ACID HYDROLYSIS OF GROUNDNUT STRAW FOR THE PRODUCTION OF ETHANOL

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FOR THE PRODUCTION OF ETHANOL

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DECLARATION

I , Amade Friday Ayegba , declare that this research work is solely the result of my effort and has never been submitted anywhere for any degree . All literature cited have been fully acknowledged in the reference

………………………………………………………………

A . F . Ayegba

CERTIFICATION

This project "Acid hydrolysis of groundnut straw for the production of ethanol"

Meets the regulations governing the award of degree of Bachelor of Engineering of the federal university of technology, Minna and is approved for its contributions to scientific knowledge and literary presentation.

.... 3/12/2007,

Engr. A . S . Kovo Date

....

Dr. M. Edoga Date

(H O D)

....

External Examiner Date

DEDICATION

To God almighty , that has been my strength and stronghold , to my family for everything I have received and my friends for their courage.

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I want to thank God for His love and mercy althrough this research and my studies, may His name be praised .To my parents Mr & Mrs Amade S . Y . whose constant support and courage has made this dream come through and to my Dad who bowed out of the race for life at the peak of my studies , may His soul rest in peace.To my siblings Juliana , Rosemary,Monday(late) , Godwin , Veronica and Theresa you are all wonderful.

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Finally , to my enormous relations for there support and encouragement may God bless you all.

ABSTRACT

The research was carried out to produce ethanol form biomass. The choice of groundnut straw for the production was based on its abundant availability and ability to grow in most part of the country. The production of ethanol from biomass requires acid hydrolysis , fermentation using Yeast to produce ethanol and carbon IV oxide , the by-product of the reaction . The production of the sample was carried out to give a yield of 179.2ml of ethanol from 500g of groundnut straw .Therafter was tested for some of the basic parameters of ethanol . The Heat of vaporization , boiling point temperature and specific gravity obtained was quit almost close to literature which implies that it will give the same performance as that of the hydrocarbon.

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CHAPTER ONE

1.0 INTRODUCTION

The a oil embargo of 1973-1974,the gasoline shortage of the summer 1974,the shortage of gasoline in Nigeria between 1994-1998 and the recent oil supply disruption in the middle East and the South-South region of Nigeria show the world extreme and dangerous dependence on petroleum products. This problem of gasoline shortage has been faced by some nations in the past and this has prompted them to seek for a cheap alternate source of fuel. Countries like Germany and South Africa has little oil but ample coal, so the make there oil from coal. Some like the United States have all of the mentioned options, others like Japan have few ,if any. A brief look at what can be done starting with the raw materials to the finished product has seen appropriation in the light of the world.

Ethanol has been used as fuel since late 19th century .However , the outburst of crude oil reduce interest in ethanol production as fuel. In the last two decades ,ethanol production as fuel has been reconsidered due to the ability to produce ethanol from low cost agricultural residue making ethanol

competitive with gasoline.

The attractiveness of ethanol as a motor fuel is due to the four characteristics giving below;

1. It is light and easily transported

2. Its heating value per gallon is high (about 2/3 of that of gasoline)

3. It can be blended up to 10 % with gasoline with no change engine turning or increase in emission and;

4. It can enhance the octane rating of unleaded gasoline.

The raw materials for ethanol fermentation have included Sugar (obtained from sugar cane guice ,cassava molecules),starch (obtained from grains), agricultural residue (from wheat, straw, corn stales)

1.1 AIMS/OBJECTIVES

The aim of this work is to utilize the abundant agro-residue present for the production of ethanol fuel which can substitute for gasoline .The agro-residue under consideration is groundnut straw.

1.2 SIGNIFICANCE OF THE WORK

The cost of the raw material for the production of ethanol from agro-residue is very low compared to that of corn feed stock. Although the process is expensive at present ,advances in biotechnology could decrease conversion cost substantially .A set target to reduce the cost of producing ethanol by 60% per gallon by 2015 has been set by the United States .In a nutshell ,the ability to produce ethanol from low-cost agro-residue is the key to making ethanol competitive with gasoline.

The efficiency of ethanol as engine fuel is appreciably high (about 73% on volume basis). Its heating value per gallon is about 2/3 that of gasoline. The use of ethanol as engine fuel has a super charging effect that increases the power output obtainable from an engine of a given size and this is due to the lower stoichiometric air-fuel ratio and its high latent heat of vaporisation.

CHAPTER TWO.

2.0 LITERATURE REVIEW

2.1 MOTOR FUEL

Gasoline is the preferred fuel for the remarkable Otto engine which emanated from an unwanted by-product to an indispensable main stay of modern life in less than one normal human life.Today gasoline in the engine of the world passenger cars alone produce more than fifty times the power generated by all of the nations central power plants.

The sources of gasoline used in car engines are:

1. Crude oil of petroleum which is formed during fractional distillation , thermal cracking , hydrocracking , reformation , alkylation and isomerization.

2. Coal hydrogenation and catalytic synthesis ; This was operated by the Germans during the world war II in 1946 . The process consist basically of the hydrogenation of carbon II oxide over such catalyst and under such condition that the product consist of hydrocarbon of various chain length and degree of saturation . The reaction equations are given below :

$$nCO + 2nH_2 \rightarrow C_2H_2\text{n}\, H2 \; + \text{n}H_2\text{O}$$

$$nCO + 2n\, H_2 \rightarrow C_2H_2\text{n} + \text{n}H_2$$

3. Coal liquefaction :This is a direct one step conversion of coal to high octane gasoline.

4. Oil shale and tar sand : This is the major potential source of gasoline. Oil shale and tar sands have not yet been exploited to any appreciable level , in the

case of tar sand s , extremely viscous bitumen must be removed from the surface of the sand grain to which it stick tenaciously . In the case of oil shale ,solid kerosene content of the shale must be thermally cracked into liquid hydrocarbon. The cost of the two processes are still great or high compared to petroleum.

2.1.2 REQUIREMENT FOR GOOD GASOLINE

To satisfy modern light performance of an automotive engine , today's gasoline must meet a given specifications . Moreover , some of their characteristics must be geared towards meeting the prevailing local conditions , for example knock resistance (which is indicated by octane number) must be adjusted to meet the need of the particular engine in which the gasoline will be used .

Knocking property is an important characteristics of petrol in the internal combustion engine , mixture of petrol and air are compressed by fast moving cylinder and ignited by a spark. The pressure develop by the combusting gas is used in propelling the cylinder . The extent of compression is limited by the characteristics of burning at normal burning condition . The speed of the flame developed is 10-15 ml . However , in abnormal cases the speed cane be as high as 1500-2500 ml . Thus is referd to as knocking or detonation .

Octane number requirement to prevent annoying , fuel wasting , potential damaging , engine knock at all engine speed and loads for gasoline must have high antiknock quality (octane number) throughout its entire distillation range .

Distillation characteristics ; For fast warm up , smooth acceleration and proper distribution of the fuel among an engine cylinder – the gasoline must vaporize increasingly as carburetor and manifold temperature rises.

Vapour pressure – In order for an engine to start at prevailing atmospheric temperature , it's gasoline must form a substantial amount of combustible vapour at that temperature which was tested : Real Vapour pressure test (ASIM method D523)

Low gum requirement – A good gasoline must be substantially free from gum foaming materials in order to avoid clogging of engine valves manifold deposites that would cause exhaust smoke and loss of engine power .

Low sulphure requirement – Gasoline containing hydrosulphide or the thiols naturally present in crude oil would be extremely offensive to the motor engine .

2.1.3 SUBSTITUTION OF GASOLINE WITH ETHANOL FUEL

Ethanol and other ethanol fuel blending has been tried many times in many countries either to utilize the surplus agricultural produce or residue or to create a market for expanded production . Ethanol use in motor fuel reached its peak between world war I and II because of over development of ethanol production for munitious in world war I , rapid expansion of European beet- sugar industry and declines in the consumption of drinking ethanol .

Properties of ethanol

Molecular formular	C_2H_5OH
Molecular weight	46.07
Specific gravity	0.7937
Heat of combustion (kJ/κg)	29,836
Boiling point (at 101.3 kJ/kg ^0C)	78.32
Latent heat of at normal boiling point(kJ/kg)	840
Vapour heat capacity(H25 ^0CkJkg/ ^0C)	1.60
Liquid heat capacity(H25 ^0C kJ/ ^0C)	2.42

Table 2.1 THE CHARACTERISTICS OF ETHANOL VERSUS GASOLINE FUEL

	ETHANOL	ISO-OCTAN
Heating value J/g	29,800	46,500
Specific gravity	0.794	0.704
Stoichiomtric A/F ratio	9	15
Latent heat of vaporization J/g	840	328
Research octane number	106	100
Motor octane number	89	100

-T o convert J/g to Btu/lb multiply by 0.430

-To convert J to calorimeter divide by 4.184-A/F

- Air Fuel ratio

Comparing the properties of ethanol with those of gasoline range hydrocarbon in the above table shows some of the advantages and disadvantages of ethanol . Firstly , on a weigth to weight basis , ethanol has only about two-third the heating value of gasoline range hydrocarbons , all of which has a heating value of about 46,500 J/g (21,100 Btu/lb) compared to alcohol 29,800 J/g (13,500 Btu/lb) . However , because ethanol's specific is higher than that of most fully boiling gasoline (0.79 versus 0.70) , the difference in heat content per unit volume is as great as the difference per unit weight compared to iso-octane , one of the light or gasoline hydrocarbon . Ethanol heat content deficiency is only about 27 %on volume basis.Because of ethanol lower stoichiometric air – fuel ratio and its high latent heat of vaporization , its use as engine fuel has a super charging effect , increasing the power output obtainable from an enine of a given size.

As might be expected from its own octane rating , 106 research octane number and 89 motor octane number ethanol has more effect on research rating than a motor and road ratings . As effect is greater with low – octane –straight run gasoline fraction and becomes less and less as base – stock and anti knock quality increases .

The attractiveness of ethanol as motor fuel is derived from four characteristics .

1. It is a liquid that is easily transportable

2. Its heating value per gallon is high (about 2/3 that of gasoline)

3. It can be blended up to 10% gasolie with no change of engine turning or increase in emission and ;
4. It can enhance the octane rating of unleaded gasoline .

The fundamental processing step in the overall ethanol fuel production remain similar , though considerable improvement in efficiency . Most motor fuel grade ethanol stock composition and ethanol yields are shown the table below :

Table 2.2 DIFFERENT SUBSTRATES FOR ETHANOL PRODUCTION AND THEIR COMPARATIVE PRODUCTION POTENTIAL.

CROP	ETHANOL PRODUCTION POTENTIAL{L/T}
Sugar cane	70
Sugar beet	110
Sweet potato	125
Potato	110
Cassava	180
Maize	360
Rice	430
Barley	250
Wheat	340
Sweet sorghum	60
Baggas and other biomass	280

Source : Winrock international 2004

Table 2.3 POTENTIAL OF DIFFERENT AGRO-RSIDUE FOR THE PRODUCTION OF ETHANOL

Agro-residue	**cellulose (%wt/wt)**	**hemicellulose (%wt/wt)**	**lignin (%wt/wt)**	**theoretical ethanol yield{l/t**
Rice straw	41.36	20.36	12.06	346.00
Wheat straw	39.63	24.07	16.97	359. 00
Groundnut straw	36.55	13.94	31.28	319.69
Rice husk	44.06	17.85	17.20	392.33
Sugarcane baggase	33.60	29.00	18.50	351.00

Source ; Iyer , Rao and Grover (2002) ; DOE (2005)

2.3 PRODUCTION OF ETHANOL

Ethanol is produced from a number of though biological or chemical reaction method.

2.3.1 RAW MATERIALS

The and variety of raw materials for ethanol production can be conveniently classified into the following types (Caro , 1991)Mollases from sugar cane sugar beet and fruit , which may be converted to ethanol directly ;

a. Starch from grain and root crops , which must first be hydrolyzed to fermentable sugar by theaction of enzymes ;

b. Cellulose from wood , agricultural waste etc which must be converted to sugar using either acid or enzymatic hydrolysis

c. Catalytic hydration of ethylene , where ethylene is produced by petroleum cracking and from natural gas , then treated with water at high temperature in the presence of catalyst to produce ethanol and :

e. Sulphuric acid hydration of ethylene

2.3.2 COMMERCIAL MANUFACTURE OF ETHANOL

Ethanol may be produced either from synthetic or chemical method or by fermentation. Ethanol is produced by several synthetic process such as ;

1.Catalytic hydration of ethylene where ethylene is produced by petroleum cracking and from natural gas then treated with water at high temperature in the presence of catalyst to produce ethanol .

$CH_2 = CH_2 + H_2O \rightarrow C_2\,H_2\,OH$…………………………………………..(1)

2.Sulphuric acid hydration of ethylene where ethylene is treated with concentrated sulphuric acid to produce ethyl hydrogen sulphate and diethyl sulphate which are then hydrolysed to ethyl alcohol and dilute sulphuric acid

3.Fermentation ; A chemical process wherein products are obtained through the activities of micro – organism and chemical changes are brought about in an organic substrate through the action of enzymes by micro – organisms .

The ethylene method is the cheapest of the ethanol production method series but the relative availability of biological material and the apparent ease of conversion to ethanol have led to the large scale , widely accepted biological method of ethanol production . The biological materials from which ethanol can be obtained includes ; corn , wheat , paper mill waste , molasses , sugar cane, wood , surplus food crops etc. These materials are collectively known as biomass which is defined as the renewable liquid fuel , derived from biological raw materials , which can be used as a substrate to petroleum fuel . Biomass are carbohydrate composed of either simple sugar (monomer and dimmers) or polymeric form of the simple sugars as in starch and cellulose with molecular weight ranging in millions .The basic steps in the biological production of ethanol is the fermentation process where specific enzymes facilitate the anaerobic conversion of the simple sugar (glucose , fructose) to ethanol with accompanying evolution of heat and CO_2. Yeast , an eucaryotic cell secrets degradative enzymes that act on the sugar substrate .

$C_6 H_{12} O_6 \rightarrow 2\, CH_3\, CH_2\ OH\ + CO_2 + \text{Heat}$ ....(2)

The reaction above is common to all biomass and it facilitated by the enzyme,diastase .However, for dissaccharides like sucrose and maltose, another enzyme, invertase, secreted by yeast hydrolyses the compounds to their individual primary sugers for subsequent fermentation. In addition, stach and cellulose materials composed of the large network of sugar monomers required first, the breaking of the complex network of monomers into sugar before fermentation can take place.

$(-C_6 H_{10} O_5 -)n + nH2O$ ……………………………………………………………………(3)

The hydrolysis is achieved by treatment with acid, base or specific enzyme appropriate for such functions. Hydrolysis of cellulose materials is more difficult principally because of cellulose crystallinity and the naturally occurring binding material (lignin) which gives wood a structural strength and which also has to be broken for the cellulose material to be reach for processing (Caro 1991). Subsequently, the complexity and overall cost of the project is increased. At the moment, data on the economics of ethanol product form cellulose are not available although plants scattered around the world utilizing cellulose raw material exist, probably operating on pilot scale or proprietary method s are in existence. Above all, the choice of material and method for ethanol production depends on a number of factors. Usually, a material which is available in abundance with a great comparative advantage in production, based on soil and natural conditions and other socio-political factors is considered for production.

Different crops thrives well in Nigeria, but results from recent studies undertaken have shown that Nigeria has the capability to become the largest producer and exporter of groundnut and its products and this is responsible for the governments re-invigorated interest in the groundnut production.

2.4.1 BRIEF DISCRIPTION

Groundnut/peanut (Arachis hypogeal L) originated in South America. It is a short herbaceous annual that produces its pod inside the soil. Groundnut was brought into West Africa through the slave trade the crop is one of the principal oil seeds in the world. Until the mid 1980's it ranked third behind soya beans and cotton seed; but now raped seed has passed groundnut in terms of world production, closely followed by sunflower seed. The emergence of raped seed and sunflower seed may be contributed to health concern by the industrial countries and the European union policy. Developing countries account for 95% of world groundnut Era and about 94% of total production.

Production is concentrated in Asian and Africa, with Africa accounting for 355 of global area and 21% of total output mainly in Nigeria, Senegal and Sudan.

2.4.2 HISTORICAL DEVELOPMENT OF GROUNDNUT IN NIGERIA

Before Nigeria become independent groundnut production, marketing and trading served as major source of employment, income and foreign exchange.

The groundnut sector provides the basics for the Agro-industrial development and contributed significantly to the commercialization, monetarization and integration of the national rural sector.

While groundnut production in the world has increase, there has been variation in Nigeria. Groundnut production in Nigeria has been beyond 1.5million tones from the late 50's up to the early 70's. however the drought of 1972 and 1973, follow by the devastating rosette disease of 1975 and 1976, increase local consumption irrigated by increase population, improved living standards and reduction in the number of farming familiar cause by the oil boom of the early 70's (which drew out a substantial number of the able labour force to the urban industries) have resulted in Nigeria becoming a net importer of groundnut particularly in the form of oil.

2.4.3 USE OF GROUDNUT

Groundnuts high contents of edible oil(50%) and protein (255) make it a popular human food . it is consumed either as a shelled nut or as oil, after pressing of the kernel, or in a range of other forms subject to various degree of processing such as peanut, butter ,sance, flour is valuable ingredient to the diet in developing countries where cereal foods . ground is s good source of mineral such as phosphorus(p), calcium(ca), magnesium(mg) and potassium(k) as well as the vitamins E,K and B .Groundnut can be used ass an enhancing ingredient in a wide range of cooked dishes.

Alternatively it can be consumed whole with or without cooking as snacks. Groundnut haulms are used as animals feed. In rural areas the empty shells provide some of the fuel used by local oil mills. Large amount of the shells are often burnt on the farm or spread on the field as a soil amendment. In addition groundnut help improve soil fertility through biological nitrogen fixation.

2.5 ETHANOL FUEL

Fuels are referred to as naturally or artificially manipulated compounds that have a source of energy and raw materials for chemical industries. They consist with oxygen of the air to produce heat energy. This material supply the requirements of the earth which they receive from the sun, the infinity energy store house and convert to chemical energy in the naturally occurring fossil fuels by the process of photosynthesis. Synthetic fuels are understood as liquid and gaseous fuels obtained by converting a carbonaceous material to another form as in fermentation of production of ethanol fuels. The fuels whether natural or synthetic are store houses of chemical energy prior to their conversion into other forms of energy. Ethanol from conversion is therefore solar energy in liquid form.

The of ethanol as fuel is necessitates by the potential chemical energy it can supply and on some other characteristics and the properties that make it equal or in some other case, even batter than fossil fuels. This properties where identified early enough to warrant its choice as the fuel for use in the late nineteen and early twentieth centuries in different application. However, the seemingly widespread acceptance of gasoline and other derivative in present times pushed ethanol to the back burners but the resulting cumulative effect from the fossil fuel use has once more offered the door of opportunity for a possible shift to alcohol fuels.

A mathematical measure of the amount of solar energy in the ethanol molecule is obtained by considering the average bond energies of the differe4nt bonds that constitute the composite structure. Ethanol is composed of carbon, hydrogen, oxygen atoms linked by bonds to form the molecule.

Assuming standard average bond energies of the different bonds, we have

C-H bonds = 413 (5) C-H = 413 kg/mol

C-C bonds = 346 (1) C-C = 346 KJ/mol

C-O bonds = 358 (1) C-O = 358 KJ/mol

O-H bonds = 464 (1) O-H = 464 KJ/mol

(Ababio,1999)

The sum of some total average bonds energies gives 3233KJ/mol and it is a measure of the amount of energy stored in an ethanol molecule, or simply put "a molecule of energy from the sum that are stored in a molecule of a compound ".

2.5.1 COMBUSTION PROPERTIES

The combustion of ethanol fuel refer to the fairly rapid reaction, usually accompanied by a flame which occur between ethanol and an oxygen carrier, often times, and air. The molecule of ethanol and air have a certain amount of energy stored in the bonds between their constituents atoms and a comparatively lower energy the new molecule formed by the reaction. The energy difference is transferred to the environments in the form of heat and the reaction is said to be exothermic. One of the most important properties of any fuel is the amount of energy obtained from it when it is combusted, referred to the as the heating value of the fuel, measure on a per unit basis (weight or volume). It is this property that gives an indication of the potential work that can be expected from the fuel.

Ethanol as am oxygenate, contained oxygen atom bonded to a hydrogen atom in the hydroxyl radical, as opposed to octane with no oxygen. During the ethanol combustion, the hydroxyl group combines with hydrogen atom to form a nuclear of water. Thus the oxygen contained in the ethanol no doubt contributes nothing to the heating value of the fuel rather it depressed it in companson with hydrocarbon fuel.

The combustion reaction of ethanol and octane fuels are shown below

C2H5OH +3(O2 +(79/21))N2→ 2CO2+3H2O +3(79/21)N2................(4)

1 : 3 : 3(79/21) 2 : 3 :3(79/21)

C8H8 +25/2O2 +(25/2)(79/2)N2→ 8CO2 +9H2O +(79/12)(25/2)N2............(5)

1 : 25/2 : 25/2(79/21) 8 : 9 :25/2(79/21)

Ethanol with about 35% weight of oxygen has about 60% of the heating value of gasoline (matherson,1990). However, since alcohol undergoes different changes as it is vaporized compressed in an engine, the outright heating value of the fuel is not as important when it is considered as a motor fuel when this is burnt a certain amount of air is required for complete combustion and the quality of air are fuel and are exactly balanced (theoretically as required by the combustion reaction), the mixture is said to be stoichiometrically correct . Often, this qualities of the mixed fuel and air is compressed as the air-fuel ratio (mixture ratio which is the amount of required for completely combust). The combustible materials in the fuel. The fact that there is oxygen in the ethanol molecule structure means that the fuel will naturally require less air for combustion as the oxygen present will be contributed during combustion to reduce the amount of air needed for the reaction. For the ethanol and octane, the AFR is calculated based on equations (4) and (5) as thus

$$\text{AFR} = \frac{\text{stoichiometric amount of air (weight)}}{\text{Stoichiometric amount of fuel (weight)}}$$

AFR ethanol = 412/46 =9.0

AFR ethanol =1716.67/114 = 15.0:1

From the above, ethanol has a lower AFR of 9:1 which is that one unit of ethanol fuel engines 9 units weight of for complete combustion while a unit of octane will completely combust with 15 units weight of air, really, ethanol needs sixty percent of the total amount of the air required for octane combustion and since the reaction can reach completion (combustion efficiency ,100), ethanol will bunr more completely than gasoline with a greater combustion efficiency and a net reduction in total pollutant emission. In addition if the heating value of the two fuels are spreaded over the total amount of materials , both combustible and non combustible (i.e per unit total volume) the value obtained will not differ from the two fuels (mathewson1980) as a result of gasoline and alcohol are about equal in what is called volumetric efficiency when burnt in a correct adjusted engine. The mixture ratio is one of the most important parameters of the combustion system as it affect the furnace performance efficiency and pollution .Usually, it is not stated as an absolute value, but as a range of flammability which is the range of the gas or vapor concentration that will burn if an ignition source is introduced . basically two factors determine weather the combustion process can take place i.e (transformation form able mixture to a rapidly combustion system)the first is that there should be sufficient energy to allow initiation of the reaction. In all, the energy can be supplied by an intensive source of localized energy such as a flame or spark and also by application of energy by means of heat and pressure. The minimum ignition energy is the parameter that characterizes this property ant it is the threshold energy the air/fuel mix must posses for ignition to occur. Closely related to the minimum ignition energy is the auto-ignition temperature ,the minimum the fuel/oxidized mixture (or a portion of it) must be heated in order for the combustion to occur, independent of the source of heat. since the combustion process is a chemical reaction, the minimum ignition energy and temperature will be determined by the activation energy. Ethanol with an ignition temperature of 423°C has a higher activation energy of a combustion reaction than gasoline with T eg=257.3°c on the surface this may infer difficulty in ethanol engine startup than in gasoline. But the choice should not be limited by this alone as safety concern are also important. with the lower ignition temperature of gasoline the fuel will ignite easily making it potentially more hazardous than ethanol which will have difficult ignition(www.rppi.org/ethanolmandate.html). Even the ignition difficult of ethanol can always be solve as will be seen in the different format of ethanol fuel use. Till further, another parameter favorable to safety use of ethanol fuel is the flash point, which is defined as the temperature to which the liquid fuel must be heated so that the vector pressure is sufficiently high for an explusive (flammable) mixture is to be form with air. Flash point generally is lower than ignition temperature and is also an indicator of potential danger when the fuel is exposed to an ignition source. Flash temperatures above room temperature mean that a fuel can safely be handle since explosive to flames or other ignition sources will not cause an explosion. Although, ethanol like gasoline has a flash point below room temperature, the higher value means that it will be slower in forming a combustible mixture than it is hydrocarbon rivals. Ignition is influenced by a number of factors among which is the composition of air /fuel mix. A minimum composition is required for the mix to be ignited irrespective of the ignition temperature been achieved. Once ignition is been initiated, combustion must be sustained for the reaction to proceed to completion (willian,2003). Now the mixture of the fuel and oxidant is not necessary able to sustain combustion , it is only when the fuel is within a flammability range that combustion, can proceed to completion. The range is defined by the lower and the upper flammability limits. Mixtures below the lower limits are described as too lean for combustion since there is insufficient amount of fuel for combustion while above the upper limits, the mixture is too reach as the amount of fuel supplied is so large that the flame is put off. Gasoline has flammability from 1.4 – 7.6 (% vol) while ethanol has it value 4.3- 19.0 (% vol) (willian,2003). The wider flammability range of the alcohol compared to gasoline permit sustainability of combustion even at very reach missions. Of course related to the flammability is the flame speed which is also a very vital characteristics, defined as the speed which a laminar flame propagates through a pre-mixture of fuel and air. At turbulent condition , the flame speed increases largely giving highly enhance combustion. Thus, ethanol with higher flame speed will combust more efficiently and release it it's heat at a faster rate.

2.5.2 COMBUSTION TEMPERATURE

Combustion system may be created thermodynamically like any other. It obeys the same laws and is under the same restrictions (Rogers 1992) the main difference however comes about from the enthalpy of formation of the species of the combustion system as this value is insignificant in systems with no chemical change since the material remains the same. In thermodynamics systems, only the sensible enthalpy of the system is considered while with combination (chemical change), additional consideration of the internal energy of the molecular bonds has to be made when fuels are combusted, the heat of formation of the product in less that that of the reactants and the difference is released to the surrounding as the heat of reaction. In practical application, the differences are stated before, is the heating value which is measured when the fuel is burnt taken into consideration the fact that combustion can never be complete. However, theoretically it is stated as the calorific value which refers directly to the heat liberated when unit mass of fuel is burnt completely in a calorimeter under special conduction. Determination of the calorific values require differences in the heat of formation of the species while the flame temperature calculations give the maximum temperature rise thermodynamically possible for any particular combustion system .The actual temperature of the products from the adiabatic Combustion of a stoichiometric mixture however, would not be as high as the calculated value partly due to heat losses and temperatures, some products of the combustion reaction one unstable. Some of the unstable molecules split into their constituents usually with an accompanying absorption of energy. The phenomenon is known as dissociation and in combination most often, water and CO_2 are the dissociating molecules.

$$CO_2 \longrightarrow CO + \frac{1}{2} O_2 \text{ ------------------------------------- (vi)}$$

$$H_2O \longrightarrow H_2 + \tfrac{1}{2} O_2 \quad \text{-----------------------------------} \text{(vii)}$$

The phenomenon of dissociation increases with the temperature and is worse off in gasoline than with adiabatic flame temperature higher than ethanol's combination is gasoline will invariably be more incomplete and inefficient as the presence of CO and the H_2 (combustible materials) indicates that not all the chemical energy in the fuel is released (Rogers, 1992). The combination products of gasoline will have a higher temperature. The effect of dissociation and inefficiency in ethanol fuel combination is not as pronounced as in gasoline because of the lower adiabatic flame temperature.

The effect of dissociation can be visualized by analysis of the combustion products for the two fuels. The efficiency can be defined in terms of the relationship between the theoretical heat release to the actual heat release or as a relationship between the theoretical and actual temperature rise.

$$\text{Neff:} \quad \frac{\text{Actual heat release}}{\text{Theoretical heat release}}$$

$$= \frac{\text{Theoretical heat release} - \text{Heat losses from products of incomplete combustion}}{\text{Theoretical heat release}} \quad \ldots\ldots\ldots\ldots\text{(viii)}$$

The theoretical of maximum heat release is simply related to the calorific value while the main products of incomplete combustion are CO and uncombusted and in combustible hydrocarbons. If we consider only CD, the presence of CO in the exhaust means that the extra sensible enthalpy release.

$$Q = CV_{co}\,[\mathrm{CO}]\mathrm{mass},\quad CV_{co} = 10.1029\,\mathrm{MJ/KG}$$

$$Q = 10.1029\,[\mathrm{CO}]\,\mathrm{mass}$$

Maximum heat released = CO fuel x [mass] fuel

$$= \frac{\left\{ 1 - [10.1029\,[\mathrm{CO}]\,\mathrm{mass} \right\}}{\mathrm{CO\ fuel} \times [\mathrm{mass}]\,\mathrm{fuel}}$$

$$= \left\{ \frac{10.1029\mathrm{ni}\,[\mathrm{CO}]\,\mathrm{mass}}{\mathrm{CO\ fuel} \times [\mathrm{mass}]\,\mathrm{fuel}} \right\}$$

Where ni = degree of association

2.5.2 VOLATILITY

Basically, all fuels function by releasing combustible gases (vapor) that are oxidized in the presence of an ignition source the volatility of fuel is the parameter that defines this property and it is the measure of the tendency of the fuel to evaporate. The quality is very important especially for fuel intended for motor engine because of vaporization does not occur readily, the fuel cannot be evenly mixed with the air and it becomes of little value in an engine. Ethanol is very volatile and it is able to form a flammable mixture with air, however, less so than gasoline with a higher vapor pressure. The higher vapor pressure (volatility) of gasoline increases the changes of its explosion from heats or sparks and so again, is potentially more dangerous than ethanol.

Related to volatility is latent heat of vaporization referred to as the amount of additional heat headed to change the liquid fuel to a gas (vapor). When a substance is about to undergo a change in form from liquid to vapor, it must absorb a certain amount of additional heat from its surrounding in other for the change to take place. Ethanol fuel has a higher latent heat of vaporization absorbs about 2.5 time that of gasoline, which means that the alcohol must absorb 2.5 times more heat than gasoline does. The heat absorbed results in combustion system cooling as heat is taken away from the engine blocks. Hence, the latent heat of vaporization is the phenomenon that is responsible for an alcohol powered engine running cooler than its gasoline fueled counterpart . in an engine, vaporization of gasoline fuel air mixture results in a temperature drop of about 40^0f (Mathewson, 1980). Under similar conditions, the temperature drop for ethyl alcohol will be more than twice that of gasoline. In fact, the phenomenon can sometimes account for a temperature drop of as much as 77^0C for ethanol as against 7^0 for gasoline under the same conditions, (Mathewson, 1980), the temperature drop of alcohol cools the air mixture entering the combustion chamber of the engine, thereby increasing the air density, mass flow rate and the soichiometric mixture of ethanol and air will be cooler than the same gasoline air mixture. As a results of this, these is over three times (by weight) as much ethanol in the engine as there is for the hydrocarbon. Even though ethanol has only 60% of the heat value of gasoline, the net gain in the volumetric efficiency is more than that of gasoline (Mathewson, 1980). The importance of a higher volumetric efficiency cannot be over emphasized as it relates to the actual power output from an engine at higher rational speed of engine, the actual power output reduced owing to the higher temperature which results in a lower change into the combustion chamber (Douglas, 1965). With the greater temperature drop associated with ethanol fuel use, there is a simultaneous increase in both volumetric efficiency and fuel mixture charge as the temperature reduction allows for additional fuel and air to enter the combustion chamber. This significantly increases the power output of engines. The power gain due to improved volumetric efficiency is on of the important reasons for the superiority of alcohol over petrol as fuel, as the increase considerably mitigates the liability of their lower heat value. This explains why methanol with a greater effect from this phenomenon is used to power racing cars. The charge cooling together with the low level of combustion temperature improves on the thermal efficiency of ethanol fuel engines.

2.5.4 OCTANE RATING

A fuel ability to resist deterioration on premature combustion is called octane or anti-knock rating. This quality is better understood by considering the combustion a certain fuel in an engine in which the compression ratio can be varied if the ratio is gradually increased, a point will be reached when the fuel will detoriate prematurely (Rogers, 1992). This is because, as the fuel air mixture is compressed, heat is generated. If the explosive mixture in an engine is compressed enough, the resulting heat will cause it to detoriate since fuel engines are designed so that flammable mixture is detoriated by the spark plug at the beginning of the downward movement of the piston following the compression stroke, pre-ignition or knock occurring during the compression stroke is undesirable (Wells, 2003). Indeed, several knock can quickly overstress and destroy an engine. Even after ignition in real life, a series of pre-flame reaction will occur in the unburnt and gases in the combustion chamber before the flame front arrives if these reaction form molecule or species that can auto ignite before the flame front arrives, knock will also occur (Williams, 2003). Thus the octane rating of a fuel reflects the ability of the unburnt and gases to resist spontaneous auto ignition under the engine test condition used. If auto ignition occurs, it results in an extremely rapid pressure rise, as both the desired spark initiated flame front and the undesired auto ignition and gas flames are expanded. The combined pressure peak arrives slightly ahead of the normal operating pressure peak, leading to a loss of power and eventual overheating fuel with too low octane rating convert chemical energy to heat rather than power, making for less efficient fuel usage and reduced engine life.

The ability to resist knock in a fuel is specified by the chemical structure of the fuel with long straight hydrocarbon chain producing large amounts of easily auto ignitable pre-flame decomposition species, while branched and aromatic hydrocarbons are more resistance. In practical applications, the unburnt gases ahead of the frame front encounter temperatures up to about 700^0c due to piston motion and radiant and conductive heating and commence a series of pre-flame reaction (William, 2003)

The method of measuring the detoriating tendency of ethanol fuels is to compare its performance with that of a heptane-octane mixture in a special engine. The octane number assigned to fuels is based on the pre hydrocarbon "octane' which is considered to be 100 and at the other end of the scale in a heptane considered to hare an octane rating of zero. Ethanol has a relatively higher anti-knock or octane rating which is better than that of gasoline. The octane rating of gasoline can be improved by the addition of additives such as ethyl lead and oxygenates which have been found to affect the flame reaction pathway. The additives work by interfering at different points in the pre-flame reactions. Unfortunately it has been observed that the levels of lead ions in the atmosphere due to automobile combustion processes are harmful to health (Rogers, 1992). Public opinions and outcries have gradually caused regulatory boches to bring in financial incentives for the use of unleaded fuel, boosted with oxygenates as octane enhancers. Ethanol has the ability to rise considerably, the octane ratings of gasoline with which it is mixed in addition to being an oxygen carrier for combustion. The effect is greatest on the poorer grades of gasoline. Then 25% blend of ethanol and a 40 octane rated gasoline will have a net increase of almost 30 points (Richandson, 1987) this increase is one of the major advantages of gasohol.

Ethanol's ability to increase octane rating means that

1. A lower grade of gasoline can be used to obtain a fuel with a certain octane rating.
2. The use of traditional pollution producing anti-knock additives such as tetra ethyl lead can be eliminated.

2.5.5 FIRE SAFETY

The fact that ethanol is less of a fire hazard than gasoline is obvious from its heat of combustion, ignition temperature, latent heat of vaporization e.t.c which all measures better than gasoline on the safety scale. Moreso , is the higher volatility and flammability of gasoline which makes it more prone to fine and explosions (www.rppi.org/ethanol/mandates.html). In any case, since ethanol dissolves in water rather than floating on it like gasoline, than its fire can be extinguished with water.

2.5.6 WATER INJECTION

The addition of OH group to the hydrocarbon chain impacts water solubility to alcohol molecules. Water solubility is infinite in alcohol with the water molecules evenly distributes within the mixture but in gasoline however, solubility is negligible as a result, pure ethanol in engine produce excellent results from concentrations of 160 proofs to the anhydrous fuel (Roberts, 1995). This is very important to the fuel producers as extra investments on additional capital to produce the anhydrous fuel become undesirable. As an extra benefit also, the water in the fuel helps to clean and lubricate the internal part of the system including valve sits, piston heads, surface and combustion chambers (Roberts, 1995).

The solubility of water in ethanol and the ability of the fuel to function effectively within the desirable water composition have been exploited advantageously in the form of water injection into engines to provide extra thrust. The point being that within certain limits, the se systems actually do increase power (Mathewson, 1980). Water has a higher latent heat of vaporization of 700But/lb (Okeke , 2003) than gasoline and ethanol respectively. Therefore, if a little water is injected into the carburetor in the form of an ultra fine mist, the latent heat of the water will cool the charge and increase volumetric efficiency considerably. In addition, when the charge is fired in the cylinder, the water is turned to a high pressure steam and provides additional power as the steam exerts pressure. There are definite limits however, to the amount of water than can be injected into the system too much will cause excessive cooling and misfiring.

The practice of water injection in a gasoline fuel engine is not as common a practice as it is with ethanol due to the insolubility of the hydrocarbons in water.

2.5.7 ENVIROMENTAL EFFECT ON FUEL USE.

The fossil fuels have over time established themselves as the manufacturers preferred choice and is such, have gained wide spread among the varied users leaving no room for other potential fuels to express their effectiveness in meeting the complex fuel requirements of modernization faced with the alarming rate of environmental degradation, it has become obvious that there is more to be considered in the choice of fuel for use than its intrinsic values and properties. The use of fuels invariably lives indelible trials on the environment and its people with attendant high capital set aside to redeem the effect on the environment. Right from man's deliberate efforts to obtain the fuels, imbalances are created as the environment is grossly exploited with the impact even more pronounced as the materials undergo further processing and purifications to produce the end products.

The fossil fuel, water gas oil, coke all consist largely of carbon and hydrogen and minor impurities but not oxygen. As depicted in the carbon cycle, they are formed by a continuous process of decomposition under high pressure of carbonaceous materials with subsequent depletion of the environment of its carbon sources. Attempts to obtain the energy sourced leads to deliberate destruction of natural vegetation, as large expanse of land are cleared to reach the treasures. Natural flora and fauna are also destroyed through occurrence of oil spillage from petroleum, sometimes condemning bodies of water. These are only some of the issues during activities aimed at obtaining the fuels. However more severe and needing more attention is the impact of the contribution of combustion and use of the fossil fuel on the environment so severe are the effects that they far exceed the combined effects of other sources of environmental degradation.

The energy need of the earth is provided by the sun and stored in plants through the process of photosynthesis. Theoretically, the combustion fuels is supposed to lead to the production of CO_2 and H_2O only. This is rarely the case in practice, as substantial quantities of products of incomplete combustion of fuels are always present; the quantity however depends on the chemical composition of the fuels. During the combustion of hydrocarbon fuels having oxygen in their structure, substantial quantities of their black fumes of the poisonous carbon monoxide and other complex emissions, arising from impurities present in the fuel are produced. The CO is the major destroyer of the ozone layer that shields the earth from direct sunrays. Recent reports on incidences of increased solar radiation in some parts of the world, especially in Europe with high rates of industrialization, are indicators of increased combination of fossil fuels with increased amount of CO produced. The effect of CO is no doubt well known but as long as manufacturers of machines and equipments continue to make use of the fossil fuels, the issue will continue to receive a mute response.

Sulphur, phosphorus and nitrogen, are some of the common impurities of fossil fuels, in addition to the oxides of carbon formed during their combustion, the impurities combined with oxygen, favored by the resulting high temperatures of combustion, to form poisonous oxides of the respective elements. One of such effects is acid rain formation during which the poisons combine with water droplets in the atmosphere especially from rainfall. The acid corrode machines and equipments pants, buildings and effects plant and animal life especially those in aquatic environment. The carbon dioxide that was thought to be the harmless product of combustion has been discovered to be the major green house gas in as much as CO_2 is a product of all combustion processes, the relative amount released in a particular combustion is prime in accessing the overall contribution of that process to the atmosphere CO_2. Lack of oxygen in fossil fuels makes complete combustion impossible, even with larger quantity of atmospheric air. Although attempts to make the combustion more efficient by converting the CO to CO_2 are desirable, the consequence will be an accumulation of CO_2 in the atmosphere. The net increase is responsible for increasing global warming as the CO_2 absorbs infrared radiation emitted from the earth's surface and reflects same back to the earth. This together with electromagnetic rays from the sun that leaks to cracks in the solar radiation shield (Ozone layer) contributes to temperature increase in the universe. CO_2 is an acid anhydride and to in the universe. CO_2 is an acid anhydride and so it also contributes to acid rain formation.

Apart from the harmful oxides of carbon, Nitrogen and Sulphur, other compounds of carbon are also produced during fossil fuel use. This includes volatile produced organic compounds (VOC's) uncombusted fuel molecules that are green house gases themselves and also combine with nitrogen oxide in the presence of sunlight and heat to destroy the ozone layer, non combustible fuels that come up as small particles (particulates). Some of the organic compounds formed in the combustion process attach to the particulates to form carcinogenic substances.

Ethanol like the fossil fuels cannot be absolutely excused from being a contributor the global climate changes besieging the earth since t he advent of industrialization. It is even truer considering the fact that all fuels are composites consisting of carbon, hydrogen and may be oxygen and since nothing, not even matter can be created nor destroyed, they will always find a way of returning to their natural state, the atmosphere is the mode and form of return of the fuels to the environment that is of concern to mankind because they are responsible for the environmental balances. Ethanol on its own has inherent properties that reduce the severity of its contributions to global pollution and concern when used for fuel. Solar energy from the sun converted into carbohydrate from the plants is directly converted into bond energies of the ethanol molecules during the process of photosynthesis, CO_2 of the air is used by plants in the presence of sunlight while combustion if the fuel also produces and releases CO_2 into the air. As a result, there is no net CO_2 accumulation in the environment since the CO_2 from combustion is continually alerted and transformed into carbohydrate in the plants. The continuous circle of photosynthesis is what makes ethanol fuel renewable. Oxygen in ethanol molecule affords the fuel a high efficiency with small quantity of co-produced. The seeming disadvantage alleged in the lower heating value of ethanol becomes an asset as the effect of the lower temperature is a reduction in the amount of acid oxides of nitrogen while SO_2 is almost completely eliminated since there is little quantity of element of sulphur in the fuel, ethanol fuel with its high octane rating can be used as an octane booster in gasoline fuel to replace the poisonous lead and other undesirable compounds used to raise the octane number of fuels. The solubility of water in ethanol further reduces the amount of NO_x and CO without compromising engine performance. With water in engine cylinder, its mass absorbs energy and its result is lower peak temperature as well as reduced CO, because of the water shift reaction.

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \text{(ix)}$$

2.5.8 ENERGY BALANCE OF FUELS

To be viable, any fuel economy should have net positive energy balance and heat means that the total energy expended in producing the fuel must be less than the energy content of the fuel (www.rppi.org/ethanol/mandates.html). Energy is quite difficult to quantify and so, is more often that not expressed in the cost equivalent. The concept is somewhat subjective since it depend on what is excluded and what are excluded from the calculation particularly when it is compared with the index of other fuels produced by other methods. But in all , the concept is used as it give an estimate of the viability of a particular fuel relative to others that can be used for the same purpose with a positive net energy balance, more energy is obtained from the use of the fuel t hat that used to produce it (www.radford.edu/nwkovarik/lad). The fossil fuels have a net positive energy balance obviously after a long history of exploitation and use that has necessitated the advancement of more effective techniques of their exploitation and production consequently, they are cheaper to produce presently. In assessing their energy balance, cost of geological survey, exploitation, transportation, refining, labor, e.t.c are estimated and compared with energy obtained from their use. (www.usda.gov/oce/oepmu/aer-813.pdf) with more stringent measures put in place to checkmate the indiscriminate destruction of the environment, efforts to remedy the situation created by the use of the fuels demands additional expenses on research and development of pollution prevention strategies, monitoring systems, purification methods e.t.c. which consequently results in the energy balance of the fuel. Ethanol fuel meets most pollution mitigations policies and son the effects of pollution remediation are less pronounced on its energy balance sometimes, even if the fuel as a positive energy balance, choice can be limited by the purpose for which it is intended, for example, if a portable fuel is desire, and coal or firewood which has positive energy balance is available, it becomes absolutely necessary to spend more energy to get a portable fuel.

Making ethanol fuel also requires the sue of energy first crop has to be grown the plant must be harvested group up and dissolved in water to make the marsh, thereafter the marsh is heated and then enzymes and yeast are added for fermentation to take place finally, the fermented marsh is boiled and the alcohol separated the concentrated in a distillation column. All these require expenditure. Various studies have been carried out to estimate the energy balance of ethanol fuel production for comparison with that of the fossil fuels. However, variation in data and assumption in such studies resulted in a wide range of estimates which makes it more difficult for comparison with gasoline since their methods of production are quite different but the USDA energy balance of about 34% that is growing and will continue to improve in the future (www.usda.gov/oce/oepnu/aer-813.pdf) this is further boosted by the fact that distillation of the fuel can be achieved using locally available non potable fuels. Like firewood in addition to the fact also that the several valuable non carbohydrate by product of the fermentation left in the marsh can be used as animal feed or sold out for other uses. This will make ethanol fuel production from biomass sustainable energy inputs for ethanol fuel balance calculation can be divided into those needed for crop production and for crop conversion for crop production includes energy for machineries, fertilizers, herbicides, and insecticides involved in cultivation, vesting and transportation of the cassava. Crop conversion involves energy consumed in equipment manufacture, chemical and or biochemical processes, separation and purification required to generate the fuel.

Balance = produced – expanded

2.5.9 TECHNOLOGY

Ethanol is produced from the fermentation of sugar by enzymes produced from specific varieties of yeast. The five major sugars are the five-carbon xylose and arabinose and the six-carbon glucose, galactose and mannose. Traditional fermentation processes rely on yeasts that convert six-carbon sugars to ethanol. Glucose the preferred form of sugar for fermentation, is contained in both carbohydrates and cellulose. Because carbohydrates are easier than cellulose to convert to glucose, majority of ethanol currently produced are made from crops that produces are made from crops that produces large quantities of enzymes for carbohydrates. Also, the organisms and enzymes for carbohydrate conversion and glucose fermentation on a commercial scale are readily available.

The conversion of cellulosic bromass to ethanol pralleles the corn, conversion process. The cellulose must first be converted to sugar by hydrolysis and fermented to produce ethanol. Celluslosic feedstocks (composed of cellulose and hemicelluslose) one more difficult to convert to sugar them are carbohydrates two common methods of converting cellulose to sugar are dilute acid hydrolysis and concentrated and hydrolysis, both of which use sulphuric acid. Dilute acid hydrolysis occurs in two stages to take advantage of the difference between hemicellulose and cellulose. The first stage is performed at low temperature to maximum the yield from hemicellulose, and the second, higher temperature stage is optimized for hydrolysis of the cellulose portion of the feed stock. Concentrated acid hydrolysis uses a dilute acid pretreatment to separate the hemicellulose and cellulose. The biomass is then dried before the addition to dilute the acid and then heated to release the sugars, producing a gel that can be separated from residual solids. Column chromatographic is used to separate the acid from the sugars.

Both the dilute and concentrated and processed have several drawbacks. Dilute acid hydrolysis of cellulose tends to yield a large amount of by products. Concentrated acid hydrolysis forms fewer by-products.

Concentrated acid hydrolysis forms fewer by-products, but for economic reasons the acid must be recycled the separation and reconstruction of the sulphuric acids adds more complexity to the process. In addition, sulphuric acid is highly corrosive and difficult to handle. The concentrated and dilute sulphuric acid processes are performed at high temperature (100 and 220^{0}c) which can degrade the sugars, reducing the carbon source and ultimately lowering the ethanol yield. Thus, the concentrated acid process has a smaller potential for cost reductions from process has a smaller potential for cost reductions from process improvements. The National Renewable Energy Laboratory (NREL) estimates that the cumulative impact of improvements in acid recovery and sugar yield for the concentrated acid process could provide savings of 14 cents per gallon, whereas process improvements for the dilute acid technology could save around 19 cents per gallons.

A new approach under consideration is countercurrent hydrolysis. Counter current hydrolysis is a two stage process. In the first stage, cellulose feedstock is introduced to a horizontal co-current reactor with a conveyor. Steam is added to raise the temperature 150^0 (no acid is added at this point). After a residence time of about 8 minutes, during which some 60% of the hemicellulose is hydrolyzed, the feed exits the reactor. It then enters the second stage through vertical reactor operated at 225^0C. very dilute sulphuric acid added to the feed at this stage, where virtually all of the remaining hemicellulose and depending on the residence time, any where from 60 percent to all of the cellulose is hydrolysed. The countercurrent hydrolysis process offers more potential for cost reductions than the dilute sulphuric acid process. NREL estimates this process may allow an increase in glucose yields to 8^0f percent, an increase in fermentation temperature to 55^0C, and an increase in fermentation yield of ethanol to 95 percent, with potential cumulative production cost savings of about 33 cents per gallon.

CHAPTER THREE

3.0 MATERIALS AND METHOD

Groundnut straw

The groundnut straw used for this experiment was obtained from a farm at kpakungu in Minna .

Yeast

The yeast, saccharomytes Cerevisiae used was gotten from a bakery at Bosso market.

Table 3.0 Table of Equipments Used

NAME	MODEL/MANUFACTURE
Milling Machine	Duram Scott
Digital Weighing balance	Mettler PM 2000
Water bath	WE 4105/Clifton
Distillation apparatus	Pyrex
PH meter	KENT EIL 7045/ 46
Thermometer	Boydler
Heating Mantle	Mettler DT 18OO
Density bottle	Pyrex , U.S.A
100ml conical flask	Pyrex , England.
Filter paper	

Table 3.1 Table of chemicals and reagents

Chemical and Reagent	Formular	**Comments**
Sodium hydroxide	NaOH	Laboratory reagent grade
Sulphuric acid	H_2so_4	Laboratory reagent grade
Iodine solution	I_2 (aq)	Analytical reagent grade
Distilled water	H_2O	Analytical reagent grade
Fehlings solution	Nil	Analytical reagent grade

3.1.0 PRODUCTION PROCEDURE.

The procedure for the production of the ethanol was carried out as follows.

1. Pretreatment
2. Mashing
3. Fermentation
4. Distillation.

3.1.1 Pretreatments / Mashing

The groundnut straws was harvested and rinsed with water to remove particles. The material was air dried at 35°c to constant weight and milled to a size of less than 2mm. At this stage, a two stage hydrolysis is performed. The milled groundnut straw is introduced into a reactor and heated to a Temperature of 121 °c (no acid is added at this point) . after a residence time of about 8 minutes during which some 60% of the hemicellulose is hydrolyzed, the feed is again heated to a temperature of 150°c very dilute sulphuric acid (i.e 4% H_2so_4) is added to the feed at this stage where virtually all of the remaining hermicellulose and depending on the residence time say 30 minutes, anywhere from 60% to all of the cellulose is hydrolysed. The PH was monitored using N_aoH and maintained at 6±1. During the second heating, at 75^oc the enzymes termamyl and neutrase are added and agitated well in the process. The mash was cooled to 60^0c and the enzymes Amyloglycosidase (4_{ml}) was added and maintained for 1hour 45 minutes by agitating. The PH was also maintained using NaOH . at the end of the 1 hour 45 minutes, the mash was filtered to remove. the spent materials from the wort. The wort was heated to 78^0c and maintained for 60 minutes to the destroy the unspent enzymes and to kill of unwanted micro – organisms. Felhing's solution test was carried out to determine the presence of the simple sugar in the sample.

3.1.2 Fermentation

It is during fermentation that the actual ethanol production takes place. 12g of bakers yeast was measured and added to the wort in a plastic rubber made to be air tight. The whole set up was kept in a cupboard in the laboratory. at the end of 7 day period, fermentation was stopped for distillation to be carried out.

3.1.3 Distillation

The ethanol produced during fermentation was contained in a mixture with water and unfermented spent materials. The distillation was carried out to first separate the liquid from the spent materials and then to concentrate the alcohol produced.

Some quantity of fermented wort was put in the conical flask of the distillation apparatus and then transferred to the electric burner. It was heated to 85^0c and he distillate received was measured it was then redistilled using sextet extraction equipment at different temperatures as given in the table overleaf.

3.2.0 TEST OF ETHANOL PRODUCTION

3.2.1 Determination of heat of Vaporization of Ethanol:

The empty bottle was filled with distilled ethanol and put on the heating mantle with thethermometer put inside the filled bottle the ethanol in the bottle was heated until it begin to boil and the boiling temperature was taken and used in calculation in appendix B.

3.2.2 Determination of the specific gravity of the ethanol:

The specific gravity of the ethanol was determined using specific gravity bottles as W_1 (g) , the empty bottle was then filled with the ethanol and weighed to give W_2 (g). the bottle was emptied and filled with distilled water and weighed to obtain W_3 the result is given in appendix B.

CHAPTER FOUR

RESULTS AND DISCUSSION OF RESULTS

4.0 RESULTS

The results for the production of the ethanol after a 7-day fermentation period are summarized in the table below.

Table 4.1.1 Table of quantity of materials

MATERIALS	QUANTITY
Groundnut straw	500g
Water (H_20)	1.0 lit
Neutrase	3.5 ml
Termamyl	3.5 ml
Amyloglycosidase	4.0 ml
Yeast	12g

Table 4.1.2 Table of PH requirement

PH	Observed	Expected
Mashing	4.5 – 4.9	5.4 – 5.6
Fermentation	4.7 – 5.0	5.9 – 6.1

Table 4.1.3 Table of Concentration of Sample after distillation runs

RUNS	1	2	3	4	5
Initial volume (ml)	750	500	300	170	100
Final Volume (ml)	500	300	170	100	85
Temperature (^{0}c)	85	82	79	78	78
Concentration (%)	38	52	64	75	83

Test for simple sugar: Brick red precipitate was obtaine

Table 4.1.4 Table of distillation range of sample

TEMPERATURE (^{0}C)	VOLUME COLLECTED (ml)
75	79
77	81
78	85
80	85
85	85

Table 4.1.5 Table of Sample Test Result

EXPERIMENT	EXPERIMENTAL VALUE	STANDARD VALUE
Temperature (^{0}C)	76	78
Heat of vaporization (j/g)	855.31	840
Specific gravity	0.797	0.8

4.1 DISCUSSION OF RESULT

The important operations during the production of the ethanol were pretreatment/mashing and fermentation in principle, the processes appear relatively simple but actually, they are a bit more complex that not all the reactions taking place have been fully understood. During the fermentation for 7 days, the PH measured before the starch was 4.6, at the end of the fermentation period a total of 750ml by volume and a relative density (R.D) measured with the hydrometer gave 0.927 which correspond to a maximum concentration of 9% ethanol in the sample. The standard boiling point of ethanol is 78^{0}c but the sample boiled at 76^{0}C. The difference was due to deviation of laboratory conditions from that of the standard. Ambient pressure of the laboratory was 714mmHg and the use of the boiling correction index to obtain the corresponding temperature at normal atmospheric pressure gave the normal temperature of 78^{0}C.

The relative density of the sample at 25.5^0C was obtained as 0.825 which is little deviation from the literature value of 0.8 at 25^0C the two values are quite close, this being due to the concentration of the sample.

The heat of vaporization obtained from ethanol sample is greater than that of the standard value. This is one the clear cut edge for ethanol over gasoline. It is reasonable considering the fact that the presence of water, with an even higher latent heat of vaporization, would lead to a higher value for the sample, over and above the value for the anhydrous fuel. The higher heat of vaporization is responsible for the greater effect of charge cooling in engines that run on ethanol (Rogers et al, 1992). On vaporization, ethanol draws some heat from the incoming air/fuel mix and the engine environment and the resultant decrease in the temperature of the mixture increases the mass flow rate into the cylinder with corresponding increase in power output. The result is that engines running on the sample will always be cooler that its gasoline fueled counterpart with a higher thermal efficiency.

At the end of the experiment, the various test of the ethanol obtained from the laboratory compared favorably with that of literature. In most of the test, the values were not exactly the same but slight deviations of experimental readings from literature values are a testimony to the reliability of the experimental results and the methods employed in carrying out the experiment.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.0 CONCLUSION

The project was successfully carried out as the aims and objectives were achieved. At the end of the experiment, the yield of the ethanol produced shows that groundnut straw in actually a viable source of ethanol fuel that can effectively serve as an alternative or substitute for the conventional fossil fuels. This was attested to by the good comparison of the sample test with that of standard values which in some cases even measure more. The closeness of the experiment to literature values of the test are an indication of the reliability of the whole experimental efforts. Moreso, the correlation is a confirmation that the sample obtained was truly a solution of ethanol.

5.1 RECOMMENDATION

The successful attainment of the aims and objectives of the experiment was not without its own share of difficulties. In view of experimental methods carried out in the production of ethanol from groundnut straw in this project, the following points are recommended.

1. The use of bakers yeast should be avoided if possible. Specially formulated brewers yeasts are well suited for ethanol production since they can survive in higher concentrations of the compound during fermentation and should be integrated into the production process.

2. Calcium hydroxide should be used instead of sodium hydroxide in the experiment to control the PH of the mashing system. The Ca^+ serves as a co-factor for amylase performance (Richardson and Cowson).

3. The experiment should be carried out at different conditions to obtain the condition that gives the belt yield of the fuel.

4. Alternative to the exogenous enzymes (both termamyl & neutrase) should be soughed after and used. Difficulty in obtaining the enzymes, especially in small quantity, was a major constraint during the experiment and when found it is always exorbitant.

In all, the prospect in the use of ethanol as a renewable fuel for the future lies basically in its potential as an excellent fuel for internal combustion engines. Its lower heating value technically rules if not for use solely as a heating fuel as the heat of combustion is the main parameter when considering fuels for that purpose automobile fuels require some other properties inherent in the fuels of which ethanol readily meets.

It is important to stress at this point that this write-up does not aim at making ethanol a total replacement for gasoline because if this is done over time, the fuel would generate its own share of environmental problems as is being experienced presently and if possible, some others not even enlisted at this point. The suggestion is that of alternation or a blend of the two fuels with more emphasis, in the direction of the renewable ethanol fuel so that the natural reserves of the fossil fuel is not depleted and the environment is not starved of natural flora and food for the sake of fuel.

APPENDIX A

MATERIAL BALANCE CALCULATION

The production of fermentable sugar from a given cellulose entails the following step.

$2\ (C_6H_{10}O_5)n + H_20 \longrightarrow nC_{12}H_{22}O_{11}$ ------------------------------------ -----(1)

Maltose

$C_{12}H_{22}O_{11} + H_20 \longrightarrow 2\ C_6H_{12}O_6$ ------------------------------------ -----(2)

Maltose glucose

The conversion of the simple sugar to alcohol by yeast is given as

$C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2CO_2$ -------------------------- ----- (3)

Glucose Alcohol

From table, the groundnut straw contains 50.49% cellulose for 500g of groundnut straw used, the mass of cellulose is

$$\frac{50.49}{100} \times 500g = 252.45g$$

Assuming complete hydrolysis of the starch, applying the stoichiometric ratio

From equation (1)

2 (162)g cellulose gives 342g maltose

252.45 cellulose will give $\frac{252.45 \times 342}{2 \times 162}$ = 266.475g maltose

From equation (2)

342g maltose gives 2(180)g of glucose

266.475 maltose will give $\frac{266.475 \times 2 \times 180}{342}$ =

= 280.5g of glucose

Similarly

From equation (3)

Mole ratio of glucose and ethanol 1:2

180g of glucose gives 2 (46)g of ethanol

280.5g of glucose will give $\frac{280.5 \times 2 (46)}{180}$

= 143.367g of ethanol

To calculate the volume of ethanol produced

Density of ethanol = 0.8g/cm^3

$$\text{Volume of ethanol} = \frac{\text{mass in gram}}{\text{Density g/cm}^3} = \frac{143.367}{0.8}$$

Volume of ethanol = 179.2 ml

MOLECULAR WEIGHT

Cellulose = 102 g/mol

Glucose = 180 g/mol

Maltose = 342 g/mol

Ethanol = 46 g/mol

APPENDIX B

SAMPLE CALCULATION

Experimentally, 750ml of fermented worts yields 85ml of C_2H_5OH.

500g of milled groundnut straw produces 85ml of C_2H_5OH theoretically.

750ml of liquor produces 179.2ml of C_2H_5OH (from material balance calculation in appendix A).

Amount of unhydrolysed cellulose ($C_2H_{12}O_6$) and oxidized ethanol (C_2H_5OH) is

$$(179.2 - 85)\ \text{ml} = 94.2\text{ml}$$

$$\text{Percentage of distillate in sample} = \frac{\text{Amount produced} \times 100}{\text{Theoretical value}}$$

$$= \frac{85 \times 100}{179.2} = 47.7\%$$

Percentage of unhydrolysed cellulose and oxidized ethanol

$$= \frac{\text{Amount of unhydrolysed and oxidized} \times 100}{\text{Theoretical value}}$$

$$= \frac{94.2 \times 100}{179.2} = 52.6\%$$

THE HEAT OF VAPOURIZATION

$$H_{v,b} = \underline{R\, T_c\, T_{br} (3.978\, T_{br} - 3.938 + 1.555 \ln P_c)}$$

$1.67 - 0.6828$

Using chemical method

Where Tc = Critical temperature in Kelvin = 516.2K

Pc = Critical pressure in atmosphere = 63 atm

R = Gas constant

Tb = boiling point in experiment = 76^0C = 349K

$$\text{Also } T_{b,r} = \frac{T_b}{T_c} = \frac{349}{516.2} = 0.6828$$

$$R = \frac{8.31}{M} = \frac{8.31}{46} = 0.1807$$

Substituting yields

$$H_{v,b} = \frac{0.1807 \times 516.2 \times 0.6828 \times (3.979 \times 0.6828 - 3.938 + 1.555}{1.67 - 0.6828}$$

$$= \frac{63.6g\,(5.19985)}{0.3872} = 855.31\ \text{J/g}$$

Calculation of specific gravity of sample product

W_1 = 25.7076g = mass of empty bottle

W_2 = 66.507g = mass of bottle filled with ethanol

W_3 = 76.8744g = mass of bottle filled with distilled water

Therefore,

$$\text{Specific gravity} = \frac{W_2 - W_1}{W3 - W1} = \frac{66.507 - 25.7076}{76.8744 - 25.7076}$$

$$= \frac{40.7994}{51.16668} = 0.797$$

Temperature correction

$T_{actual} = T + 0.00012\,(760 - P)\,(273 + T)$

P = Ambient pressure of laboratory environment

T = Boiling point of sample as recorded in the laboratory

P = 214mmHg

$T = 76^0C$

$T = 76 + 0.00012\,(760 - 714)\,(273 + 76)$

$= 76 + 1.9264 = 77.93^0C \quad \approx 78^{0\,C}$

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