

Hydrolysis of Cellulose Wastes: Feasibility of Fuel Ethanol as Alternative to Gasoline from Petroleum as a Usable Energy Source in Nigeria

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Abstract: It is generally believed that fossil fuel aside its environmental implications in terms of its high carbon emissions and pollution characteristics is rapidly depleting. New energy source that is not only abundant in supply but more fungible in today's value chain and with potential as future green fuel is required to fill the gap. Research has shown that biomass possesses such characteristics to serve as alternative to the fossil fuel energy. Of all the fuels gotten from biomass, Ethanol is the most common and widely used. Ethanol was originally produced to serve as wine and for medicine, but today the use of ethanol are many ranging from production of organic chemicals to source of organic energy for heating, lighting and locomotion. Ethanol apart from synthesis is prepared from agricultural biomass by conventional method. Conventional methods as applied in many farms are expensive and has greatly increased the cost of food because of competition between consumers and industrialist for raw food materials. A modification of this method, use of cellulose waste and development of an efficient technology are necessary for cheap production, if ethanol is to be used, in place of gasoline. The paper discusses the various methods, techniques, technology, and reaction conditions necessary to produce low price ethanol, and at the same time surveys the possibility of the use of ethanol as alternative to gasoline as a usable energy source.

Keywords: Biomass, Fuel Ethanol, Hydrolysis, Renewable Energy

1. Introduction

Global increase in population have resulted to high increase in energy usage. Fuels have become more important as man discovers more uses for it. Fossil fuels have long provided the energy needed for internal combustion engines, power plants etc [1]. The so called age of petroleum is now giving way to a new age as fossil fuel source deplete rapidly. This rapid exhaustion rate of fossil fuel coupled with other factors such as increasing cost of fossil fuels due to increasing cost of extraction, environmental pollutions from fossil fuel combustions are major determinants drivers in the search for a new energy source; a renewable energy, one that

is abundant in nature and more environmentally friendly. Among the pollutants associated with fossil fuel combustion are unburned hydrocarbon, nitrogen oxides, carbondioxide, carbon monoxide etc. These gases such as Carbondioxide, has been blamed for a wide range of environmental problems such as acid rain and global warming. Owing to these increased efforts have been put into research aimed at development of a green fuel with low carbon as the desired fuel for the future. Biofuels have shown to possess the potentials and prospects of future green fuel.

Bio-fuels are liquid or gaseous fuels synthesized from residues of plants or plant matter, e.g. agricultural crops, municipal wastes and agricultural and the by-product of

forestry. Liquid bio-fuels are utilized as alternative fuels for transport, just like other alternative fuels such as liquid natural gas (LNG), compressed natural gas (CNG), liquefied petroleum gas (LPG) and hydrogen. Bio-fuels can considerably decrease the road transport emissions if deployed. They have proven to decrease carbon emissions, thereby helping to increase energy security. Various types of biofuels exist, and are synthesized from varieties of crops through different processes. Biofuels main classification are biodiesel and bioethanol.

Bioethanol among other biofuels have been recognized to be most globally used alternative fuel. This is because it has contributed immensely to a cleaner environment for the future through the reduction in crude oil consumption, possessing high oxygen content and high octane number in addition to its non-toxicity and reduced emission characteristics when it is compared to gasoline [2-5].

1.1. Ethanol and Its Uses as Fuel

Ethanol, also referred to as ethyl alcohol with the chemical formula C_2H_5OH , is a flammable, clear, colorless and slightly toxic chemical compound with acceptable odour. Ethanol, also referred to as ethyl alcohol with the chemical formula C_2H_5OH , is a flammable, clear, colorless and slightly toxic chemical compound with acceptable odour. It can be made either from petrochemical feedstocks by the acid-catalyzed hydration of ethene, or by the fermentation of biomass materials. Globally, the ethanol produced synthetically represents about 3-4% of the whole ethanol production while others are produced by biomass material fermentation. Bioethanol represents the ethanol produced from biological materials. Bioethanol fuel mainly is made by the process sugar fermentation. These are present in grains,

such as corn, grain sorghum, and wheat, as well as potato wastes, sugar cane, switch-grass, rice straw, urban wastes, and yard clippings [6].

The main sources of sugar required to produce ethanol come from fuel or energy crops. These crops are grown specifically for energy use. Research is ongoing on the use of municipal solid wastes to produce ethanol fuel.

Bioethanol is biodegradable, low in toxicity and causes minimal environmental pollution if spilt. Ethanol burns to produce carbon dioxide and water. Ethanol is a high octane fuel and has replaced lead as an octane enhancer in petrol. Ethanol blending with gasoline can be used to oxygenate the fuel mixture to enable it burn more completely and reduces polluting emissions.

Varieties of agricultural products can be fermented to produce ethanol – wheat, corn, sorghum, potatoes, cane sugar, molasses etc. the fermentation is capable of yielding 2.6 gallons of ethanol from one bushel of grain. Two main by-products are normally produced – (i) distillers grains- this is a high protein residue which is valuable as livestock feed. (ii) Carbon dioxide. The three products – ethanol, distiller's grain and carbon dioxide are produced in approximately equal amounts.

The basic ethanol production process from grains and starchy substances first requires an enzymatic chemical reaction with starch and water to produce simple sugar. A second stage in the reaction is fermentation in which yeasts converts the simple sugar to ethanol. Carbon dioxide is released during this second conversion process. The alcohol – water mixture is then separated by fractional distillation to obtain fuel grade ethanol, leaving behind distiller's grains. Carbon dioxide bubbles off, or is collected if needed [7].

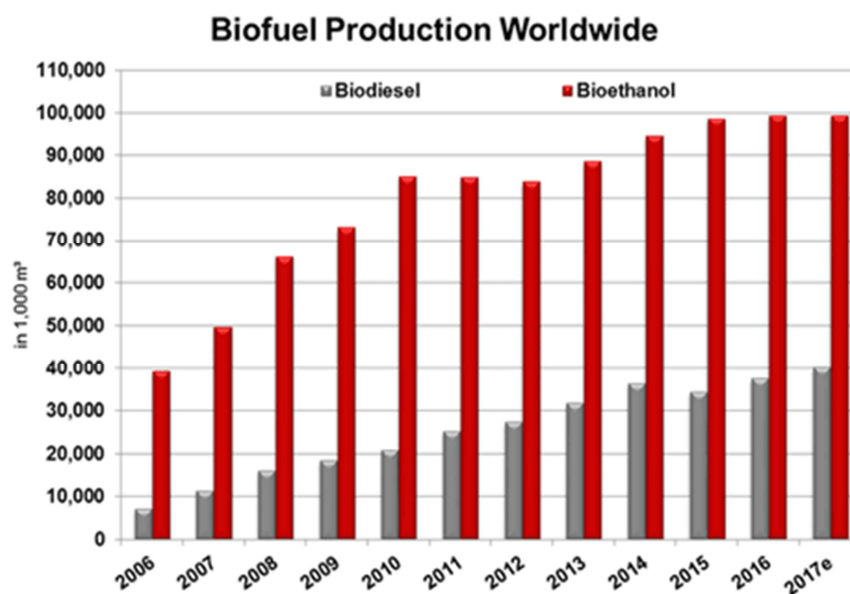


Figure 1. World biofuels production [8].

Figure 1 shows the trends in the increase in production of biofuels and bioethanol globally. It can be seen from figure 1

that there is increasing production as a result of increasing demand for biofuels.

1.2. Biomass Feedstock for Bioethanol Production

Bioethanol is gotten by fermenting sugar contained in various kinds of biomass:

Sugar-rich biomass, mainly sugar beet and sugarcane;

(ii) Starch-rich biomass, grain (e.g., barley, wheat, corn, rice), potatoes, sorghum, cassava; and

(ii) Cellulose-rich biomass, straw, wood (residues), corn cobs and stalks, grass, paper and more.

About half the world's bioethanol production makes use of sugar crops as feedstock, mainly sugarcane and beets. Many of the remaining ethanol is made from starch crops, mainly grains e.g. corn and wheat. It is easier to make ethanol from sugar crops, since the fermentable sugars are more readily available than other feedstocks. 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. The disadvantage of producing bio-ethanol from sugar or starch is the high cost of the feedstock [9]. Thus, there is a possibility of competition between the production of food stuffs for food and for industrial usage for fuel. Therefore, bioconversion of cellulosic biomass into bioethanol is very important to be developed since this resource is more economical and is available easily.

1.3. Cellulosic Ethanol

Cellulosic materials such as agricultural and forest residues, crops and herbaceous materials in large quantities are available in many countries with various climatic conditions, making them suitable and potentially cheap feedstocks for sustainable production of fuel ethanol. Few decades ago, much interest has been given to research on the conversion of cellulosic materials to ethanol [10]. Cellulosic materials are generally widespread and abundant in nature. Being abundant and outside the human food chain makes cellulosic materials relatively cheap feedstocks for

bioethanol production. Cellulosic materials are comprised of lignin, hemicellulose, and cellulose, often called Lignocellulosic materials. One of the main functions of lignin is to provide structural support for the plant. Generally, trees have higher lignin contents than grasses. Unfortunately, lignin which contains no sugars, encloses the cellulose and hemicellulose molecules, making them difficult to reach.

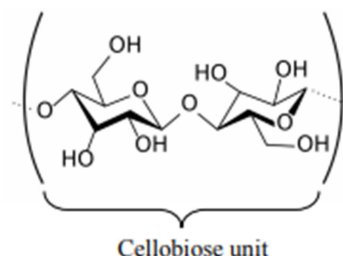


Figure 2. Chemical structure of cellulose [11].

Cellulose molecules consist of long chains of glucose molecules much like starch molecules, although with different structural configuration. These structural features with the encapsulation by lignin makes cellulosic materials more difficult to hydrolyze than starchy materials. Hemicellulose also comprises long chains of sugar molecules but contains, in addition to glucose (a 6-carbon or hexose sugar), pentoses (5-carbon sugars). To complicate matters, the exact sugar content of hemicellulose varies depending on the type of plant. Since 5-carbon sugars comprise a high percentage of the available sugars, the ability to recover and ferment them into ethanol is crucial for the efficiency and economics of the process [11]. Figure 2 shows biomass feedstock contributions to ethanol production.

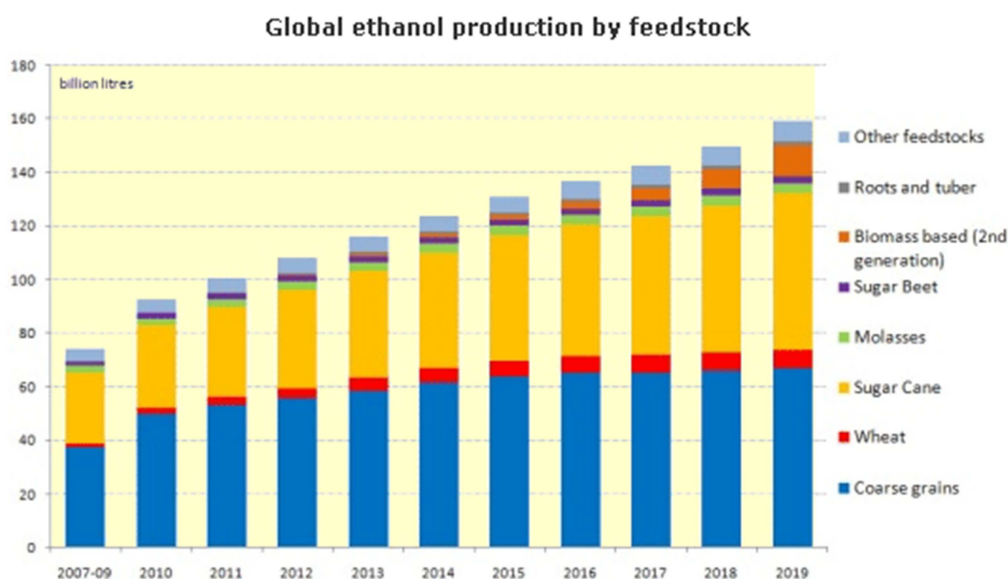


Figure 3. Global ethanol production by agricultural feedstocks [12].

2. Production of Bioethanol

The production of bioethanol as a useable energy source is not a simple process. A considerable amount of energy, equipment and process control are required if ethanol is to be produced in commercial quantity. A number of methods for the production have been developed.

2.1. Conventional Method

A basic process flow diagram for the production of ethanol by the conventional method is shown in figure 4.

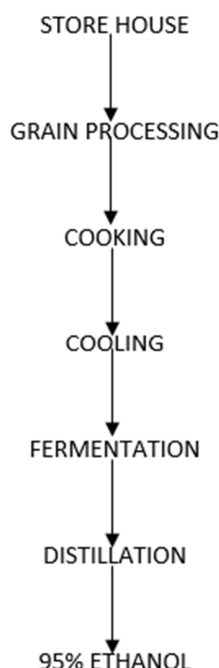


Figure 4. Ethanol Production Flow Diagram.

i. Storing – the grains are collected, dried and stored in the storehouse

ii. Processing – in the processing, the grains are ground to expose the starch molecules. A hammer mill with a 3/16 inch screen is normally used.

iii. Cooking – here the grains in form of slurry is cooked. Water (about 15 to 30 gallons per bushel of grains) is added to the ground to form slurry. The pH of the slurry is adjusted using acids or alkali to between 6.0 and 7.0. An enzyme, amylase is added to the slurry to ensure complete breakdown of the starch. The slurry is then cooked for thirty minutes or an hour at about the boiling point temperature to gelatinize the starch and sterilize the mixture. Cooking is best accomplished with steam or fired cooking. The mixture is stirred during cooking.

iv. Cooling – more water is added (about 15 to 20 gallons per bushel) and the mixture is cooled from 85° – 90°F. Cooling is normally accomplished in a heat exchanger. The heat removed can often be used to preheat the water entering the steam boiler. It is during this dilution and cooling process that most of the starch is converted to simple sugars. Additional time may be needed for complete conversion to occur.

v. Fermentation – in fermentation section, brewer's yeast and second enzyme (glucose – amylase) are added to the mixture. Stirring is needed to distribute the enzyme and yeast. The mixture is allowed to ferment, converting the simple sugar to ethanol. The temperature of the mixture during this process which takes about 48 to 72 hours should be maintained at 85°F to 90°F. This may require the removal of the heat produced during fermentation. As fermentation progresses, the pH of the mixture decreases. At the end of the fermentation, the mixture will contain about 6 to 12 percent alcohol, water and distiller's grains. The alcohol – water mixture is referred to as beer.

vi. Distillation – in distillation section, ethanol is separated from the fermentation mixture. Ethanol boils at 173°F and water at 212°F. This difference in boiling temperature is made use in the separation of ethanol and water. The mixture is heated to vapourise ethanol at 173°F, then followed by collecting and condensing the vapour to liquid ethanol. The first distillation contains about 50% of water. A second distillation is carried out and this removes 45% of the water leaving only 5% of the water in ethanol in the mixture for distillation. The wet distiller's grains are available as livestock feed.

The 95% ethanol is either denatured and sent to the storage tank or concentrated more by refluxing with benzene to produce 100% anhydrous ethanol. We have been discussing the conventional production, which is now operational in many agricultural farms in the United States of America, Brazil and other countries. Based on this conventional method, ethanol is produced from:

Cassava, Maize, Sweet Potatoes, Palm wine, Rice, Ubereagu (a local berry from which wine was subsequently prepared), Sugar cane (leading to exhaustive use of sugar can viz:

(i) Production of crystalline sugar

(ii) Fermentation of molasses for ethanol and carbon dioxide production

(iii) Dilute acid or enzyme hydrolysis of husk (chaff), followed by fermentation to produce ethanol, carbon dioxide and distiller's feed. The distiller's feed serve as animal feed.

However, the conventional method of ethanol production has many limitations: (i) It is cumbersome, (ii) It involves many operations, (iii) It is inefficient, requires much heat, gives out a lot of waste water, and as such ethanol of high cost.

Hydrolysis, fermentation and distillation processes in the conventional method consume large amount of energy. Cooking to gelatinize the starch prior to enzymatic hydrolysis consumes 17% of this energy [13] and this energy is part of the large processing energy demand that has made the economic feasibility of on-farm small scale ethanol production base on conventional method questionable, and conventional method involves many stages. Other effective and less costly methods are now developed.

2.2. Continuous Method

In this process, some of the operations (iii, iv and v) are combined. Cooking and fermentation take place in one vessel. Fermentation is continuous. Used water and yeast are

recycled. The main advantages are [14]: (i) Reduced labour, (ii) Reduced energy, (iii) High yield, (iv) Simple operation, (v) Reduced waste water

2.3. Use of Koji Amylase

Cost was further reduced by removing energy required for gelatinization of the starch prior to fermentation by enzyme hydrolysis without heating. A glucose – amylase was developed by Koji known as Koji-amylase. With the use of Koji-amylase continuous method, it is possible to produce low cost ethanol in good yield (89.6%). The use of Koji-amylase in hydrolysis of starch and cellulose waste has the following merits: (i) The use of dilute acids is eliminated, (ii) Energy of gelatinization is removed, (iii) Maintains high yield of ethanol, (iv) Lower production cost

3. Raw Materials for Bioethanol Production

As earlier pointed out, apart from synthesis, the main raw materials for the production of ethanol are agricultural commodities, there are two basic methods of producing ethanol from agricultural waste: the conventional method known otherwise as the first generation method and the use of cellulose waste known as second generation method

3.1. Cassava

Cassava has its origin in tropical America, and appears to have been cultivated there for about 4000 years, the plant has spread from South America to other tropical and subtropical countries of the world. The most important area of the cultivation of Cassava are East and West Africa, Brazil, Indonesia, Malaysia, Thailand and Philippines. The plant is a perennial bush plant, reaching a height of 3 metres depending on the plant strain. The tuberous roots usually contains 25 – 30% starch and at times 40% starch. In Nigeria the period of harvest for maximum yield of starch ranges from eight months to sixteen months and at times twenty four months depending on the strain. It is a major source of food.

3.2. Sweet Potatoes

Sweet potato is a major tuber which is grown in Nigeria. It is heavily cultivated in Benue, Plateau and Kwara states. It is grown in very many other parts of the country particularly in

Kano, Zaria, Sokoto, Maduguri, Abeokuta, Oyo, Sapele, Onitsha, Badagry and Ikeja. It thrives in swampy area and is a major source of food particularly as a supplement for yam, cocoyam and other carbohydrates.

3.3. Palm Wine

Palm Wine is the palm sap obtained by tapping a palm tree. It is a beverage and of economic importance to the farmer. The two main sources of palm wine are oil palm wine tree and raphia palm tree. Raphia palm grows in swampy areas. Palm wine contains a heavy suspension of live yeast and bacteria. In this respect palm wine differs from grapes and other fruit wine, which at the time they are drunk are usually devoid of all the organisms responsible for the initial fermentation. The juice contains 10 – 12% sugar – mainly wine. The sources of these micro-organisms are not known, but it is claimed that these microbial contaminations might have originated from the indigenous flora of the palm trees and from equipment used in collecting the wine. Cassava, Potatoes and Palm wines are few selected examples. They are used primarily as food for man and animals, rather than for ethanol production. This increases the cost of ethanol.

3.4. Cellulose Wastes

Most of the raw materials used in conventional method are agricultural commodities that serve as food for both man and other animals leading to high cost of ethanol production. Efforts are now being directed to cellulose waste of agricultural, forestry and municipal residues. Acid hydrolysis is a potential attractive technique for upgrading the value of cellulose wastes by converting them to glucose. The glucose can then undergo biological and chemical processing for further conversion to ethanol. New York University has carried out expensive work on developing technology with emphasis on the crucial steps of converting the waste cellulose to glucose continuously. These studies have led to the development of a high dilute acid hydrolysis process. One key feature of this process is its ability to accept many types of cellulose waste both wet and dry. The system to date has been tested utilising paper pulp and dry hardwood sawdust resulting in high conversion yields and good energy efficiencies [15]. The glucose from cellulose wastes can also be used as the basic material for the manufacture of many volume organic chemicals.

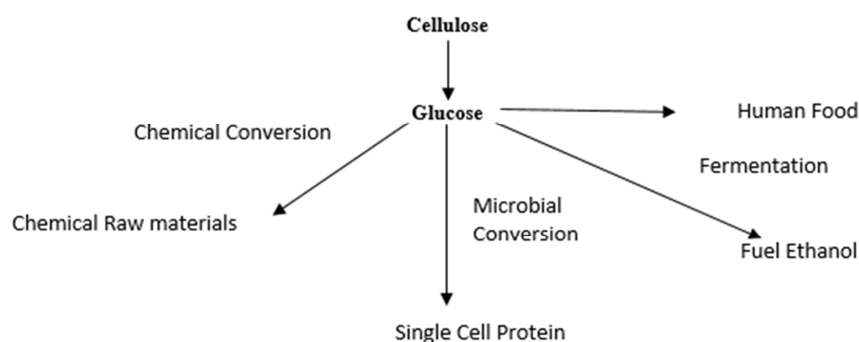


Figure 5. Waste Cellulose Utilization.

A reliable, high-yielding, energy-efficient process based on cellulose waste would have many advantages, compared to the conventional corn processing technology now being used.

Table 1. Comparison of Properties of ethanol and gasoline as transport fuels [16].

Property	Ethanol	Gasoline
Chemical formula	C ₂ H ₅ OH	Various
Oxygen content by mass (%)	34.8	0
Density at NTP (kg/l)	0.79	0.74
Lower Heating value (MJ/kg)	26.95	42.9
Volumetric energy content (MJ/L)	21.3	31.7
Stoichiometric AFR (kg/kg)	9	14.7
Energy per unit mass of air (MJ/kg)	3.01	2.95
Research octane number	109	89-95
Motor octane number	89.7	85
Boiling point at 1 bar (°C)	79	25-125
Heat of vaporization (KJ/kg)	838	180-350
Reid vapour pressure (psi)	2.3	7
Flammability limits in air	0.28-1.99	0.26-1.6
Laminar flame speed at NTP	40	28
Adiabatic flame temperature (°C)	1920	2002
Specific CO ₂ emissions (g/MJ)	70.99	73.95

From the table above although gasoline has more heating capacity than ethanol, ethanol has less CO₂ emissions characteristics than gasoline which makes it good when used as blends in gasoline fuelled vehicles.

4. Discussions

The use of ethanol are many- ranging from the synthesis of organic chemicals, to the manufacture of rubber, solvents; to sources of organic energy for heating, lighting and locomotion. It is a promising substitute for gasoline, but it is expensive.

The method for the production of ethanol, which is operational in many agricultural farms, is the conventional method. The conventional method is cumbersome, involves many operations and Labour. It requires much heat, give out a lot of waste waters and produces fuel ethanol of high cost

Costs for the production of ethanol by fermentation must be reduced if fuel is to replace petroleum based liquid fuels. One such method to reduce the costs of production is the combination of a number of operations in the conventional process. This is seen in continuous processes where cooking, cooling and fermentation take place in one operation in a single vessel, and used water and yeast are recycled, thereby saving costs. Another such method of reducing costs of production is to lower energy inputs through the elimination of the cooking step presently required for starch gelatinization.

The use of Koji-amylase that requires no prior gelatinization of starch holds promise for not only the elimination of the cooking step, but also maintain present ethanol yields, lowering energy inputs and lowering production costs. Work by Ueda and his group with Koji-amylase on raw ground corn gave 88.0%, 99.9%, 90.2% and

91.1%. This is encouraging. Gelatinization of raw ground corn was not necessary prior to hydrolysis by Koji-amylases. The amylases produced by Koji were to degrade the raw starch to fermentable sugars. Elimination of this cooking steps lowers energy inputs of ethanol production and eliminates the need for cookers.

Thus, operation cost, and capital cost can be reduced for both large and small-scale industries when compared with the conventional method. All ingredients were combine in one vessel so fermentation occurred simultaneously with hydrolysis – as sugars were formed, the yeast hydrolysed them to produce ethanol. Combining all these process in one vessel reduces handling and management. Thus cost for time, Labour and management are reduced and the use of dilute acid is completely eliminate in the production of ethanol from cellulose wastes.

The conventional raw material for the production of ethanol are Wheat, Corn, Sorghum, Potatoes, Molasses and Cassava etc. these competes with their use as food, making the ethanol produced expensive. The introduction of cellulose waste in the production of fuel ethanol is a welcomed alternative.

Dilute acid hydrolysis of cellulose, followed by fermentation to ethanol offers an attractive alternative for the production of ethanol as an alternative usable energy source. In addition to ethanol production, glucose from cellulose waste can be used as the basic raw materials for the manufacture of many valuable organic chemicals. The much needed food materials (agricultural commodities) are replaced by cellulose wastes, and the use of dilute acid can be replaced by Koji-amylases.

With adequate technology, proper reaction conditions and use of cellulose wastes, fuel ethanol can serve as valuable substitute for gasoline as a usable energy source.

5. Conclusion

The reason for the promotion of fuel ethanol as substitute for gasoline is mainly because the fear of fossil fuel run out and the environmental pollutions it portrays. An eco-friendly environment has become the dream of many economies. Increasing the use of bio-fuels for energy generation purposes is of particular interest nowadays because they not only allow mitigation of greenhouse gases but provide means of energy independence even offer new employment possibilities. Many countries have long used bioethanol as blends and the possibility of ethanol domination is imminent as fossil fuel prices rises and technological breakthroughs in ethanol production especially from cheap and relatively more abundant cellulosic biomass reduces the cost of ethanol production, making it economically competitive to its gasoline counterpart. Nigeria as a nation should adopt the ethanol economy by investing in ethanol production from cellulosic waste. This will be an additional revenue to the government and help boost the Nigeria economy.

6. Recommendations

There should be a cellulose Hydrolysis plant situated in Nigeria to utilize the vast cellulosic waste generated in the country as feedstock for the production of Ethanol. The Ethanol produced can be blended to gasoline to achieve transport fuel of high quality and performance. Furthermore the construction of Cellulose Hydrolysis plant in Nigeria will aid in reducing cellulosic waste generated in the country thereby converting them into useful transport chemical products. Lastly, veering into Ethanol production from Cellulose waste will provide employments to the teeming unemployed youths in Nigeria, provide additional revenue to government via tax and royalties.

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