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Research Paper

Evaluation of the Effects of Mixing Ratio on the Percentage Yields in Bioethanol Production from Corncob and Maize

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ABSTRACT
This paper report the study of production of bioethanol from corncob and maize which in effects to minimize energy cost and substituting nonrenewable energy by using renewable resources. The feedstock for this project work was gotten from a local market in Ekiti State, Nigeria, and then taken for further pretreatment processing. Corn dry milling process was employed in this project work. The production process was carried out in four main stage namely pretreatment, hydrolysis (first and second stage), fermentation and distillations. The first stage diluted acid hydrolysis was used as chemical in pretreatment stage and the process variables were fixed at the best optimum condition. Fermentation of the hydrolyzate was performed using Saccharomyces cerevisiae at 30^{o}C temperature, 5.0 pH and 72hrfermentation time.A comparison of different ratio of corncob and maize, and the corresponding yield from the ratio was taking. Three mixing ratio was considered Viz; 30% corn cob and 70% maize(Sample A), 40% corn cob and 60% maize(Sample B), 50% corn cob and 50% maize(Sample C)and the percentage ethanol yield of the three samples were taking which are 85% ethanol was produced from Sample A, 78% ethanol from sample B and finally 65% ethanol from sample C. Therefore, the best mixing ratio with the highest production of ethanol is sample A.
KEY WORD: *fermentation, corn cob, hydrolysis, distillation, and renewable*

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I. INTRODUCTION

Oil and gas exploration and production has become a dominant sector of the world energy and other economic sectors since the last century. In Nigerian perspective, since the discovery of commercial reserves in the Niger Delta region in the mid-1950s, the sector has increasingly dominated the agriculture and solid minerals exploitation for both the source of energy and revenue to the country. Currently, these commodities accounted for over 90% of both foreign exchange benefits and total government revenues(Chiaramonti, D. P., 2007).

However, continuous reliance by the country on only one sector is unsustainable, especially considering the fact that the current respective proven reserves of 37.22 billion barrels and 181 trillion cubic feet of oil and gas could only last for the next 25 to 30 years. This could be attributed to the rapid increase in population and energy consumption and the associated development in science, technology and socio-economic activities.(Cardona, C., and Sa'nchez, O., 2007)

Energy consumption has increased during the last century due to the world population development and growth (Sun, 2002). Nowadays, the increasing problem of the CO_2 emissions due to energy consumption, besides to the future petroleum scarcity, has strengthened the interest in alternative, nonpetroleum-based sources of energy. They are increasingly associated with the emissions of greenhouse gases, majorly CO_2, leading to climate change, emergence of drought, spread of diseases and variation in population sizes of both plant and animal species (IPCC, 2007).

Within the last 20 years, about 75% of human made CO_2 emissions were from burning of fossil fuels. Nigeria is the largest emitter of these undesirable gases from the sub-Saharan Africa, and particularly, the second worlds' biggest gas flare, contributing immensely to the global atmospheric pollution. The oil and gas exploration and production being dominant in only a portion of the country, accounted for only few job opportunities to less than 1% of the over 140 million inhabitants of the country. This can also be connected with the continuous rise in poverty levels among the rural communities and the persistent rural-urban migration over the years. Nigerian government recently indicated the incorporation of biofuels production, particularly bioethanol and biodiesel to be a good option. The production of these fuels could enhance fuel use in automotive industry, electric power generation and rural development, including agricultural mechanization and light industrial goods development, and in ensuring that the common man is fully benefitted from the country's economy (Azih, 18-21 June, 2007).

Bioethanol is fermentation of alcohol. It is ethyl alcohol produced by microbial fermentation processes, as opposed to synthetically produced ethanol from petrochemical sources. It is produced through distillation of the ethanoic which emanating from fermentation of biomass-derived sugars. It can be utilized as a liquid fuel in an internal combustion engines, either neat or blends with petroleum. The flash point of ethanol is the lowest temperature (i.e. 12.8°C) where enough fluid can evaporate to form an ignitable concentration of vapour and characterizes the temperature at which ethanol becomes flammable in air. The ignition point of ethanol is the minimum temperature at which it is able to burn independently (i.e 425°C).

Ethanol has a high octane rating 99, which is a measure of a fuel's resistance to pre-ignition, meaning that internal combustion engines using ethanol can have a high compression ratio giving a higher power output per cycle. (Walker, 2010). Bio-ethanol feedstock can be divided into three major groups which are: sucrose-containing feedstock, starchy materials, and lingo-cellulosic biomass. In the short-term, the production of bio-ethanol as a vehicular fuel is almost entirely dependent on starch and sugars from existing food crops (Ohgrem, K., Bura, R., and Lesnicki, G., 2007)

The issue of energy security resulting from the depletion of world petroleum reserves, increase in the price of petroleum, crude and products, and environmental concerns about air pollution caused by the combustion of fossil fuels, the search for alternative fuels has gained importance.The availability of biofuel feedstock is what led to increased energy security (Hassan, M. H., and Abdulkalam, M. D., 2013). Nevertheless, the use of gasoline in transportation sector is increasing and the trend seems to be moving upward considerably. The development and implementation of alternative sustainable energy in this sector have been given a priority globally including Nigeria (Patrick, S. O., Abdullahi, Z., and Bello, I. M. , 2013). Nigeria's target of being among the leading biofuel producing countries is an appealing one. The current realization of the diversification of various existing feedstock could justify the effort of the country in biodiesel production drive (Abila, 2010).

Nigeria mainly depends on fossil fuel as the dominant primary source of energy, which accounts for over 90% of Nigerian foreign exchange earnings (Oniemola, P. K., and Gbenga, S., 2009). The fear of escalation in the price of petrol, depletion of the total volume of oil reserve (as the oil experts speculate), and increase in air pollution and emission of pollutants are deemed as negative effects of using petroleum fuels. Therefore, it has become necessary for Nigeria, which faces many economic challenges, to find and provide alternative sources of energy. If achieved, it will help immensely in reviving the gradual dwindling of Nigeria's economy. The Nigerian National Petroleum Corporation (NNPC) has since made a clarion call on this issue, and the final conclusion drawn is that Nigeria needs economy diversification, especially in the oil sector (NNPC, 2008).

The high prospect of Nigeria for biofuel production is mainly due to large acreage of fertile land with abundant potential feedstock. However one issue that can be taken as a matter of high magnitude is the sustainable economic diversification, which aims at providing the alternative sources of fossil fuel(NNPC, 2008). An observation here is that this will bring a lot of changes, in terms of economic development, to the nation. Employment availability would become a reality (Lee, 2007). Opportunities for rural development would also be a key priority. For rural settlers, implementation of biofuel production will help create massive employment, from agricultural perspective, for feedstock cultivation. This is of key priority because as the agricultural activities increase, it will directly increase the annual farm output thereby attracting demand for businesses (Agba, A. M., Ushie, F. I., Michael, S. A., and James, O., 2010).

Moreover, as an agricultural activity, islabour intensive, the rural settlers will have increase in their expenditure due into increase in personal income. A study by Dauvergne and Neville indicated that the success of Brazilian bio based ethanol production was due to subsidy of the agricultural facilities(Dauvergne, P., and Kate, J.N., 2010). Maize is one of the principal food crops in Nigeria. The crop ranks firstly in terms of productivity and secondly in area coverage. According to the data obtained from the International Maize and Wheat Improvement Center (CIMMYT), Ethiopia is the third largest producer of maize in Eastern and Southern Africa.

Corn cob is an important byproduct, for every 100 kg of corn grains; approximately 18 kg of corn cobs are produced. However byproduct is simply disposing to the environment while such residues may contain valuable materials; their current economic values are less than the apparent cost of collection, transportation and processing for beneficial use. Corn cobs contain 32.3-45.6% cellulose, 39.8% hemicelluloses - mostly composed of pentosan and 6.7-13.9% lignin (Ohgrem, K., Bura, R., and Lesnicki, G., 2007). However, the primary industrial yeast used in bioethanol production, Saccharomyces cerevisiae converts only hexose sugars such as glucose and is not able to co-ferment glucose and xylose. Thus, corn cob can be used for the production of second generation biofuel. In addition to environment benefit, ethanol production from corn cob can stimulate community based jobs and economic growth.

The focus on biofuel production may be a worthwhile endeavor in view of world's development woes. By investing in biofuel production, a lot of development potentials exist which include:Provision of employment,Economic diversification, Provision of cleaner environment; a pathway for low carbon energy alternatives, and Poverty reduction and many potential opportunities (Abila, 2010). The integration of a biofuel economy would help to reduce the rise in fuel prices in Nigeria by providing a steady income to local farmers. Moreover, Nigeria is the leading producer of corn in Africa and needs to develop a significant ethanol industry, so as to have presence in the global market. Therefore, it is of the utmost importance that Nigeria as a country starts implementing biofuels production as part of her means of economy development (Agbro, E. B., and Nosa, A. O., 2012). Thus, this paper provides an overview on the production of bioethanol from the mixture of corn cob and maize focusing on the potential yield of three different variations of the mixtures.

II. MATERIALS AND METHOD

Materials

The materials used to run all experiments are listed below:

Chemicals: Sodium Hydroxide (NaOH, min. assay 98% BDH cellulose), Sulphuric acid (H_2SO_4, (98%), Dextrose sugar, Yeast extract, Urea, MgSo4.7H2O, Yeast (Saccharomyces cerevisiae)

Equipments: Digital balances Fig. 1(a) (model= Sartorius with 0.01mg sensitivity, and model EP214C), Vacuum Filter (model =BN 3 STAATLICH), Sieves (mesh size of 2.0 mm), Shaking Incubator Fig. 1(b), pH- Meter Fig. 1(c), Vertical Autoclave,Ovens- Loading model 100 -800, Pycknometer, spectrophotometer (Perkin Elmer), Gin Vac HT4 Evaporator, Alcoholmeter.

(a) Digital Balance | (b) ShakingIncubator | (c) pH meter

Fig. 1 Equipment used for measurement during sample preparation

Methods

The method in the production of ethanol employed in this study is Corn dry-milling process and it was carried out in five steps viz: (i) biomass Preparation (Sample preparation), (ii) liquefaction (Pretreatment), (iii) hydrolysis (saccharification)(iv) fermentation and (v) distillation and recovery (Bioethanol separation).

Sample Preparation

The Corn used in this work was obtained from a market in Otun-Ekiti, Nigeria. The main aim of the research was to produce ethanol from the mixture of corn cob and maize and to determine the yield of the different ratio of the mixtures, sample A: 70% maize – 30% corn cob, sample B: 60% maize and 40% corn cob, sample C: 50% maize and 50% corn cob. The maize (i.e. seed) Fig. 2(a) was removed manually from the cobs, Fig. 2(b), separating the corn from the cob, Fig. 2(c), then the cobs and maize were broken down separately into small pieces with the aid of a wooden mortar and pestle, Fig. 2(d) in such a way that it will be suitable to go through the grinder. They were then milled into powder with a grinding machine, Fig. 2(e). The powder form of the maize, Fig. 2(f) was then mixed with powder corn cob in the specific ratiosstated above for the preparation of the samples in Fig. 2(g).Grinding of the feedstock into powder form gives the surface area of the sample increased which enhance the contact between hemicellulose and cellulose with dilute acid to reduce cellulose crystallinity.

(a) maize corn

(b) Removal of corn from cob

(c) Separation of corn from cob

(d) manually size reduced sample

(e) Milling of the corn

(f) Powder corn

(g) Various Samples of the corn

Fig. 2 preparation of samples with different mixing ratios

Pretreatment

The purpose of the pretreatment was to reduce cellulose crystallinity and increase the porosity of the materials. Pretreatment met the following requirements: improved the formation of sugar, avoided the degradation or loss of carbohydrate, avoided the formation of by-product inhibitors and was cost effective.

Acid pretreatment

In this study dilute tetraoxosulphate (vi) acid pretreatment method with 1.5% concentration was used. Each sample of the mixture was pretreated inside autoclave and heated at temperature of 120^{o}C for 30 minutes. After that, it was cooled and filtered. The filtrated was preserved in another conical flask prepared for this purpose and kept it for fermentation. The residue was washed twice by distilled water to remove tetraoxosulphate (vi)acid from it and kept it for hydrolysis purpose. corn cobs and maize powder was fed as batches and every batch contains 50 g of screened corn cobs powder with a ratio of 10:1(v/w) water to the sample. In sample pretreatment for all batches acid concentration of 1.5%, temperatures of 120^{o}C and retention time of 30 minutes were used.

Dilute Acid Hydrolysis

Dilute acid hydrolysis is an easy and productive process. Research works on the dilute acid hydrolysis of different lignocellulose materials have defined optimal process. The acid hydrolysis procedure started with adding of diluted sulfuric to the non-soluble component from pretreatment steps and the corncobs were hydrolyzing in the reactor. Next separate the solid particles from the liquid in the hydrolysate by vacuum filtration (to remove the non-fermentable lignin portion). After separating the solid part, the solid part is washed with distilled water. Finally, mixing the soluble component with the previously filter solution from the pretreatment step for the next procedure.

PH Adjustment

Before addition of any micro-organism to the above prepared solution, pH of these samples has to be adjusted. Otherwise the micro-organism will die in hyper acidic or basic state. A pH of around 5.0 -5.5 is maintained. Pretreated and hydrolyzed solutions are mixed, shaken substrate primarily checked for pH using a pH meter. Since, the mixed solution is more acidic media, and then it would maintain the pH by adding sodium hydroxide solutions.

Fermentation

Microorganism used for fermentation are Baker's yeast, *Saccharomyces cerevisae*used for fermentation was cultured on yeast extract agar. In order to prepare the media, one should have the favorable condition for yeast growth or to supply the required amount of nutrients.

Fermentation Medium: 200ml of production medium was prepared according to the requirements of Saccharomyces cerevisiae, containing 4 gm dextrose, 2gm dry yeast extract, 4gm peptone, 1 gm Urea, 1gm $MgSO_4.7\ H_2O$ and 200 ml make up distilled water. The pH 5 and autoclaved temperature of 121°C was maintained for 15 minutes.After that, 1gm of yeast *Saccharomyces cerevisiae*(instant premium) was added to the above 200 ml media in a 250 ml conical flask. Next the conical flasks were properly covered with aluminum foil. Finally the conical flask was then placed in a shaking incubator for 24 hours, a temperature of 30^{o}C and 200rpm

	
Sterilization mation	Media after sterilization

Fig. 3 Equipment for the fermentation process in the production of

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Sterilization

The reactor and all the equipment that were used for fermentation purposes were sterilized (autoclaved) and the sterilization was carried out at a temperature of 121^{o}C for 15 minutes.

The Procedure for Fermentation

Set shaking incubator in Fig. 1(b) at 30^{o}C and 200 rpm and then mix the prepared sample Fig. 1(f) with the media prepared in the shaking incubator using sterilized funnel. The parameters of fermentation i.e. fermentation time, yeast concentration (yeast proportion) and fermentation temperature were set to be at 72 hour, 10% (with the proportion of 1:10 that is the prepared media and sample respectively) and 30^{o}C respectively. And after 72 hours of fermentation, the samples were taken out and distilled.

Bioethanol Separation (Distillation)

Distillation was the last step in the production process experiments. It is the purifications steps. Distillation is the method used to separate two liquid with different boiling points. However, to achieve high purification, several distillations are required. In this experiment separation was used by simple distillation at a temperature of 85 ^{o}C. Finally the bioethanol from the three samples was harvested with small amount of water.

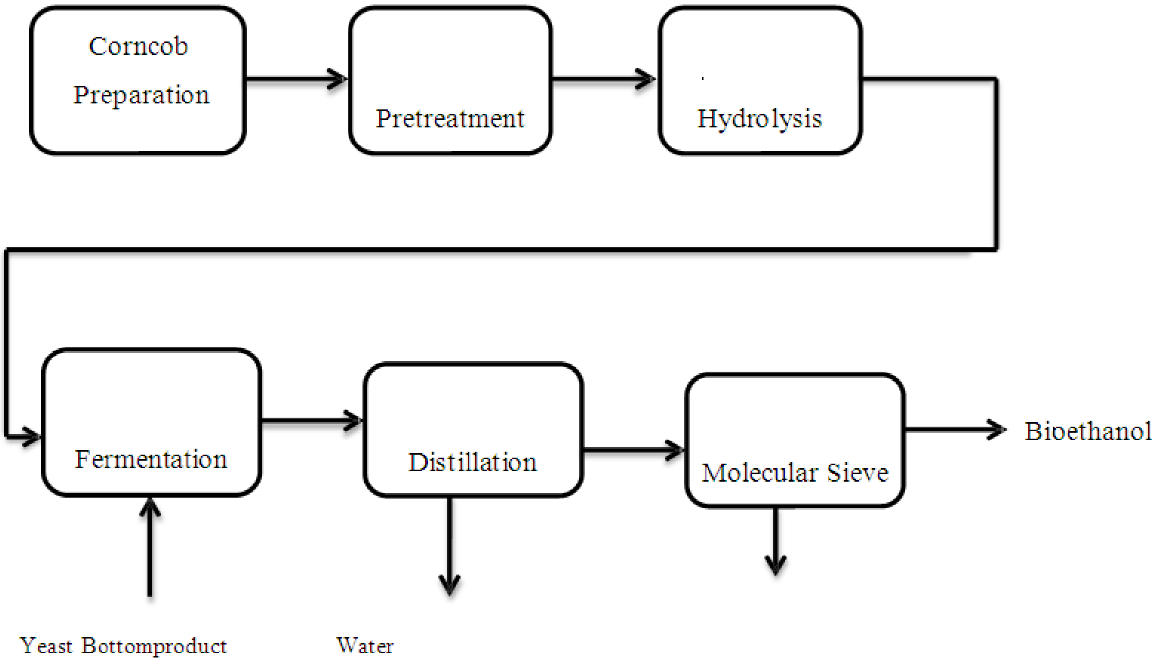

Fig.4Productionprocessofbioethanolfrom the mixture ofcorncob and maize.

III. RESULTSANDDISCUSSION

Here, statisticalanalysisand percentage yield ofeach sample were discussed.

Table 1Mixing ratio

%Maize	%Corncob	Sample
70	30	Sample A
60	40	Sample B
50	50	Sample C

The production process (Pretreatment, hydrolysis, fermentation and distillation) was repeated for each of the sample of the mixture

Percentage Yield

In this study, it was discovered as listed in Table 2 and depicted in Fig. 5, that the sample with more maize yielded more ethanol and the lesser the quantity of maize the lesser the yield of ethanol.Thedeterminationofcelluloseandhemicellulosecanbeappliedto quantifythetheoretical productionofbioethanol.However,Saccharomycescerevisiaeonlyconvertsglucose.Inthis study,corncobcontainedhighcontentsofthetotalcelluloseofapproximately50%cellulose. Thelowertheligninconten ttheeaserhydrolysiscondition,anddecreaseformationoftoxic chemicals suchas,aromatic,polyaromatic, phenolicandaldehydic.

Table2Percentage yield of each sample at different mixing ratios

Sample	%Yield
Sample A	85
Sample B	78
Sample C	65

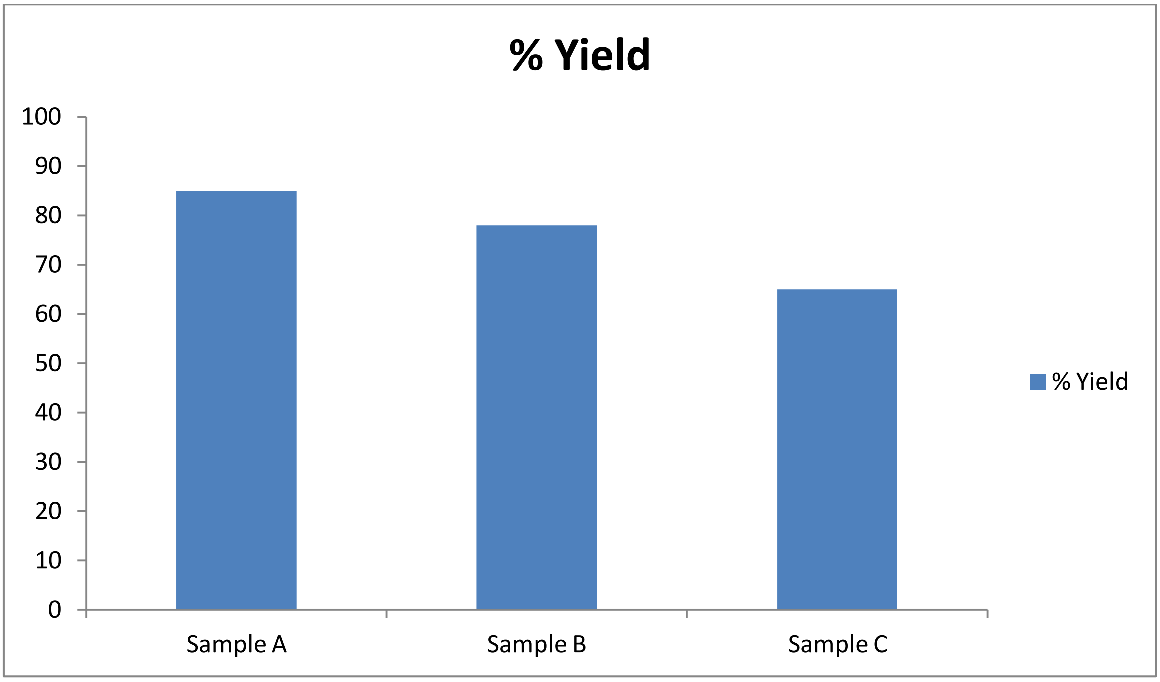

Fig. 5 percentage yield of the samples at different mixing ratios

IV. CONCLUSION

This study examines the possibility of corncob for bioethanol production. The conversion of corncob to bioethanol was carried out with dilute acid pretreatment, dilute acid hydrolysis, fermentation and distillation process steps.

In this study,two-stage diluted acid hydrolysis was used and the effect of the hydrolysis process variable (temperature, time and acid concentration) in the yield of bioethanol was investigated and optimized using response surface methodology. Positive yield of ethanol was obtained at a high acid concentration and low temperature as well as at high temperature and low acid concentration.

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