	20.0
Specific gravity	0.79±0.02	0.79±0.02
Boiling point °c	78.39±0.1	78.43±0.05
Refractive index	1.41± 0.02	1.41±0.02
pH	6.4±0.2	6.5±0.2

Table 1: Physicochemical Characteristics of Bioethanol Extracted From Guinea Corn Husk and Groundnut Shell.

Data are mean± Standard deviation of triplicate results.

Properties	Groundnut shell	Guinea corn husk	Astm Standard
Pour Point (°C)	2.3	3.80	97
Cloud Point (°C)	8.70	12.40	23
Octane Number	55	61	99
Flash Point (°C)	42.10	40.40	93

Table 2: physicochemical properties of bioethanol extracted from Guinea corn husk & groundnut shell

Samples	Cd	Cr	Cu	Fe	Pb	Mn	Hg	Zn	Ni	Co
Gs	0.005	0.004	0.003	0.051	0.003	0.003	0.001	0.054	0.011	0.011
Gh	0.004	0.002	0.001	0.049	0.003	0.002	0.003	0.051	0.006	0.011

Table 3: Results of the Heavy Metal Concentration (Mg/L) Of Bioethanol From Groundnut Shell and Groundnut Shell

Key; Gs- Groundnut Shell, Gh –Guinea Corn Husk

3.2. Discussion

3.2.1. Percentage Yield

The result presented in the table 1 indicated the percentage yield of the produced bioethanol from 1kg of groundnut shell was 20.0% while the guineacorn husk was 22.0%, this indicates that during fermentation the yeast (*S. cerevisiae*) utilize the glucose as a source of carbon and energy. The low percentage yield of fuel yield from the two substrates is too small compared to the economic value of ethanol (65% minimum), In pretreatment with dilute sulphuric Acid, the structure of the cellulosic biomass will be altered to make cellulose more accessible to the enzymes that cover the carbohydrate polymers into fermentable sugars rapidly and with greater yield.

Research groups presented some result with xylose fermenting *S.cerevisiae* (Sonderegger, *et al.*, 2004). Application of such microorganisms would definitely increase ethanol yield from lignocellulosic biomass. (Piout *et al.*, 2007).

3.2.2. Specific Gravity

The result presented in the table 1 indicated the specific gravity of the produced bioethanol of the two samples being 0.79 which is in total agreement with the standard obtained from ASTM (Range 0.78-0.85), it is noted that, the more the water content the higher the specific gravity of the liquid. And this indicates that it can be used as a solvent for chemicals and also in the production of liquid detergents.

3.2.3. Boiling Point

The result presented in the table 1 indicated the boiling point of the produced bioethanol of two substrate. It was observed that the boiling point which varies from 78.39°C (groundnut shell) to 78.43°C (guineacorn husk), this implies that the boiling point fell within the specification value (78.5°C).

3.2.4. Refractive Index

The refractive index of the produced bioethanol was determined and result obtained as presented in table 1, which indicate that the refractive index of the two sample was 1.41 which is a little higher than the standard of ASTM 1.36. The essence of measuring the refractive of the fuel is to verify the purity of the fuels, it can be deduced from the results obtained that the bioethanol produced is pure.

3.2.5. PH

The pH of the two samples (groundnut shell and guinea cornhusk) is 6.8, and 6.7 respectively it fell within the specification (6.5-6.8) which implies that the experimental ethanol was neither acidic nor alkali. The pH below the specification indicates a strong increase in the risk for developing reflux diseases.

3.2.6. Flash Point

Is the minimum temperature at which a fuel must be heated for it to ignite air- vapor mixture. The result as presented in the table 2, it indicate that the flash point of the produced bioethanol were 40.40 and 42.10 for groundnut shell and guinea corn husk respectively. This implies that the produced bioethanol is less flammable than the standard bio fuel. Also the lowest temperature of ignition for bioethanol is 12.8°C (Walker, 2011)

3.2.7. Cloud Point

The cloud point is also an important property of bioethanol fuel, also it is a criterion for low temperature performance of a fuel. Cloud point is the lowest temperature at which a cloud of wax crystals first appear in the fuel when it is cooled (Lang *et al.*, 2001). The results of cloud point of produced bioethanol as presented in the table 2 indicated that the cloud point was 12.40 and 8.70 (groundnut shell and guinea cornhusk) respectively, which is lower than the standard of ASTM 23°C.

3.2.8. Pour Point

The pour point is the lowest temperature at which the fuel or bioethanol cannot be moved (freezing point). These properties are related to the use of bioethanol in the cold temperate regions especially in hail region or snow region (Lang *et al.*, 2001). The pour point of the produced bioethanol was determined and obtained as presented in table 2 which are 3.80 and 2.30 for groundnut shell and guinea corn husk respectively. Which is lower than the standard ASTM 5.30°C, which is an indication that the bioethanol produced can be used even in polar regions where atmospheric temperature is not less than 5°C.

3.3. Octane Number

Is a measure of ignition quality of fuel the higher the octane number, the higher octane number the better its ignition properties and the better it is used as a bioethanol fuel. Reported by Oando (2016). The high octane number of ethanol makes its blend achieve the same octane boosting or anti-knock effect as petroleum derived aromatics like benzene. Aside high octane number Ethanol has a high evaporation heat and high flammability temperature that influences the engine performance positively and increases the compression ratio. The blend E85 consisting of 15% unleaded gasoline and 85% ethanol has a prevalent usage as alternative fuel because of its advantage over pure ethanol which has a high risk of cold starting problem. (Walker, 2011).

3.4. Heavy Metals

Heavy metals are harmful in the environment, as a result of both natural and anthropogenic activities, and humans are exposed to them through different pathways (Wilson and pyatt 2007). Heavy metals like iron, copper and manganese occur naturally in the environment and could serve as plant nutrients depending on their concentration. Ingestion and eventually accumulation of toxic heavy metals such as lead, cadmium, chromium etc.

Many of these trace metals are highly toxic to humans such as Hg, Pb, Ni, Cd, As etc. their presence in surface and underground water at above background concentration is undesirable (Radojovic and Vladimir, 1992). Some have also been identified as deleterious aquatic ecosystem and human health (Bhatia, 2001). The summary of the results of heavy metals in the samples were reported in table 3.

3.5. Copper

The concentration of copper reported in this work showed that, groundnut shell has the value of 0.003mg/l, guinea corn husk having the value of 0.001mg/l. The concentrations of copper in the samples were below the permissible limit of 30mg/l and 190mg/l set by WHO/FAO and (DPR, 2002) target and intervention values for metals in soil, food and vegetables. The values reported were lower than the ones reported by Abubakar and Ayodele (2002). Copper deficiency, even though rare, is associated with hyperchromic, microcytic anaemia resulting from defective hemoglobin synthesis (Umar & Ebbo, 2005).

3.6. Zinc

The result obtained for zinc in groundnut shell was 0.054mg/l while guinea corn husk has a concentration of 0.051mg/l. Despite widespread use of zinc for domestic purposes, electroplating, paints in alloys, and dyes, the values obtained are still far below the threshold limit values of 60mg/l and 900mg/l approved by WHO/FAO and (DPR, 2002). It could be deduced, therefore, that the values obtained for zinc in this work were not harmful, but further works need to be carried out before making my conclusive statement, since deficiency of it (zinc) has been found to retard growth and maturity and produced anemia (parker, 1987).

3.7. Lead

Lead is a toxic heavy metal, which can be taken up by plant from the soil, thereby interfering with the food chain (Tsafe, 2001). The concentration of lead in groundnut shell is 0.003mg/l while in guinea corn husk is 0.003mg/l. All the samples concentration of this lead element compared to WHO/FAO and (DPR, 2002) values of 2mg/l and 530mg/l. Lead is known to exert its most significant effect on the nervous system, including motor disturbances, sensory disturbances, the hematopoietic system and the kidney, and ultimately major brain damage (Macrea *et al*, 1993). Lead ingestion has been associated with deteriorious health effects, including disorder of central nervous system (NAS, 1982). Lead is widely known to be toxic even at low concentration especially in young children (Ang *et al*, 2003).

3.8. Chromium

The concentration of chromium in groundnut shell is 0.004mg/l while guinea corn husk is 0.002mg/l and are below WHO/FAO and (DPR 2002) standard 380mg/l. The presence of chromium could be the discharge of waste of products from industries into the environment, by the activities of cement, paper, leather tanning, and paint industries (Umar and Ebbo (2005). The concentration of chromium in the samples are far below the value (182mg/l) reported by Ekwumemgbo and Audu (2006).

3.9. Cadmium

The concentration of cadmium reported in this work showed that groundnut shell has the value of 0.005mg/l while guinea corn husk has the value of 0.004mg/l. The obtained values in this work were far below the values (1mg/l and 17mg/l) in food and vegetables adopted by WHO/FAO and (DPR 2002). The presence of cadmium could be the discharge of waste products from industries to the environment, battery chargers and mechanical workshops. The results deviated from the findings of Iwegbue *et al*, (2004) and Nwajei *et al*, (2007).

4. Conclusion

The findings of this study have shown that, the bioethanol production from these agricultural wastes through fermentation process would make good biomass fuel.

In view of this, the production bioethanol from agricultural by-products Such as groundnut shell and guinea corn husk can greatly serve as alternative source of fossil fuel and also serve as a measure in curbing the environmental hazard caused by emission of greenhouse gasses.

In conclusion, therefore an efficient and good environment friendly bioethanol can be produced from agro-waste residue, also the general high durability rating of the bioethanol could be edible (i.e. consumed) as it contains no heavy metals. Therefore the bioethanol produced from groundnut shell and guinea corn husk is not economical because the percentage yield is low.

Considering the cost effectiveness, in addition to being a means to control environmental pollution, the use of groundnut shell and guinea corn husk for ethanol production is concluded as not worthwhile venture since the percentage yield is very small.

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