SYNTHESIS AND CHARACTERIZATION OF BIOFUELS FROM VARIOUS NIGERIAN CROPS FOR INTERNAL COMBUSTION ENGINES

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CERTIFICATION

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DEDICATION

This work is dedicated to my Lord and Saviour Jesus Christ in whom are hidden all the treasures of God’s wisdom and knowledge

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NOMENCLATURE

EPA	Environmental Protection Agency
ASTM	American Society of Testing and Materials
IEA	International Energy Agency
VOME	Vegetable Oil Methyl Ester
JME	Jatropha Methyl Ester
GHG	Greenhouse Gas
FAO	Food and Agricultural Organization
NEB	Net Energy Balances
LPG	Liquefied Petroleum Gas
RON	Research Octane Number
MON	Motor Octane Number
TEL	Tetra Ethyl Lead
TML	Tetra Methyl Lead
TBA	Tertiary Butyl Alcohol
MTBE	Methyl Tertiary Butyl Ether
FFV	Flex Fuel Vehicle
USDA-ARS	U. S. Department of Agricultural, Agricultural Research Services
IBUS	Integrated Biomass Utilization System
CFP	Coal Fired Plant
FFA	Free Fatty Acid
MeOH	Methanol, EtOH Ethanol
CSTR	Continuous Stirred Tank Reactors
BOCLE	Ball-On-Cylinder Lubricity Evaluator
HFRR	High Frequency Reciprocating Rig
FAME	Fatty Acid Methyl Ester
NREL	National Renewable Energy Laboratory
HDPE	High Density Polyethylene
CFPP	Cold Filter Plugging Point

OSHA	Occupational Safety and Health Act

ABSTRACT

Bio-fuels (Biodiesel and Bio-ethanol fuels) are synthesized from various Nigerian crops (palm(*Elaeis Guineensis*) wine, raffia(*Raffia Vinefera*) trunk, sugar cane*(Saccharum L),* physic nut seed (*Jatropha Curcas*), castor bean seed(*Ricinus Communis*), sandbox seed (*Hura Crepitans*) and African bush mango nut (*Dika Nut*) (*Irvingia Gabonensis*)) to serve as alternative fuels for internal combustion engines. The direct base-catalyzed trans-esterification process is employed in the biodiesel production using methanol and a homogeneous base (sodium hydroxide) as alcohol and catalyst respectively. Bio-ethanol was obtained through fermentation and distillation from sugar cane, raffia trunks and palm wine and then purified. Physical properties of the bio-ethanol and various petrol bio-ethanol blends such as vapour pressure, octane number, flash point, heating values, auto ignition temperature and density were evaluated. The neat biodiesel and bio-ethanol fuels and its blends are characterized using the American Society for Testing and Materials (ASTM) methods. The evaluated properties for the biodiesel fuels are density, kinematic viscosity, pour point, flash point, cloud point, heating value and cetane number. These properties are compared in relation to the international standards for petrol and diesel engine fuels. The octane number increased from *86* at E_{10} to *105* at E_{90}. The calorific value decreased from *44.22MJ/Kg* at E_{10} to *30.10MJ/Kg* at E_{90}. The optimal petrol-bioethanol blend of E_{20} was recommended for Nigerian vehicles running on spark ignition engines. Biodiesel yields of *67%*, *68.5%*, *69.32%* and *56%* were obtained from *jatropha, dika, castor and sandbox oils* respectively. Cetane values of *59.4, 52, 50* and *50* and kinematic viscosities of $4.2mm^2/s$, $3.2mm^2/s$, $10.75mm^2/s$ and $4.2mm^2/s$ were obtained for *jatropha, dika oil, castor and sandbox biodiesel* respectively. The results of the characterization showed that the produced fuels are alternative fuels that can be used on modern diesel and petrol engines with little or no engine modifications.

Keywords: ***Bioethanol; Biodiesel; Transesterification; Octane Number, Cetane Number; Fuel Properties***

CHAPTER ONE

INTRODUCTION

1.1 GENERAL BACKGROUND

The ever rising cost of fossil fuel internationally has forced major world economies, which are also major importers of fossil fuel, to examine renewable and cheaper alternatives to fossil fuel to meet their energy demands. Biodiesel and bio-ethanol have emerged as the most suitable renewable alternatives to fossil fuel as their quality constituents match diesel and petrol respectively. In addition they are less polluting than their fossil fuel counterparts. Environmental concerns and the desire to be less dependent on imported fossil fuel have intensified worldwide efforts for production of biodiesel from vegetable oils and ethanol from starch and sugar producing crops.

The petrol and diesel engines are one of the most efficient power plants in use today, consequently, they enjoy wide application in road, rail and marine transportation as well as power generation. Petrol and Diesel engines conventionally runs on petrol and diesel fuels which is a fossil fuel and whose production and combustion result in the emission of gases that have adverse effects on human health and environment. The greenhouse gas emissions from the combustion of diesel and other hydrocarbon fuels have been identified as the major causes of climate change and global warming. Climate change and global warning are serious contemporary challenges that face humanity. The numerous and varied effects of climate change on the environment, human life and the economy of the nations are becoming increasingly obvious and real. Expectedly, the phenomenon is provoking global concern as shown by world summits, local and international conferences on climate change and global warming held at different places and times like the Kyoto, Japan in 1997, Hague, Netherlands in 2000 and Copenhagen, Denmark in December 2009. Pragmatic steps like setting of drastic emission cut targets for both developing and developed nations have been taken. The Kyoto Protocol was aimed at stabilizing greenhouse gas concentration to prevent a dangerous anthropogenic interference and according to the United Nations Framework Convention on Climate change, the protocol has been ratified by 187 States as at November, 2009.

Global warming is the increase in the average temperature of Earths near surface air and oceans. This increase in global temperature has caused changes in the global climate patterns described as climate change [Ofoh, 2009; Lu, et. al, 2007].

Both the U S Energy Departmental report of 2008 and the 2007 Report of the Intergovernmental Panel on Climate Change associated global warming with rise in sea level, flooding, changes in rainfall pattern, deforestation, glacier retreat, increased precipitation and high hurricane power dissipation index. On human health, global warming has been linked with increase in cardiovascular diseases, asthma, and other lung diseases due to the concentration of ozone at ground level [McMichael, et al, 2003]. Hales, et al [2002], and Rogers, et al [2004] associated global warming with wide spread of diseases like dengue fever and malaria. There are predictions that global warming may substantially fuel itself by causing the loss of carbon from terrestrial ecosystem leading to an increase in the level of atmospheric carbon dioxide and the release of methane gas from methane clathrate [Cox, et al, 2007]. Both carbon dioxide and methane are greenhouse gases.

The emerging consensus is that global warming in the recent decades has been caused primarily by the greenhouse gas emissions from the production and processing of fossil fuels, their combustion in the factories, power generation, transportation and other human activities like deforestation and urbanization [Ofoh, 2009; Barma, et. al.2010]. These activities have increased the concentration of greenhouse gases in the atmosphere. The concentrations of carbon dioxide and methane have increased by 36% and 148% respectively and fossil fuel burning has produced three-quarters of the increase in carbon dioxide from human activity over 20 years. [EPA 2007; IPCC, 2000; Pearson, and Palmer, 2000]. Transportation in industrialized and developing countries constitutes the largest and most rapidly growing user of world’s oil reserve and hence a major source of greenhouse emissions [Giri, 2004,].

Besides the issues of health and environment, the over dependence on fossil fuels as major sources of energy has raised the issues of energy security and incessant price increases. Fossil fuels are non-renewable and the fast depletion of their reserves could lead to their exhaustion in the near future hence a possible global energy crises may emerge.

Consequent upon these challenges, many counties are today turning to fuels from biomass and other non- petroleum sources to substitute or supplement the conventional fuels. Alternative fuels from bio-resources are considered biodegradable, renewable and environmentally friendly [Prasad,et al 2010]. Among the alternative fuels that are gaining global interest particularly for internal combustion engines are bio-fuels like Bio-ethanol and Biodiesel. While bio-ethanol is considered a good alternative fuel for petrol engines, biodiesel is considered as good alternative for diesel engines.

Biodiesel is an ester-based, oxygenated, non-toxic and biodegradable fuel synthesized from renewable sources like animal fats, refined and used vegetable oils [Narasimharao, et al, 2007; Somerville, 2008]. According to the UN Bio-fuel report, biodiesel is the most commonly used bio-fuel in Europe and some other continents with Germany and France being the largest producers in the world. Biodiesel provides a reduction in harmful emissions such as SO_x, CO, HC, Polycyclic Aromatic Hydrocarbons, particulate matters as well as reduction of carbon dioxide emission which is a major cause of global warming. It is being used in U S and Europe to reduce air pollution and dependence on fossil fuels. Biodiesel is considered safe to handle and transport, contains no sulphur and low aromatics. Biodiesel fuels have good combustion characteristics because of high cetane number and oxygen content. Its high lubricity prolongs the life of the engine and fuel systems. [Korres, et al 2002]. Bio-ethanol and Biodiesel fuels have favourable engine performances comparable to petrol and diesel fuel respectively. They produce higher thermal efficiencies than petrol and diesel fuels due to their low heating values [Quick, 1989]. They are the only alternative fuel to have a complete evaluation of emission results and potential health effect submitted to the US Environmental Protection Agency [EPA] under the Clean Air Act section 211[b].

As a result of these qualities, increasing research attentions are being paid to the development of bio-ethanol and biodiesel globally. Currently, edible and non-edible crop oils are being investigated for biodiesel production. Some commonly used feedstocks in different countries are soybean in US, rapeseed in UK, Karanja and Jatropha in India and palm oil in Malaysia, Indonesia and Nigeria.[Jorg, and Sascha, 2008, Nagarhalli, et al. 2010]. Similarly, edible and non-edible sugar feedstock are also being investigated for bio-ethanol production and some commonly used feedstock in different countries are, sugar cane in Brazil and USA, wheat and barley in Europe, palm wine, palm sap and cassava in Western Africa and maize in USA and Central Africa [Ocloo and Ayernor, 2010, Tangka et al, 2011].

This work involves three main processes namely,

- The synthesis of bio-fuels as alternative fuels for internal combustion engines from various Nigerian crops (palm wine, sugar cane, raffia trunk, physic nut seed oil, castor bean seed oil, sandbox seed oil and African bush mango nut oil).
- The characterization of the produced bio-ethanol and biodiesel fuels in accordance with the American Society of Testing and Materials (ASTM) test methods and,
- The evaluation of the physical properties of a wide range of ethanol petrol blends.

The alcohol chosen for the transterification process is methanol because of its low cost, high product yield, availability and allows simultaneous separation of glycerol [Edgar, et al. 2005, Bunkyakiat, et al. 2006]. Base- catalyzed technique is preferred because it is considered a very economical method requiring only low temperature and pressure and gives high conversion yield of up to 98 percent with minimal side reactions and reaction time [Watanebe, et al. 2004]. The catalysts favoured for this work is sodium hydroxide because it is cheaper and locally available, though potassium hydroxide is easier to use because it dissolves faster in methanol. The properties of the biodiesel fuel that are of interest are, density, viscosity, calorific (heating) value, pour point, flash point, cetane number, iodine number, ash content and cloud point while the properties of bio-ethanol fuel that are of interest are, vapour pressure, octane number, flash point, Heating values, auto ignition temperature and density.

1.2 STATEMENT OFTHE PROBLEM

Humanity has depended on fossil fuels for many decades as its major source of energy. This has led to increase in the demand and use of fossil fuels with some far reaching economic and environmental consequences. The increase in the demand of fossil fuels has led to incessant rise in their prices as well as the fear of exhaustion of their reserves.

There is also a growing concern about the environmental effects of the use of fossil fuels. The disturbing global warming and climate change are associated with greenhouse gas emissions from the combustion of fossil fuels.

These challenges have provoked global search for alternative fuels that are renewable, cost effective, and environmentally friendly. Biodiesel and bio-ethanol are widely believed to be one of the possible candidate fuels to meet these needs. It has low emission profile and does not contain sulphur and carcinogens like poly aromatic hydrocarbons and nitrous poly aromatic hydrocarbons. Biodiesel and bio-ethanol contains some amount of oxygen [11% and 35% by weight respectively] and has higher cetane and octane numbers respectively, both of which improve combustion with resultant low emission profile. The production of bio-ethanol and biodiesel are currently engaging the attention of the international community and many nations of America, Europe and Asia have made a lot of progress in this regard. Nigeria with large population and high consumption rate of fossil fuels is expected to be actively involved in the development of bio-fuels in order to cut down greenhouse emissions and make up for the shortfall in local fuel supply.

This project represents an effort to address these problems associated with fossil fuels by producing an alternative fuels (bio-fuels) from organic and renewable sources which will have performance characteristics similar to conventional fossil fuel. This will enlist Nigeria among the nations making frantic efforts to cut down greenhouse emissions in order to mitigate the effects of climate change.

1.3 OBJECTIVES OF THE WORK

The objectives of this research work are:

- The synthesis of bio-fuels (bio-ethanol and biodiesel) as alternative fuels for internal combustion engines from locally available feedstock which includes; sugar cane, palm wine, raffia trunk, physic nut seed oil, castor bean seed oil, sandbox seed oil and African bush mango nut oil. The seed oils have high oil yields and low iodine values which make them suitable for the production of quality fuels.
- Characterization of the produced neat biodiesel fuels in accordance with the American Society for Testing and Materials Methods and compares their qualities with the standard ASTM properties of biodiesel and diesel fuels. The following properties are of interest; densities, viscosity, flash point, pour point, heating value, cloud point, cetane number, iodine number and ash content.
- To publish the physical properties of a wide range of ethanol petrol blends and studies the effect of blend on these properties. The following properties are of interest; vapour pressure, octane number, flash point, calorific value, auto ignition temperature and density.

1.4 JUSTIFICATION

This research work is justified by the current global search for alternative fuels and energy sources that are both renewable and environmentally friendly. This search has been informed by the obvious negative consequences of the over dependence of humanity on fossil fuels for transportation, industry, power generation etc. These fossil fuels are exhaustible and this raises the issue of energy security. They are also the major sources of greenhouse gases like carbon dioxide which is a major contributor to global warming and climate change. This work involves the production of fuel that is generally considered as cleaner, biodegradable and non-toxic. This is believed to contribute to the global efforts to control the environmental effects of the use of fossil fuels such as global warming.

This work will stimulate interest in the harnessing of these abundant bio-energy resources available in the country. This has the multiplying effects of promoting agricultural activities, generation of rural employment, provision of rural infrastructures and the enhancement of the standard of living of rural dwellers. Nigeria is endowed with huge natural resources and factors deployable for bio-energy production like large arable land and favourable climate conditions.

Another aspect of this work involves the determination of the properties and performance characteristics of the produced bio-ethanol and biodiesel. The results will expectedly add to the existing knowledge on fuels from non- petroleum sources as well as confirms the suitability of these fuels for existing internal combustion engines vis-a-vis the ASTM standards. This will be very useful for engine designers and users.

Finally, the under listed benefits of bio-fuels justifies the production of bio-fuels. Some of these benefits include; creation of employment, rural development, poverty alleviation, foreign exchange, energy security, emission reduction, biodegradability, non-toxicity, higher cetane and octane numbers, high flash point for biodiesel fuels, high auto ignition temperature for bio-ethanol fuels, lubricity, renewable, adoptability, oxygenated fuel, e.t.c.

1.5 SCOPE OF THE WORK

This work is focused on the synthesis and characterization of Biodiesel and Bio-ethanol from various Nigerian crops (palm wine, sugar cane raffia trunk, physic nut seed oil, castor bean seed oil, sandbox seed oil and African bush mango nut oil) as alternative fuels for internal combustion engines.

It is limited to the evaluation of some of the physical properties of the fuels and does not cover chemical properties.

CHAPTER TWO

LITERATURE REVIEW

2.0. BIO-FUELS – AN OVERVIEW

2.1 BIOENERGY AND BIOFUELS

Bioenergy is a renewable, non-fossil energy obtained from the combustion of biomass, most often in the form of fuelwood, biogas or liquid biofuel[Richard and NeBambi, 2010]. Liquid biofuels can be bioethanol, biodiesel or straight vegetable oil. While bioethanol(ethyl alcohol) is a chemical compound, biodiesel is a mixture of compounds that varies in physical properties according to the feedstock used to produce it. Liquid biofuels can replace petrol and diesel for transport use and can be used in stationary engines to generate electricity, pump water and mill food grains as well as for cooking and lighting. The IEA report “Biofuels for Transportation” (2004) has summarized the potential benefits and cost of biofuels, ethanol included. See Table 2.1.

Table 2.1: Potential Benefits and costs of Biofuels (Source: IEA, 2004)

Potential benefits	Potential costs
• Energy security	• Higher fuel cost
• Balance of trade	• Increases in some air emissions
• Lower GHG Emissions	• Higher crop and crop product prices
• Reduced air pollution emissions	• Other environmental impacts, such as land use change and loss of habitat
• Vehicle performance	
• Agricultural sector income, jobs and community development	
• Waste reduction	

2.1.1 First, Second and Third Generation Biofuels

Levels of technological development for biofuels are defined as first, second and third generation [CGIAR 2008]. The first generation biofuels are the fuels which are the fuels now in common use are produced from conventional agricultural crops by well-established technologies such as biodiesel from oil crops and ethanol from sugar and starch producing crops. The important biofuel crops are maize, sugar cane and sugar beet for the extraction of sugars to produce bioethanol and soyabean, rapeseed and oil palm for the extraction of oil to produce biodiesel. The second-generation biofuels on the other hand are produced from the agricultural waste - mainly the lignocellulosic material. However they require advanced production (conversion) technologies. Technologies for second and third generation biofuels remain under development. They offer prospect of producing biofuels from non-food sources such as fast growing trees, grasses and carbon-rich waste materials. These future technologies will also have the capability of converting algae and bacteria into oils that can replace petroleum fuels. The need to optimize resources and minimize waste also has prompted research into the production of higher value chemicals and commodities as by-products of biofuel feedstock processing. Brazil's sugarcane industry has adopted this bio-refinery concept, using the waste bagasse left after sucrose extraction as a fuel to produce electricity. Overall, high energy conversion efficiencies and least cost of production are the key factors for selecting biofuels for the future.

2.1.2 Bioethanol and Biodiesel

Bioethanol: Sucrose is extracted from the plant stem or tuber of sugar-rich crops, fermented and then distilled to produce bioethanol (alcohol). Crops rich in starch, such as maize and cassava, need a pre-treatment to convert the starch into fermentable sugars. Bioethanol is commonly blended with petrol in proportions of up to 5 percent (E5) for which no engine modification is required.

Biodiesel: Trees, shrubs and herbaceous oilseed plants may be used for the production of biodiesel through trans-esterification – a process by which alcohol is added to vegetable oil in the presence of a catalyst. The seeds of oil-rich plants are hulled and pressed to extract the oil which is then filtered. Methanol is added to the raw vegetable oil, using sodium (or potassium) hydroxide as the catalyst.

The product is a vegetable oil methyl ester (VOME) or, in the case of jatropha, jatropha methyl ester (JME). Biodiesel has very similar properties to petroleum diesel.

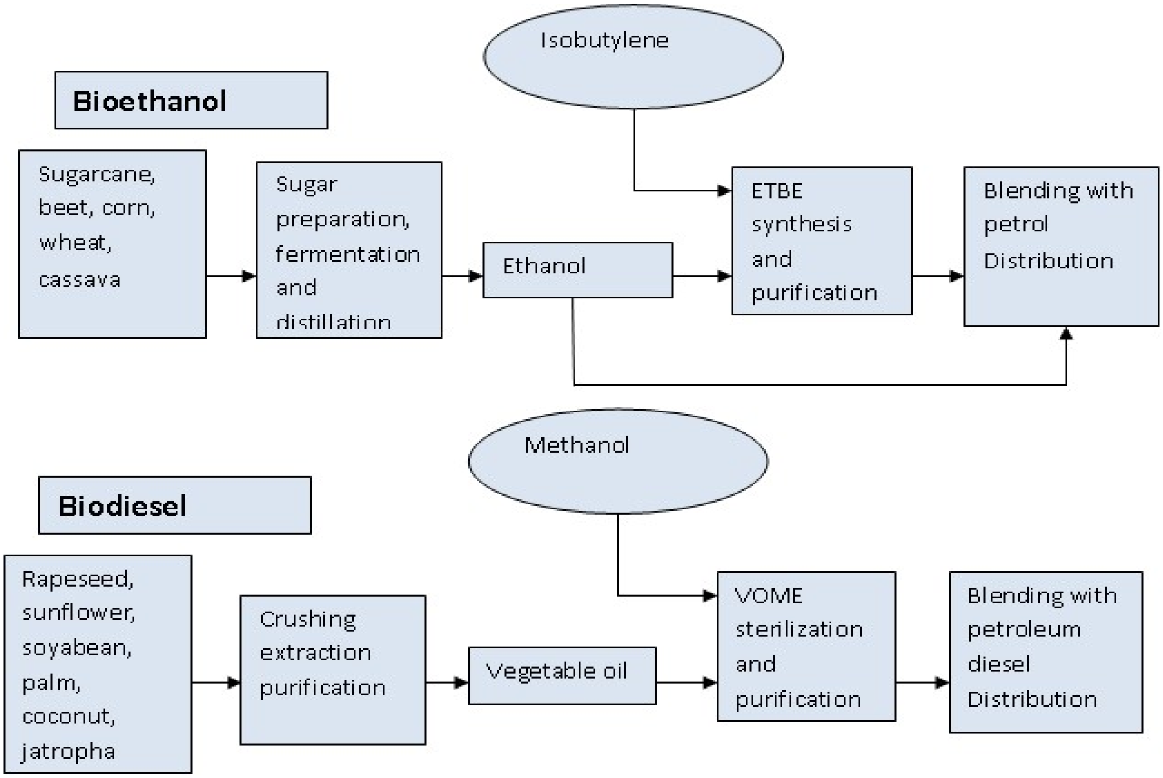


FIGURE 2.1: Bioethanol and Biodiesel Production Processes

Figure 2.1 illustrates the basic processes of converting plants to transport fuels.

2.1.3 Straight Vegetable Oil

Extracted and filtered vegetable oil can be used directly as a fuel in suitable diesel engines without undergoing the trans-esterification process [Achten et al., 2008]. While there are issues with poor performance, increased maintenance, reduced engine life and engine manufacturers who void warranties if vegetable oils are used, there is now considerable experience with using straight vegetable oil in suitably modified diesel engines [De Jongh and Adriaans, 2007; Cloin, 2007].

2.1.4 Growth Drivers of Biofuels

Growth of the biofuel industry is being driven by government policies in three main areas. This includes policies aimed at mitigating climate change, improving energy security and using biofuel production as a strategy to support rural development. Mandates and targets for inclusion of biofuels in petrol and diesel, together with subsidies and border protection in the form of import tariffs and quotas, are the means by which governments provide the impetus to drive biofuel growth. The United States of America (USA) leads in production-related subsidies while other countries, including the European Union (EU) and Brazil, largely use tax exemptions as the policy instrument for the promotion of biofuels.

Climate change: The need to slow or reverse global warming is now widely accepted. This requires reduction of greenhouse gas (GHG) emissions, especially reduction of carbon dioxide emissions. Using cultivated and non-domesticated plants for energy needs instead of fossilized plant remains such as mineral oil and coal reduces the net addition of CO_2 to the atmosphere. In addition, biodiesel produces fewer particulates, hydrocarbons, nitrogen oxides and sulphur dioxides than mineral diesel and therefore reduces combustion and vehicle exhaust pollutants that are harmful to human health.

Energy security: The search for renewable energy is being driven by volatile crude oil prices and the perceived threat to national security of over-dependence on foreign supplies. Crude oil prices are likely to increase over the long term as fossil reserves diminish and global demand increases, particularly in the newly emerging economies of Asia and Latin America.

However, the potential of biofuels to enhance energy security is limited. Globally, the huge volume of biofuels required to substitute for fossil fuels is beyond the capacity of agriculture with present day technology. For example in 2006/7, the USA used 20 percent of its maize harvest for ethanol production, which replaced only three percent of its petrol consumption [World Bank, 2008]. More significant displacement of fossil fuels will be likely with second and third generation biofuels [SOFA, 2008].

Rural development: Government policy in support of rural development, the third main driver of biofuel growth, has been enabled by the large demand for biofuel feedstocks and the import substitution potential of biofuels. In OECD countries, biofuels are seen as a new market opportunity due to their ability to absorb surplus agricultural production while maintaining productive capacity in the rural sector. In developing countries, biofuels can contribute to rural development in three main areas: employment creation, income generation and by replacing traditional biomass, which is an inefficient and unsustainable energy resource, with modern and sustainable forms of bioenergy.

Economies of scale and the vertical integration required for biofuel production allow little scope for small farmers to benefit. This is particularly true in bioethanol production and will be even more so with second- and third-generation biofuels, unless specific efforts are made to include small farmers in biofuel production schemes. There is more potential for biodiesel to be produced on a smaller scale, although maintaining consistent quality standards will be a problem. Small-scale production of straight vegetable oil requires the least economies of scale and has the greatest potential to benefit small farmers and rural development.

2.1.5 World Biofuel Scenario

Worldwide, oilseed crops occupy an area of 166.36 million hectares with a production of 295.6 million tonne and productivity of 1777 kg/ha [FAO, 2003]. In India, area under oilseeds is 23.7 million hectares with a production of about 25 million tonne and a productivity of just about one tonne/hectare. The oilseed production in the country presently meets only 20-40% of its total edible oil requirements and the rest is met through imports.

2.1.5.1 Global Biodiesel Production Scenario

Biodiesel is a fast-developing alternative fuel in the U.S. and Europe. Pilot plants for power generation and encouraging adaptation by fleet operators have established biodiesel as a viable and sustainable alternate fuel. The biodiesel production from vegetable oils during 2004-05 was estimated to be 2.36 million tonne globally. Of this EU countries accounted for 1.93 million tonne, U.S. produced 0.14 million tonne and rest of the world 0.29 million tonne [Parikh, 2005]. The EU usage of vegetable oil for biodiesel has been rising at about 30% annually in the last two years. In EU, rapeseed is the main source of oil for biodiesel, while in the U.S. soybean oil is used for manufacturing biodiesel. Malaysia - the largest producer of palm oil has set up three palm biodiesel plants with a combined annual capacity of 60,000 tonne.

2.1.5.2 World Ethanol Production

With the provision of addition of 5-10% of ethanol in petrol and diesel in most of the crude oil importing countries, there has been a substantial rise in ethanol production in last few years. Among the ethanol producing countries, Brazil produces the maximum amount of ethanol (15099 million liters/year) followed by the U.S. (13381 million liters/year), China (3649 million liters/year) and India (1749 million liters/year). Sugar cane is the major source of ethanol in Brazil, while in the U.S. it is produced from corn [Peterson, 2006].

2.1.5.3 Ethanol Production from Crop Residues

Enough availability of crop residues as a source of feedstock is obviously mandatory for the production of second-generation biofuels. Annual crop residue availability in the world is estimated to be about four billion tonne, of which the U.S. and India account for one billion tonne. Lignocellulosic residues of cereal crops like corn, rice, wheat, sorghum and millet are best suited for ethanol production and are estimated to be about 3 billion tonne/annum in the world and 0.4 billion tonne/annum each in the U.S. and India respectively [Lal, 2006]. These are large quantities and a substantial part of these residues may suitably be used for biofuel production.

The potential of bioethanol production from waste crops and crop residues was estimated by Kim and Dale (2004). According to them there are 74Tg (Tg = Teragram = 1012 Gg = 1 million metric tonne) of dry waste crops in the world that have a potential to produce 49 GL (gigaliter or 1 billion liters) of bioethanol/year. It was also estimated that conversion of 1.5 Pg (Pg = Petagram = 1015Tg = 1 billion metric tonne) of dry lignocellulosic residues of seven crops viz. corn, barley, oat, rice, wheat, sorghum and sugar cane, could produce an additional quantity of 442 GL of bioethanol per year. This potential bioethanol production of 491 GL could replace 353 GL of petrol or about one-third of the global petrol consumption. The ethanol production potential of residues from lignocellulosic crops ranges from 0.26 to 0.31 L Kg-z. The net energy yield of perennial crops ranges from 220-550 GJ/ha/yr, that of grasses 220-260 GJ/ha/yr and that of sugar cane 400-500 GJ/ha/yr [Hamelinck and Faaij, 2006].

Use of lignocellulosic agricultural residues for energy production is thus very favorable and offers good economic prospects for the future of biofuels. EU has set a target of 1 billion liters of second generation bioethanol production to be achieved by 2012 [de Miguel, 2006]. The prominent high potential fuels are ethanol produced from agricultural residues rich in lignocellulose, synthetic diesel via Fischer-Tropsch, methanol and hydrogen [Arthur D. Little, 1999; Katofsky, 1993; Turkenburg, 2000; Williams et al., 1995]. These four fuels are in attractive stages of development.

2.1.6 Comparison of Biodiesel and Bioethanol

Before striving for commercial scale biofuel production from food crops, it would be of paramount importance to determine whether biofuels provide any benefit over the fossil fuels they replace. This needs a thorough analysis of the direct and indirect inputs and outputs for their full production and use life-cycles. To become a successful substitute for a fossil fuel, an alternative fuel in addition to having superior environmental benefits over the fossil fuel should also be produced economically and in sufficient quantities to meet the energy requirements. Hill et al. (2006) analyzed the net societal benefits of corn grain (Zea mays ssp.) for ethanol and soybean (Glycine max) oil for biodiesel-the two important alternative transportation fuels in U.S.

The study showed that both corn grain ethanol and soybean biodiesel recorded positive Net Energy Balances (NEB). The NEB for corn grain ethanol was recorded as 25% more energy than required to produce it. However, the soybean biodiesel provided 93% more energy than needed in its production.

As far as the life-cycle environmental effects were concerned, the study showed that both corn and soybean production have negative environmental impacts through movement of agrochemicals especially nitrogen (N), phosphorus (P) and pesticides from farms to other habitats and aquifers. Data on efficiencies of net energy production from agrochemical inputs in corn and soybean reveal (after partitioning these inputs between the energy product and co-products), that biodiesel uses only 1.0% of the N, 8.3% of the P and 13% of the pesticides on weight basis. Although blending ethanol with petrol at low levels as an oxygenate was reported to result in lower emissions of carbon monoxide (CO), total life-cycle emissions of five major air pollutants [CO, VOC, PM10, oxides of sulphur (SO_x) and oxides of nitrogen (NO_x)] are higher with the "E85" (85% corn grain ethanol-petrol blend) than with petrol per unit of energy released upon combustion [Hill et al., 2006]. The study further revealed that production and use of corn grain ethanol releases 88% of the net green house gas (GHG) emissions of production and combustion of an energetically equivalent amount of petrol. On the other hand life-cycle GHG emissions of soybean biodiesel were recorded to be 59% of those for diesel fuel. Because fossil fuel energy use imposes environmental costs not considered in market prices, benefits of biofuel to society not only depend on its cost competitiveness compared to fossil fuel but also on its environmental costs and benefits vis-à-vis its fossil fuel alternatives. Subsidies for otherwise economically uncompetitive biofuels are justified if their life-cycle environmental impacts are sufficiently less than for alternatives. Table 2.2 summarizes the most significant fuel properties of ethanol compared to those of petrol and diesel.

Table 2.2: Properties for Ethanol, Petrol and Diesel

Property	Ethanol	Petrol	Diesel
Chemical Formula	C_2H_5OH	C_4 to C_{12}	C_3 to C_{25}
Molecular Weight [g/mol]	46	100-105	≈200
Carbon [mass%]	52.2	85 - 88	84 - 87
Hydrogen [mass%]	13.1	12 - 15	33 - 16
Oxygen [mass%]	34.7	0	0
Density at 20°C [Kg/l]	0.792	0.72 - 0.78	0.81 - 0.88
Viscosity [cST]	1.52(20°C)	0.4-0.9(16°C)	2-6(37°C)
Boiling Temperature, 1atm [°C]	78.4	27 - 225	288 - 340
Reid Vapour Pressure, [kPa]	16	50 - 100	0.1 0.15
Flammability Limit, 20°C [vol%]	3.3 – 19	1.0 - 8.0	0.6 - 5.5
Stoichiometric Air/Fuel Ratio	9	14.5 - 14.7	14.6 - 16
Flash Point [°C]	12	-42	74
Autoignition Temperature [°C]	423	257	≈315
Heat of Vaporization [kJ/kg]	910	330 – 400	225 – 600
Heat of Combustion [kJ/kg]	26900	42000 - 44000	42800 -45300
Heat of Combustion [kJ/liter]	21300	≈32000	≈37200
Research octane no.	108	90 – 100	N/A
Motor octane no.	92	81 – 90	N/A
(R+M)/2	100	86 – 94	N/A
Cetane Number	--	5 – 20	40 – 55
Water Tolerance, volume %	Completely miscible	Negligible	Negligible
Carbon Dioxide Emission [kg/kg fuel]	1.91	3.18	3.20
Energy per CO_2 Emission [MJ fuel energy/kg CO_2 emitted]	14.1	≈13.5	≈13.8

Sources: Sinor 1993(Sinor et al,: Current and Potential Future performance of ethanol fuels, SAE tech paper 930376) and US department of energy, office of energy efficiency and renewable energy, alternative fuelsndata center

2.2 FUELS

Fuel is any substance that produces heat energy when reacted with oxygen of the air or substance that liberates heat when it burns. Fuels are the major energy sources for engines employed in transportation, power generation, space heating and industrial applications. They occur in gaseous, liquid and solid forms. Liquid and gaseous fuels are considered superior to the solid fuels because, firstly, they are easier to handle and transport to distant places through pipelines, secondly, they do not leave much residue after burning and produce very little smoke during combustion, and thirdly, they burn more easily and have higher heating values than solid fuels.

Fuels can be classified as Conventional and Alternative fuels. Conventional fuels are those that are traditionally used in internal combustion engines like petrol, jet fuels, diesel and fuel oils. Majority of the conventional fuels are fossil fuels.

Fossil fuels are nonrenewable and are the most developed fuels for internal combustion engines. They are believed to have been formed from the decay of organic materials under pressure and elevated temperature below the earth surface over millions of years. They composed mainly of hydrogen and carbon hence they are designated as ***HYDROCARBONS***. Alternative fuels are those that are recently finding increasing applications in internal combustion engines. Some of them are nonpetroleum based fuels that are synthesized from renewable sources. The dominant ones are Hydrogen, Alcohols, Biodiesel, and Biogas.

Table 2.3: Classification of Fuel

Type of fuel	Natural	Synthesized

Solid	Wood, peat, lignite coal	Coke, charcoal, briquettes
Liquid	Petroleum	Petrol, kerosene, fuel oil, alcohol, biodiesel, benzol, shale oil, etc
Gaseous	Natural gas	Petroleum gas, producer gas, coal gas, coke, biogas, blast furnace gas, sewer gas, carbureted gas, synthesis gas, etc.

2.2.1 Solid Fuels

The popular type of solid fuel that has been used extensively by man in the early centuries was coal. It was a major source of energy in England when pieces of black rock called ***SEA COLES*** were discovered to be combustible. It was used as domestic fuel and in fact became the fuel of the industrial revolution when it was used for metallurgical processes, glass making and steam engines. In spite of the advent of petroleum fuels, coal is still enjoying some reasonable applications particularly is steel industries. Coal is classified as black coal or brown coal [lignite].It contains mainly carbon, hydrogen, oxygen, sulphur and ash in different proportions depending on its source. Although considerable local variations might be found, a typical analysis by weight could be; Carbon 83%, Ash 9%, Oxygen 4%, and Hydrogen 3%. Coal is used either directly in solid form where it is normally pulverized or sometimes gasified. Coal gasification is an old process dating back to about the end of eighteenth century and the process produces low energy gases such as producer gas and water gas. The use of these gases is now being superseded in many places by natural gas and liquefied petroleum gas. The main product of gasification process is usually methane which can be used in gas engines.

Wood charcoal is obtained by destructive distillation of wood. Coke consist of carbon, mineral matter with about 2% sulphur and small quantity of hydrogen, nitrogen and phosphorous. It is a solid residue left after the destructive distillation of certain kinds of woods or coal. It is smokeless and clear and can be produced by several processes that are mainly used in blast furnace to produce heat and at the same time to reduce the iron ore.

Analysis of Coal

There are two methods used for the analysis of coal: ultimate analysis and proximate analysis.

Ultimate analysis is an accurate chemical analysis by mass of the important elements in the fuel. Here the elements usually included are carbon, hydrogen, and sulphur.

Proximate analysis is another analysis of coal which gives the percentages of inherent moisture, volatile matter, and combustible solid (fixed carbon). The fixed carbon is found as remainder by deducting the percentages of the other quantities. The volatile matter includes water derived from the chemical decomposition of the coal, the combustible gases (hydrogen, methane, ethane, etc) and tar (a complex mixture of hydrocarbons and other organic compounds). Table 2.4 below shows the ultimate and proximate analysis of coal.

Table 2.4: Ultimate and Proximate analysis of Coal

<table>
<tr><th colspan="8">Ultimate analysis</th></tr>
<tr><th>Fuel</th><th>Rank</th><th>C</th><th>H</th><th>O</th><th>N</th><th>S</th><th>Mineral matter</th></tr>
<tr><td>Anthracite</td><td>101</td><td>88.2</td><td>2.7</td><td>1.7</td><td>1.0</td><td>1.2</td><td>5.2</td></tr>
<tr><td>Medium rank coal</td><td>401</td><td>81.8</td><td>4.9</td><td>4.4</td><td>1.8</td><td>1.9</td><td>5.2</td></tr>
<tr><td>Low rank coal</td><td>902</td><td>75.0</td><td>4.6</td><td>10.7</td><td>1.6</td><td>2.1</td><td>6.0</td></tr>
<tr><td>coke</td><td>-</td><td>90.0</td><td>0.4</td><td>1.9</td><td>-</td><td>-</td><td>7.7</td></tr>
<tr><th colspan="8">Proximate analysis</th></tr>
<tr><th>Fuel</th><th colspan="3">Inherent moisture</th><th colspan="3">Volatile matter</th><th>Fixed carbon</th></tr>
<tr><td>Anthracite</td><td colspan="3">2</td><td colspan="3">6</td><td>92</td></tr>
<tr><td>Medium rank coal</td><td colspan="3">3</td><td colspan="3">39</td><td>58</td></tr>
<tr><td>Low rank coal</td><td colspan="3">10</td><td colspan="3">42</td><td>48</td></tr>
</table>

2.2.2 Petroleum Fuels

They are the most used fuels for internal combustion engines because they are available in large quantity, have high energy density, and ease of delivery. Like coal, petroleum fuels are classified as fossil fuels which are believed to have been formed by the decomposition of organic materials over a long period. The discovery of crude oil and natural gas widened the fuel matrix and they replaced coal in many areas like transportation, space heating, industrial applications and power generation. Crude oil which is the source of petroleum fuels consists of many hydrocarbons and other compounds like oxygen, nitrogen, sulphur, nickel, chlorine, lead etc. However, the composition of crude oil depends on age and geological conditions under which it was formed. Older deposits such as some of the Middle East deposits tend to have a greater percentage of lighter hydrocarbons while the young deposits have more of hydrocarbons with high molecular weight. Crude oils with large amount of sulphur [>0.5wt%] and other mineral impurities are referred to as ***SOUR CRUDE*** while those with low sulphur content [< 0.5wt%] are called ***SWEET CRUDE.*** Crude oils can also be classified according to the type of residue that remains after the lighter fractions are distilled. The major classes are; *The Paraffin based crude; The Asphalt based crude; The mixed based crude*

The carbon mass carbon fraction ranges from 83-88% while the hydrogen mass fraction range is 10-16%. The bulk of the hydrocarbons in petroleum belong to the paraffin series. These compounds sometimes called Alkane hydrocarbons are a saturated group with general formula $C_nH_{2n+2.}$ Examples are Methane, Ethane and Propane. Paraffins are classified according to the arrangement of the chain of carbon atoms. Some have single long chain while others have branched and cyclic chains. The concentration varies from crude source to source and even from oil well to oil well. The physical and chemical properties of the crude oil hydrocarbon can influence the way refineries process the crude and also impact the performance of the refined fuels. For example, branched chain paraffins have compact molecular structure and greater resistance to auto-ignition in engine combustion. Other hydrocarbon types in crude oil are Cycloalkanes (naphthenes), Alkenes [Olefins] and Aromatics. These families exhibit general characteristics due to their molecular structure such as,

(i) The Anti-knock quality: This appears to be poorest in the normal paraffin and improves down the line with aromatics offering the best resistance to detonation in spark ignition engines.

(ii) Fuel suitability: The suitability of fuels for compression ignition engines is in the reverse order of their suitability for spark ignition engines. For example, fuel with high anti-knock ability is good for high performance S I engines but unsuitable for use in CI engines.

(iii) Boiling point: Generally, as the number of carbon atoms increases, the boiling point rises.

(iv) Heating value: As the proportion of hydrogen atoms to carbon increases, the heating value generally increases.

The common fuels that are derived from crude oil which are possibly used in internal combustion engines are;

2.2.2.1 Liquefied Petroleum Gas (LPG).

This is the compressed and liquefied light end petroleum fractions. It is composed of mainly propane, with low concentration of ethane and butane extracted from natural gas and crude oil where they are dissolved and are stored as liquid under pressure. The boiling points at atmospheric pressure are propane -2^{0}c and butane -0.5^{0}c. A strong smelling substance called *ethyl mercaptan* is added to the LPG gas cylinder to help in the detection of gas leakage. Studies on the use of LPG on automotive engines have revealed some promises and difficulties which include.

(i) LPG can be used as a petrol replacement in modern engines with no major engine modifications [except the addition of LPG storage tank and fuel metering system]. However, engine timing advance is also needed.

(ii) LPG combustion implementation occurs with a more uniformly distribution air /fuel mixture in the combustion chamber compared to gasoline and this leads to a slight improvement in combustion and engine efficiencies.

(iii) It has very high knock resistance

(iv) It contains negligible toxic components

(v) The main constituent of LPG is propane , the lower carbon to hydrogen ratio, the higher the octane rating and the ability to form a homogeneous mixture inside the cylinder and this reduces the of emission greenhouse gases, NO_x, PAH and aldehyde

(vi) It does not cause fuel dilution of engine oil which is often the problem with the gasoline engine

(vii) It also has the advantage of reduced cylinder wear and extended engine oil life.

(viii) It has lower peak pressure during combustion than conventional fuels, which generally reduces noise and improves durability.

On the other hand, the use of LPG in internal combustion engines has some problems which include

(ix) Low calorific value [885 kcal/m^3] which results in lower power output compared with gasoline with a calorific value of 928 kcal/m^3

(xi) Use of LPG in diesel engines results to a problem due to its low cetane number and thus the auto-ignition temperature needed is considerably high necessitating the increase of the compression ratio to impracticably high level

(xii) In LPG engine, the fuel is preheated and vapourized in a heat exchange pressure regulator before it is mixed with air in the carburetor, resulting in high mixture temperature and low power output

(xiii) Propane vapour flammability limits in air are wider than those of petrol which makes LPG ignite more easily.

2.2.2.2 Automotive Petrol

It is a blend of hydrocarbons derived from crude oil and is used to fuel spark-ignition engines. Petrol contains hundreds of individual hydrocarbons which range from n-butane to C_{11} hydrocarbons such as methyl naphthalene. The olefin content of petrol commonly ranges from 5% to 20% but can vary depending upon the nature and amount of the blend stock utilized. The boiling range for petrol is 29.4^{0}C to 226.7^{0}C. In the main, the properties of commercial petrol are influenced by both refinery practice and by the nature of the crude oil refined. An important property of gasoline is the anti-knock quality denoted by the octane number which affects the engine design and operating conditions. It is used to rate petrol into grades such as Regular and Premium. Engine knock is measured by two ASTM methods; namely, ASTM D-2699 [identified as the

Research Octane Number-RON] and D-2700 [identified as the Motor Octane Number-MON]. The difference between RON and MON is termed "***Sensitivity***". The sensitivity value represents the effect changes in operating conditions will have on knock properties of the fuel and this can be influenced by the hydrocarbon composition of the fuel. Fuels with higher percentages of unsaturated and aromatic compounds have high sensitivity. Linear paraffin in fuel is less sensitive, while highly branched paraffin can be more sensitive.

Advances in the field of engine design have led to the development of more efficient and high performance engines which require more complex fuels and lubricants for their operations. To meet the high performance requirements as well as achieve good storage characteristics, numerous chemicals called **"Additives"** are mixed into the gasoline.

Basically, a fuel additive is a material used at low concentration either to improve the performance of a product with respect to some existing properties or to confer on the product some entirely new properties. Some of the gasoline additives are compounds containing oxygen, nitrogen, lead, halogen, phosphorus, nickel, manganese and iron.

A convenient way of classifying petrol additives is according to the applications for which they are intended. Some of the common types are,

(i) Anti-oxidants: They help to prevent oxidative degradation and formation of gum in gasoline (particularly cracked ones) under storage. Thermal and catalytic cracking process increase the yield of gasoline per barrel of crude oil and the cracked components [olefinic hydrocarbon] have higher octane numbers than straight-run paraffin petrol and hence allow increased compression ratio. However, the olefinic compounds oxidize easily, giving rise to pre-knock peroxides, and gum formation in the engine.

(ii) **Anti-knock**: They are used to raise the resistance of fuel to detonation so that the fuel can be used in higher compression ratio engines. The earliest types are Tetraethyl Lead [TEL] or Tetramethyl Lead [TML]. They help to prevent engine knock by raising the temperature at which petrol begins to burn and by slowing down the speed of combustion. However, due to the presence of lead in petrol, it was practically impossible to use catalytic converters to cleanse pollutants from the exhaust gases. Attempts have been made to produce unleaded high octane fuels through catalytically reforming and isomerisation of the feedstock but such fuels are very expensive. Another approach in the recent is the use of some oxygenates to blend petrol. The common ones are methanol, ethanol, tertiary butyl alcohol (TBA), and Methyl tertiary butyl ether (MTBE).

(iii) **Detergents/Deposit controllers:** They are added to prevent deposit build up on fuel systems parts, such as carburetors, fuel injectors, inlet valves, valve seats and guides

(iv) **Anti-icing:** Anti-icing additives like Dipropylene glycol and Isopropyl alcohol act as antifreeze to prevent the formation of ice on the carburetor throttle plates and orifices during cold weather which can interfere with the mixture flow into engine cylinder.

(v) **Corrosion Inhibitor:** They reduce corrosion and rust in the fuel system and fuel handling facilities. The two common types are copper corrosion inhibitor which helps to prevent sulphur, hydrogen sulphite and mercaptan attack on copper and ferrous metal inhibitor, which prevents water/oxygen initiated corrosion of iron and steel system components.

(vi) **Metal Deactivators:** They chelate metals which may act to catalyze fuel oxidation reactions

(vii) **Demulsifiers:** They are used to help prevent the detergent additive from emulsifying with water; emulsified detergent will not perform.

(viii) **Dyes:** They are used for identifying gasoline grades and types. This helps to prevent accidental mix-up of gasoline types.

2.2.2.3 Aviation Fuels

The common ones are Aviation Gasoline and Aviation Turbine fuel or Jet fuels.

Aviation gasoline is very complex fuel with more stringent specifications than motor spirit It contains a high concentration of alkylate and high octane aromatics. Sulphur content as well as paraffin content is more injurious to this fuel as operation under -60^{0}c is severely hampered due to crystallization of paraffin compounds. Sulphur is presumably kept below 0.05% in order to eliminate the possible pollution and corrosion problems. With the advent of modern jet engines, the demand for aviation gasoline is has gradually declined.

Modern jet engines use fuels that are blended primarily from straight run kerosene or from wide-cut kerosene/naphtha blends off of the atmospheric distillation unit. It contains virtually no olefins with very limited amount of aromatics. High aromatic content can cause high carbon deposit in the engine. A total aromatic content of >30% can cause deterioration of aircraft fuel system elastomers and can lead to fuel leakage. Pour point of this fuel is of extreme importance and should not be higher than -30^{o}c as international flights always visit lands of caprice climates. High smoke point is essential for clean combustion. Jet fuel sulphur content normally ranges from 0.20wt% to 0.40wt%. Metal corrosion may result when high sulphur fuel is burned.

2.2.2.4 Diesel Fuels

Diesel fuel is next in popularity to petrol as automotive fuel. It contains fractions boiling off from approximately 523K to 625K, namely, straight run distillate, cyclic oil, various gas oils and heavy cracked distillates. These higher boiling point fractions contain about 20 times more sulphur than those from which gasoline is derived. Kerosene or jet fuel may be blended into the diesel to improve the low temperature viscosity and handling characteristics. Diesel is thicker than gasoline and has different burning characteristics, hence requires a different engine design and fuel system. The qualities of diesel fuels can be appraised in terms of the following properties, volatility, Viscosity, sulphur content, cetane number, iodine number, relative density, cloud point, pour point, flash point, and calorific value and auto-ignition temperature.

Diesel fuel comes in several different grades, depending upon its intended use. It is a mixture of various petroleum-derived components, including paraffins, isoparaffins, naphenes, olefins and aromatic hydrocarbons, each with their own physical and chemical properties. Diesel is required to satisfy a wide range of engine types, differing operating conditions and duty cycles as well as variations in fuel system technology, engine temperatures and fuel system pressures. It must also be suitable for a variety of climates. The most commonly used guidelines for diesel fuel quality are established by American Society for Testing and Materials (ASTM) international. ASTM specifications are established by consensus, based on the broad experience and close cooperation of producers of diesel fuels, manufacturers of diesel engines and fuel systems as well as other interested partners like the Society of Automotive Engineers (SAE) International. The ASTM standard for diesel fuels is ASTM D975. These standards cover seven grades of diesel fuel oils. These grades are numbers 1-D (S15), 1-D (S500), 1-D (S5000), 2-D (S15), 2-D (S500), 2-D (S5000) and 4-D. The grades are listed in order of increasing density and viscosity. In other words a 2-D grade is denser and of higher viscosity than grade 1-D. The parenthetic numbers such as (S15) refer to the maximum sulphur level thus 2-D (S15) refers to No. 2 diesel with a maximum of 15 parts per million (ppm) sulphur. This is an ultra-low sulphur diesel used in high speed engines with relatively high loads and uniform speeds and also in engines requiring fuels having higher volatility. The S5000 grades are for off-road use only. The No 4-D covers the class of more viscous distillates and blends of these distillates with residual fuel oils. These fuels are used for low speed and medium speed engines employed in services involving sustained loads at substantially constant speed. They are also used in marine and certain industrial diesel applications.

Table 2.5 shows the summary of ASTM Specifications for Diesel Fuels and their importance.

Table 2.5: Summary of ASTM Specifications for Diesel Fuels

PROPERTY	IMPORTANCE
Cetane number	Measure ignitability, reduce knock and smoke
Cetane index/Aromatic limit	Limits aromatic content of fuel to prevent adverse emission impact, reduce knock & smoke
Volatility	Deposits, Wear, exhaust smoke
Viscosity	Injector wear & spray pattern, pump wear, Filter damage

Sulphur Content	To protect emission control equipment
Low Temperature operability	Flow properties, filter plugging
Water sediment &content	Filter plugging, injector wear, increased corrosion
Lubricity	Injector and pump wear
Ash content	Injector and fuel pump, piston & ring wear, engine deposits.
Corrosion	Protect copper, brass, bronze fuel system parts
Flash Point	Safety during fuel handling & storage
Carbon Residue	Fuel system deposits, combuston chamber deposits

Source: US National Institution of   Source :US National Institute of Automotive Service Excellence

The petroleum industry uses a number of commercial fuel additives to meet and maintain diesel fuel properties. They are added at very low concentrations usually at the parts-per million level, and do not add significant volume to the fuel. The US EPA has a list of approved additives as summarized on Table 2.6.

Table 2.6: Types and Functions of Diesel Fuel Additives.

Types Of Additives	Functions of Diesel Fuel Additives
Cetane number improver	Improves ignition quality by raising cetane number, better starts, reduces white smoke
Lubricity improvers	Improves lubricity, better injector & pump lubrication
Detergents/Dispersants	Clean injectors, better spray patterns
Antioxidants	Extend storage life, inhibit oxidation, and reduce gum precipitate formation.
Stabilizers	Inhibit oxidation and extend storage life
Metal deactivators	Deactivator copper compounds in fuel thereby promoting long storage life
Biocides	Inhibit bacterial and fungi growth, help prevent fuel filter plugging.
Pour point depressants	Low temperature operability, improves cold flow

	properties
Cloud point Depressant	Reduce temperature at which paraffins solubilize
De-icers	Prevent fuel line freezing
Anti-foam Agents	Reduce foaming when filling tank
Smoke suppressant	Promote more complete combustion, reduce exhaust smoke
Rust preventors	Reduce formation of rust in fuel systems storage tanks
Demulsifiers/Dehazors	Used to increases the rate of water separation from the fuel
Dyes	To identify types of diesel for regulatory compliance

Source: US National Institute of Automotive Service Excellence,

2.2.3 Properties of Hydrocarbon Fuels

Some important properties of common hydrocarbon fuels used in internal combustion engines include;

(i) Flash Point: This is the temperature at which a fuel vapourizes enough to ignite and burn when in contact with an open flame. The flammability and combustibility characteristics of a fuel are directly related to the flash point. The flash point is also related to the level of fire risk in the transportation and storage of the fuel. According to Occupational Safety and Health Act [OSHA], compounds with flash point values $<37.8^{o}c$ are considered flammable.

(ii) Spontaneous Ignition Temperature: This is the minimum temperature to which the fuel must be heated in the presence of air to promote self-ignition without the need for a concentrated source like spark or flame. In a situation where fuel is stored in high temperature, spontaneous ignition temperature gives an idea of fire hazard potential, for example, in supersonic flight where fuel can undergo kinetic heating. For large molecules, thermal agitation leads to bond breaking and formation of smaller molecules which reaction with oxidizer. In combustion, smaller and more compact molecules can withstand thermal agitation more than larger ones. Thus denser fuels which contain higher properties of large molecules have low spontaneous ignition temperature.

(iii)Cloud Point: Some fuels and oils contain wax which separates from the other components of the fuel at very low temperature. As the wax separates, the fuel turns cloudy or milky. The temperature any which crystallized wax becomes visible is known as the cloud point. The wax can accumulate on fuel filter media and can lead to plugging of small orifices and lines. The plugging temperature is commonly referred to as the Filter plugging temperature.

(iv) Pour Point: This is the temperature at which the quantity of wax in the fuel causes it to gel. When near its pour point, the fuel can become very thick and pumping through the fuel lines becomes difficult thus resulting to engine hunting.

(v) Volatility: This is the tendency of a liquid fuel to evaporate. This fuel property is of basic importance in carbureted engines because of its major influence on the vapour-air ratio in the cylinder at the time of ignition. In engines burning a uniform mixture of fuel vapour and air, the vapour- air ratio must be not less than about 0.5 times the stoichiometric value for satisfactory ignition and flame propagation. It is obvious therefore that the volatility of the fuel must be sufficient to give at least this vapour-air ratio at the time of ignition under all operating conditions including starting and warming up from cold.

(vi) Calorific or Heating Value. It is the quantity of energy released as heat when a unit mass of the fuel is completely burnt. For engineering purposes, heating value is usually used.

Combustion reactions of hydrocarbon fuels yield water as one the products and the heating value depends on the state of the water at the end of combustion i e whether vapour or liquid. If the water is in the liquid phase, we have the higher heating value [HHV] and if the water is in the gaseous phase, then we have the lower heat value [LHV]. The temperature of the exhaust gas in the engine is higher than the condensation temperature of water vapour hence it is not possible to utilize in the engine the energy released through the condensation of water vapour. Consequently, the lower heating values are usually used in engine performance calculations.

(vii) Octane Number. It indicates the ability of a gasoline to resist engine knock or detonation. The higher the fuels octane number, the grater the amount of heat and compression the gasoline can withstand before abnormal combustion or knocking occurs. Since higher compression ratios in an engine result to increased power output and thermal efficiency, high octane number is a desirable quality. There are four basic methods of determining the octane number of gasoline, namely

- Research Method [Research Octane Number or RON].
- Motor Method [Motor Octane Number or MON].
- Road Method
- Research Motor Average Method.

The research and motor methods are the most popular and the octane number is determined using ASTM method. The Antiknock Index is the average of the research and motor numbers. Octane numbers are determined using n-heptane that has an octane number of 0, and isooctane that has an octane number of 100. The octane number of an unknown fuel is based on the percentage volume of a mixture of octane and n-heptane that matches it in pre-ignition characteristics. These tests are conducted in a special test engine with variable compression.

(viii) **Cetane Number.** It rates the ignition properties of diesel fuels. In other words, it is a measure of a fuel's willingness to ignite when it is compressed. This factor influences ease of starting, duration of white smoke after start-up, drivability before warm-up and intensity of diesel knock, roughness and deposit formation in an engine. The higher the cetane number, the more efficient the fuel. Studies show that biodiesel has higher cetane number than diesel fuel because of its oxygen content. Cetane rating is determined using an engine test specified in accordance with ASTM method D613 which involves an engine test comparison with reference fuels using a single cylinder variable compression ratio engine like that of octane number. The primary reference fuels are normal cetane, a straight –chain paraffin having excellent ignition quality [rating of 100] and heptamethyl-nonane, a compound with poor ignition quality [rating of 15]. The percentage of cetane in a blend of these two fuels giving the same delay as the fuel under test is taken as the cetane number of the test fuel.

(ix) **Flammability Limits.** These are the minimum and maximum concentrations of fuel vapour in air below and above which the mixture are un-ignitable. A vapour-air concentration below the lower flammable limits is too lean to ignite, that is, there is not enough fuel to cause ignition while a concentration above the upper flammable limit is too rich to ignite, because there is insufficient oxygen for the reaction to propagate away from the source of ignition. Flammability is an important factor in the development of safe practices for handling and storage of pure liquids or liquid mixtures. Knowledge of flammable limits at elevated temperatures and pressures is also needed in order to ensure safe and economically acceptable operation of chemical processes.

(x) Viscosity. This is the measure of the resistance of a liquid fuel to flow or to shear forces. This property effects the operation of fuel injection equipment particularly at low temperatures when the increase in viscosity lowers the fluidity of the fuel. Biodiesel has a higher viscosity than petrodiesel and high viscosity leads to poorer atomization and engine performance.

(xi) Iodine Value. This is a measure of the amount of iodine required to saturate the olefins bonds in oil. It indicates the level of instauration. It is determined by noting the amount of iodine in grams absorbed per 100ml of the oil sample under test. The iodine absorption occurs at double bonds positions thus a higher number indicates a higher number of double bonds in the oil sample and the greater the polymerization potentials. For biodiesel fuels, the more the double bonds, the lower the cloud point because they resist solidification at lower temperature. The iodine number affects oil viscosity, oxidation stability during storage, cloud point polymerization tendency and the formation of engine deposit. Oils with iodine value less than 25 like coconut oil (with 10) can be used in an engine as neat fuel. Table 2.7 shows the iodine value of common vegetable oils.

Table 2.7 Iodine values of some vegetable oils.

Oil	Iodine Value	Oil	Iodine Value
Coconut	10.2	Rapeseed	98
Palm kernel	37	Cotton seed	105
Mutton tallow	40	Soybean	130
Beef tallow	50	Linseed	178
Palm oil	54	Sardine	185

Groundnut	93	Castor seed	88
Dika nut	92	Physic nut	97
Sand box	130		

Oil seed	**Oil Extraction (kg per 100kg of seed)**	**Oil seed**	**Oil Extraction (kg per 100kg of seed)**
Castor seed	50	Copra	62
Cotton seed	18	Groundnut	42
Mustard seed	35	Palm kernel	36
Palm fruit	20	Rapeseed	37
Soybean	14	Sunflower	32

2.3 Synthetic Fuels

These are fuels that do not occur naturally but are formed or synthesized from other substances. Synthetic fuels are presently being developed to serve as alternative fuels for automotives. The growing demand for crude oil, the dwindling reserves, the desire for clean air and the problem of global warming and environmental pollutions, have sparked off new interest in the search for alternative fuels and sources of energy for the future. Some of the common synthetic fuels are Hydrogen, Alcohol, Biomass fuels, etc.

2.3.1 Hydrogen

Hydrogen is one of the most promising alternative fuels for automotives. It has the advantages of a high heating value on a mass basis (twice that of any hydrocarbon fuel), low air pollution effect, abundance in nature and the capacity to be produced from many sources; it also has high flame velocity, wide flammability limit, and high diffusivity. However, hydrogen is known to have low vapourisation temperature of about -253°C at atmospheric pressure and this makes it difficult to be stored and transported; it has low ignition energy which may cause abnormal combustion and high cost of production.

Hydrogen can be produced from many sources, the major one being water. There are two methods of hydrogen production from water. The first method involves the use of high temperature heat to directly decompose water. This method is called ***thermo chemical decomposition***.

$$6FeCl_2 + 8H_2O \quad = \quad 2Fe_3O_4 + 12HCl + 2H_2\ (650^oC)$$

However, this method is associated with problems of corrosion and material compatibility.

The second method is called ***"Electrolysis***" which uses electric power to decompose water. It involves the passage of an electric current through water by means of *inert electrodes*. As water is virtually a non conductor, an electrolyte such as KOH is added. Equivalent amounts of O_2 and H_2 are liberated at the anode and cathode respectively.

$$2H_2O = \quad 2H_2 + O_2 + \text{Energy}$$

2.3.2 Alcohol

It is speculated that alcohol has the potential to revolutionize the world's fuel technology trend, particularly in the field of transportation. The reasons behind the significance of alcohol as an alternative fuel for internal combustion engines include:

- Alcohol can be manufactured from a variety of widely available raw materials or non petroleum sources
- There are improved and demonstrated technologies for the production of alcohols (such as fermentation, thermochemical conversion, etc.)
- Alcohols have favourable combustion characteristics such as clean burning, resulting in reduced pollution.
- It has high octane performance (106), high latent heat, boiling point and flash point.

However, alcohol is still expensive to be used as automotive engine fuel. Due to high latent heat, alcohol does not vapourize easily, hence cold starting is difficult. It also burns at about half the rate of gasoline hence it demands a high ignition timing. Very wide and easy access to alcohol as engine fuel will ultimately result in human abuse of alcohol, thus precipitating great social problems.

Ethanol and methanol are the two alcohols that can serve as alternative fuels for internal combustion engines. They are derived from either hydrocarbons or biomass. Methanol is produced by the thermochemical conversion of wood and lignocellulosic materials while ethanol is produced by fermentation of cellulose, sugar or starch bearing feedstocks. Examples of the types of biomass used in the production of ethanol are;

Sugar bearing feedstock ------ sugarcane, molasses, sugar beets

Starch bearing feedstock ------ cassava, cereal crops, grains, sorghum and potatoes

Cellulosic feedstock ------------ wood, straw, organic waste

The production of alcohol from the above raw materials can be divided into three stages, namely,

- Pre-treatment in order to obtain a sugar solution
- Fermentation and
- Separation and distillation of the alcohol.

With the exception of the pre-treatment stage, the above processes are the same for all feedstock. It is easiest to produce alcohol from sugar-bearing raw materials, because the sugar found in the plants is already in a fermentation form. A more or less complex pre-treatment process is required in order to obtain a fermentable substance from the other two feedstock materials.

2.4 Bioethanol

Bioethanol as a motor fuel in the transportation sector, mainly for road transportation, has been subject to many studies and much discussion. Furthermore, the topic involves not only the application and engine technical aspects, but also the understanding of the entire life cycle of the fuel, well-to-wheels, including economical, environmental, and social aspects. It is not, however, the aim of this report to assess every single one of these aspects. The present report aims to address the technical potential and problems as well as the central issues related to the general application of bioethanol as an energy carrier in the near future. A suitable place to start studying a fuel is at the production stage, and bioethanol has been found to have a potential to mitigate greenhouse gases, depending on the production method. This and a potential for replacing fossil fuel-based oil (and being renewable) are the main reasons why ethanol is considered and implemented. Therefore, we must focus on two central questions related to ethanol implementation: how much carbon dioxide (CO_2) can be mitigated and how much fossil fuel can be replaced? A number of life cycle assessments have been performed in order to provide estimates. These assessments have generally shown that bioethanol has very good potential and can mitigate CO_2 emissions very effectively, but It has also been shown that the potential for both fossil fuel replacement and CO_2 mitigation is totally dependent on the method used to produce the fuel. Bioethanol can be made from a wide range of biomass resources, not all equally effective at mitigating CO_2 emissions and replacing fossil fuel. The Brazilian ethanol experience has in many ways shown the way for the rest of the world, not least in the production stage. Brazil was the first and biggest producer of bioethanol, but the United

States, China, India, and European Union have since then increased their production dramatically.

Overall, bioethanol represents the best alternative transportation fuel; its use is projected to increase significantly and remain high. As transportation fuel is a very big sector globally, a shift toward more bioethanol usage will potentially have great consequences in many areas of life, driving the need for more comprehensive evaluation methods and regulations. Among the concerns are the principles of sustainable development, particularly the need for the definition of indicators, regulations, and criteria; not unlike those implemented in the forestry sector.

The most apparent problems in producing the biomass and then processing it to bioethanol are pollution and usage of water, use of fossil fuels in production, soil degradation, and land use conflicts. At the layman's level, perhaps the most intensely discussed concern to date has been the food versus fuel problem. Clearly, we should not deprive people of food in order to produce transportation fuels. As has been stated by the United Nations Food and Agriculture Organization, the problem at the present time seems not to be a lack of food production capability, but rather, economical politics — namely, trade barriers. Aside from that, it has been discussed whether any real potential for greenhouse gas mitigation potential exists with the current forms of ethanol production, especially outside Brazil, since another greenhouse gas, nitrous oxide (N_2O), seems to be emitted when the feedstock crops are grown. This gas is a very powerful greenhouse gas, about 300 times stronger than CO_2. There have been investigations showing a negative potential; that is, bioethanol would be a greater contributor to global warming than regular fossil fuels (gasoline). Another very important issue is the conservation of the natural carbon reservoirs. When land is converted into farm land, there is a possibility of releasing more CO_2 into the atmosphere than the biofuel would be able to mitigate, even over a long time.

Currently, much effort is being put in to solving the problems of the second-generation ethanol technology, the way of producing bioethanol from cellulosic biomass. There is wide agreement about the advantages of this technology, for example, the use of much cheaper feedstock, because several highly efficient (energy) crops can be used, as well as biomass waste such as straw and corn cobs. Another advantage is a very high efficiency, that is, a high yield per area of land used.

Lately there has even been talk about using algae as feedstock, thereby avoiding land use conflicts. Nevertheless, many remain to be resolved before this technology can be used on a wider scale, mainly improvement of cost efficiency as well as process efficiency.

Ethanol has been shown to suit different kinds of integrated production scenarios. In Brazil the processes of producing ethanol and power have now been integrated at many locations with success. Previously the excess biomass, that is, bagasse, was burned under open air rather than being converted to power. This has a significant effect on the overall efficiency of the fuel production. In the United States, massive corn-based ethanol production creates opportunities for production of animal feed. In Denmark integrated production of second-generation bioethanol, biogas, hydrogen, and solid fuel pellets has been demonstrated to be exceptionally efficient at utilizing the biomass waste product straw, as well as reusing process water. The idea behind this method is to imitate nature by reusing the waste products from one process as feed for another process. Yet another facility has demonstrated the integrated production of power, district heating, and first-generation and second-generation bioethanol. The solid carbon that remains from the ethanol production is burned in an efficient power plant, which then supplies the ethanol process with cheap, low-grade steam. The fuel properties of ethanol differ from those of gasoline. Depending on the application, that is, the type of blend used or whether it is used neat, the vehicle special specifications for some parts to function properly. First, ethanol is hygroscopic, and an effort is required to avoid water contamination and the ensuing problems.

Moreover, production methods favor a content of water, because water can be removed only to a certain degree by normal distillation (up to about 95 percent purity), and then another relatively energy costly process removes the remaining water. This makes an argument for using the fuel containing some amount of water. Unfortunately, ethanol has poor blending properties when mixed with either diesel or gasoline, if the ethanol contains more than a very small amount of water.

Phase separation occurs and can, in the worst-case scenario, make the fuel inapplicable or, in other cases, cause all kinds of fuel system and engine problems. These blending problems depend on ambient temperatures and the blending ratios of ethanol, gasoline, and water, and therefore determine the choice of technology for a particular region or country. The worst blending problems occur when low-percentage-ethanol blends containing water are used in cold climates.

Mid-and high-percentage blends can contain much more water, posing fewer problems, and in Brazil, ethanol containing 7 percent water is used widely. The strategy behind this Brazilian watery ethanol fuel is to minimize production costs, because less effort/energy is needed for removing water from the ethanol.

Another issue related to cold climate markets is cold starting or, more precisely, engine start problems and excessive start-up emissions. These problems are related to the use of high percentage-ethanol blends such as E85 and are even more pronounced using neat ethanol.

Ethanol does not contain the light hydrocarbon compounds that make gasoline a relatively good fuel at cold ambient temperatures. The evaporative and flammability properties also contribute to this problem. Nevertheless, there are solutions to these problems. The evaporative properties are also problematic regarding safety and pollution of the environment. Ethanol is more flammable at conditions normally occurring in the fuel system of vehicles and can therefore pose a danger, but preventive measures can be taken. The evaporative properties and the chemical properties can in many cases cause high evaporative emissions from the fuel system, compared to petrol application, and even higher emissions for diesel vehicles.

However, this problem is worse for low-percentage-ethanol blends, and high percentage-ethanol blends and neat ethanol seem to offer improvement compared to petrol (but not diesel).

In terms of engine technical possibilities, almost all ethanol is used in gasoline vehicles, because petrol blends well with ethanol, compared to diesel. In Brazil ethanol application is mandatory in petrol vehicles, with the use of E25 and E100. In Sweden the use of E85 is fairly widespread and in several other countries the use of E5 and E10 is mandatory. Further increases in ethanol applications are somewhat limited by the unfortunate properties of ethanol use in regular petrol vehicles. The general limit for these vehicles is set at about 5–10 percent ethanol in petrol. In the United States and Sweden, the flex fuel vehicles (FFVs) currently on the road are compatible with blends ranging from 0 to 85 percent ethanol content. These vehicles have demonstrated the technical feasibility of running on ethanol fuels with a high renewable content, without higher cost.

Certainly, there are fuel compatibility issues, especially for older vehicles. Corrosion and other types of damages can occur in the fuel system, ultimately resulting in engine failure. Ethanol fuels are therefore not recommended for vehicles made before 1986.

2.4.1 Bioethanol as Energy Carrier — General Issues

This section draws attention to some of the most important issues of large-scale ethanol production. An in-depth discussion of ethanol production is beyond the scope of this report, but review of the literature indicated several important issues that should be addressed here.

2.4.2 Distribution

In the distribution of ethanol, especially petrol /ethanol blends, the problems are mainly those associated with using existing petrol pipelines because of the corrosive and watery nature of ethanol. Furthermore, fuel stations present safety and storing issues.

Nevertheless, years of practical experience have shown that ethanol can be distributed without major problems, using different procedures than those used for petrol. Ethanol is usually distributed in a system specifically designed for it, so that blending issues, for example, water and dirt problems, are avoided, at least until the fuels are mixed at the service stations.

2.4.3 Production

Ethanol is the largest biofuel in the world and is expected to remain so. Figure 2.2 shows how ethanol accounts for a relatively small fraction of the total fuel demand globally. The main suppliers of ethanol are the United States and Brazil.

The production of ethanol increased dramatically from 1975 to 2003, and it therefore seems important to discuss how ethanol is used most rationally. Figure 2.3 shows how ethanol production, mainly for fuel purposes, has risen in these years.

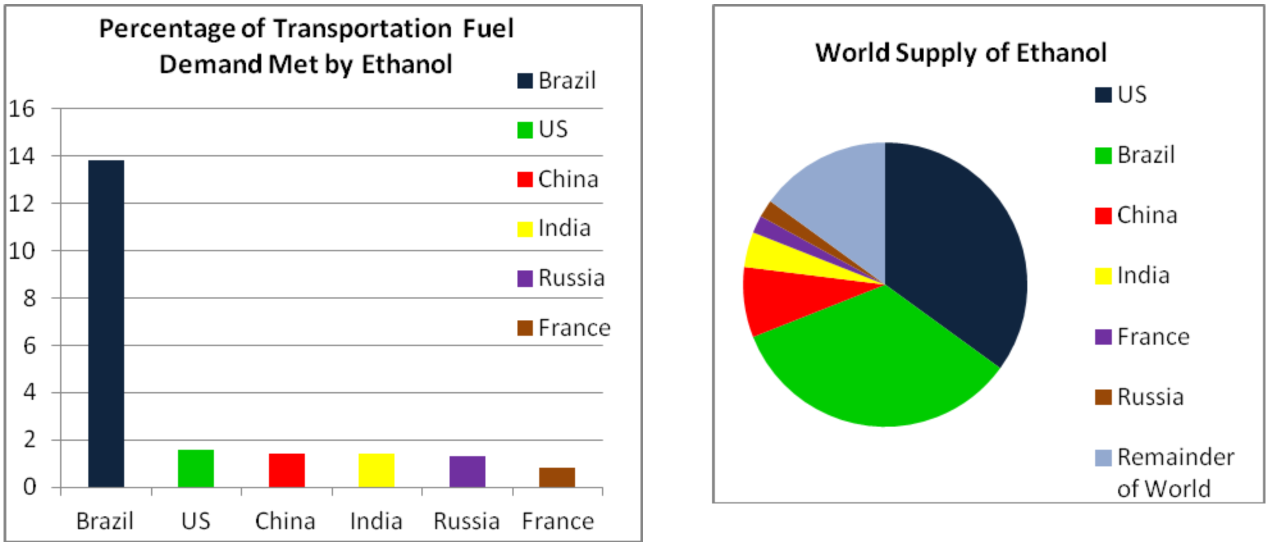


Figure 2.2: World Supply and Demand Met Figures (Source: Fichera and Kueter, 2006, Energy Information Administration, 2003, and Renewable Fuels Association, 2005)

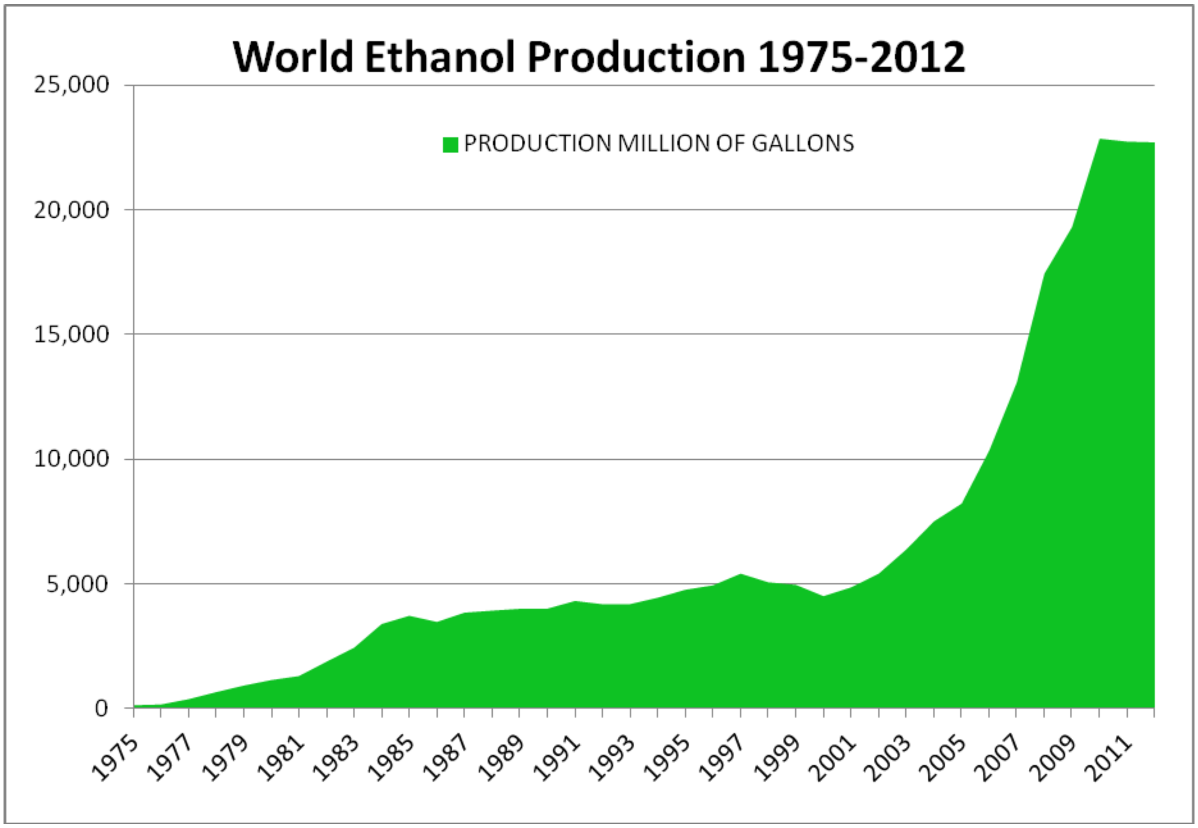


Figure 2.3: World Ethanol Production (Source: RISE6)

First, a continued massive increase in ethanol production and usage will have tremendous effects on the people, economy, and ecosystems of the planet. The IEA projects an average annual growth rate of 6.3 percent for consumption of liquid biofuels from 2005 to 2030, most of that being ethanol [Larsen and Peterson 2007]. Second, an increasing dependency on the fuel will demand reliable production. Therefore, growing of the feedstock crops used for ethanol production must done in a sustainable way.

Sustainability, according to findings reported at the Rio Conference 1992, includes economical, social, and ecological concerns, and it seems necessary to consider all three concerns when deciding whether to use ethanol as a motor fuel extensively. According to the Brundt land report definition of sustainability (1987), sustainable ethanol must provide a solution that satisfies the needs of today without compromising the needs of future generations (ARIC Atmosphere). Economics strongly influences the technical solutions a community or region chooses and thus influences the environment in different ways. At present, it makes more economical sense to keep producing ethanol using first-generation technology, even though the actual GHG gas mitigation and emission benefits in some cases seem rather limited [Wang 2005].

Socially there are heated discussions, at many levels around the world, about the food or fuel issue, but other issues such as regional agricultural development and international trade relations are also important. In terms of ecosystems, the discussions concern topics such as the need to preserve valuable ecosystems, for example, the Amazon rainforests of Brazil, and to ensure the quality of local soil and water.

2.4.4 Bio-ethanol Feedstock

Bioethanol is usually made by fermenting sugar contained in various kinds of biomass: Sugar-rich biomass, mainly sugar beet and sugarcane; Starch-rich biomass, grain (e.g., barley, wheat, corn, rice), potatoes, sorghum, cassava; and Cellulose-rich biomass, straw, wood (residues), corn cobs and stalks, grass, paper and more. About half the world's bioethanol production uses sugar crops as feedstock, mostly sugarcanes but also beets. The majority of the remaining ethanol is produced from starch crops, mainly grains such as corn and wheat [Larsen and Peterson, 2007]. Practically no ethanol is produced from cellulose-rich biomass commercially, but commercial plants are planned [Reed 2007].

Not surprisingly, the most efficient way to produce ethanol today (in terms of cost and CO_2 mitigation) is via Brazilian sugarcane. The feedstock, which is the major contributor to the cost, grows very fast there, and production methods have been refined. Furthermore, it is relatively easy to make ethanol from sugar crops, since the fermentable sugars are more readily accessible than other feedstocks [Larsen and Peterson 2007]. Cellulosic ethanol production is now at a stage where trials of different feedstocks are being conducted. The aim is to find crops that increase the biomass output as well as reduce the negative environmental impacts. Also of interest are the types of land (quality) the feedstock can grow on because of land use issues. Agricultural fertilizers are having significant environmental impacts, such as marine eutrophication, global warming, resource depletion, groundwater contamination, and stratospheric ozone destruction [Crews and Peoples, 2004]. Thus since the purpose of using ethanol is partly to mitigate global warming, the use of synthetic fertilizers in the production of feedstock for ethanol should be reduced.

Some crops can naturally fixate nitrogen from the air, for example, peas, and thus reduce the need for fertilizers. Growing these crops alongside other crops is called intercropping, which has been found to reduce the need for both fertilizers and pesticides in the case of wheat and peas combination [Thomsen et al, 2007]. Other crops do not need as much fertilizer and will still provide very good yields. Switch grass (or prairie grass) is one of the more promising examples of feedstock crops for second-generation ethanol production because of its high yield, low fertilizer requirements, soil restoring properties, good disease and pest resistance, and low cost of production [Samson and Omielan, 2007; University of Nebraska 2008].

A joint USDA-ARS (U.S. Department of Agriculture, Agricultural Research Service) and Institute of Agriculture and Natural Resources (U.S.) study has found, that cellulosic ethanol production from switch-grass could reduce GHG emissions up to 94 percent compared to gasoline.

The switchgrass is intended for growing on marginal lands, and the researchers estimated an ethanol yield of 85 percent of what is currently achieved on class 1 farm land with corn ethanol in the United States. The study was based on a 20-acre trial. Switchgrass is not a solution for first generation ethanol production, however, since it is almost purely cellulosic.

The development of feedstock for ethanol is at a stage where new methods are on the way, while the old practices still exist alongside. In order for the new methods to gain a foothold, a prerequisite is maturation of second-generation ethanol production processes and, in particular, methods for cost-effective breakdown of the strong lignocellulosic molecules of biomass.

2.4.5 Production Methods

As discussed later, the production method is the key factor determining the degree of sustainability of ethanol. There are great differences in the life cycle effects of ethanol produced by different feedstocks and by different methods.

2.4.5.1 First Generation Technology

The traditional production of ethanol follows these general steps:

1. Milling of biomass to break it down to finer parts, a substance called the meal; (This stage can be done either wet or dry; dry processing in some cases can save nearly 50 percent of the total energy used to produce the ethanol [Larsen and Peterson 2007].)

2. Cooking and liquefaction, in which the meal is mixed with water and enzymes and cooked into a mash;

3. Saccharification, a secondary enzyme is used to produce sugars that can be fermented;

4. Fermentation of sugars with yeast to form CO_2 and watery ethanol (about 10 percent pure);

5. Distillation of the wet ethanol to concentrate the ethanol up to 95 percent;

6. Dehydration of the remaining 5 percent water to make fuel-grade ethanol; and

7. Denaturing, usually with gasoline to make the ethanol undrinkable.

The main inputs are feedstock, enzymes, yeast, energy, water, and denaturant. The main outputs are ethanol, CO_2 and co-products, which are used as animal feed called distillers' grain (DDGS). The CO_2 is often captured and purified to be sold to other industries [Chiasson 2007].

In some places, in Brazil, for example, the energy input for ethanol production comes from the crop used as feedstock. To provide heat for the boiling and distillation processes, the leftover biomass (bagasse) from the sugarcanes is combusted. In many other cases the energy comes from fossil sources, typically natural gas or coal. Thus, the impact on the effective CO_2 mitigation benefit of the fuel depends on whether the first or second option is used. Low temperatures generally characterize the majority of the energy used in ethanol production.

The cooking process normally happens at about 80°C and distillation at about 100°C [Chiasson 2007]. From an energy-efficient viewpoint, it therefore seems appropriate to use waste heat from other processes such as electricity generation instead of high worthy/quality energy such as natural gas, coal, or even biomass.

2.4.5.2 Second Generation Technology

Second-generation ethanol, also called cellulosic ethanol, is produced in almost the same way as first-generation ethanol. The pre-treatment needed to access the fermentable sugars in the ligno-cellulosic plant materials, however, is much more difficult and may, depending on the feedstock, require acid, pressurized steam, special enzymes, or a combination. These methods can result in undesirable toxins that inhibit the following fermentation process. Once decomposed, the biomass requires a fermentation process in which both hemicellulose (C_5) and cellulose (C_6) sugars must be processed.

A state-of-the-art report [Larsen and Peterson 2007] has identified important research tasks for second generation ethanol production: Pre-treatment and decomposition processes that create a minimum of toxic fermentation inhibitors and use fewer chemicals; Reduction of enzyme costs (The price of enzymes has gone down significantly recently, but this is still a problematic issue for full-scale commercialization.); Techniques for processing at high solid levels (i.e., minimizing water and thus energy use);

Development of microorganisms that can tolerate inhibitors and ethanol and can process both C_5 and C_6 sugars; Higher degree of process integration to reduce water consumption; and Recovery of lignin waste products for use in power production, for example. Almost all ethanol is currently produced by the first-generation technology. Second-generation technology is at a stage where a great deal of research is being conducted. Pilot and demonstration plants are running, but commercial plants are not in operation, although several are in the planning phase. The status of commercialization of cellulosic ethanol (by 2007) is as follows: 15-20 pilot plants worldwide, mostly small-batch operations; two demonstration plants open (Ottawa and Japan) with 2–3 others to open later in 2007; 15-20 commercial plants being built worldwide; and Large range of feedstocks being investigated [Reed, 2007]. The major advantage of cellulosic ethanol is the low cost of feedstock, which as mentioned can be agricultural or forestry residues or more dedicated energy crops such as willow and switchgrass. Another advantage is that second-generation production does not conflict, in the same way as first-generation ethanol, with production of human food. Unfortunately, the economics of cellulosic ethanol are currently at a stage where the low cost of feedstock does not outweigh the high cost of production.

The advantages of second-generation technology over first-generation technology are mainly as follows:

Much higher utilization of the individual plant, providing higher production efficiency and yield per hectare;

Fewer or no conflicts between food and fuel interests because other types of crops or even agricultural waste can be used (There can be a conflict due to the use of arable land.), cheaper feedstock, possibly more sustainable feedstock production, and Very high CO_2 mitigation, up to 94 percent.

The IEA projects that widespread usage of second-generation technology will be a reality after the year 2020 [IEA, 2007], Integrated Approaches

Ultimately production of ethanol could be combined with the production of chemicals, power, heat, food, animal food, and fuel [Personal Interview 2007]. Ethanol production could also use various resources such as household waste and agricultural waste. Gasification and gas-to-liquid fuel processes could be used in the production of ethanol and other fuels [Personal Interview 2007]. Another option would be to integrate the production of biodiesel and ethanol to minimize the transportation of biomass. As discussed later, biodiesel has shown promising properties for blends of ethanol and diesel. If the biodiesel is made from, for example, palm oil, only the palm fruit is used. Integrated biofuel production could include cellulosic ethanol production from the biomass left over from the palm tree, thus utilizing more of the palm, or electric power could be co-produced by using mostly waste heat for fuel production.

On a global basis, electricity production from thermal power plants generally loses 55–65 percent of the fuel energy as relatively low-temperature waste heat, although there are cases in which the heat is recovered and used for district heating or other purposes. Thus a huge potential exists and incentives exist for process integration of ethanol and power production, in order to reduce CO_2 emissions simply because the low temperature waste heat principally does not cause extra CO_2 emissions.

The few second-generation ethanol pilot plants worldwide provide examples of interesting concepts that might also inspire other industries. Among these are two Danish concepts; Maxifuel and IBUS (Integrated Biomass Utilization System, the Venzin vision). Maxifuel integrates the production of ethanol, biogas, hydrogen, and solid fuel pellets. The concept aims to reuse or recirculation process streams in order to reduce the environmental impact. The biogas production is added as a way of cleaning and reusing the process water, but is also beneficial to the overall energy balance and economy [Biogasol APS 2008]. The philosophy is that the waste or coproduct of one process must be used as input for the next so that the waste streams are minimized.

The IBUS concept integrates a biomass/coal-fired power plant (CHP) with first-and second-generation ethanol production. The products are ethanol, solid biofuel, animal feed (DDGS), and fertilizer. The ethanol process receives low-cost steam and efficiently produced power from the power plant, while the power plant receives high-quality solid biomass fuel, a leftover from the ethanol process. Integrating these two processes achieves a reduction in investments, because no power/steam unit is needed for the ethanol plant [Kristensen, 2007]. Both the IBUS and Maxifuel concepts claim to have solved all major bottlenecks and barriers for cellulosic ethanol production; the only challenge remaining is the up-scaling of the process into a cost-effective industrial production.

2.5 Biodiesel

Biodiesel fuels are methyl or ethyl esters of long chain fatty acids derived from renewable organic sources like vegetable oils and animal fats. They can be used in neat form or blended with diesel fuel to run normal diesel engines. When blended with diesel fuel, the blends are denoted as B_{XX}, with XX representing the percentage of biodiesel contained in the blend by volume. For example, B_{20} means 20% biodiesel and 80% diesel fuel. Some national and international specifications for biodiesel are ASTM D6751 (US), DINV51606 (Germany), EN14214 (European Committee for Standardization), ONC 1191(Austria), UN110635 (Italy), SS155436 (Sweden), BIS (India), and CSN656507 (Czech Republic).

2.5.1 Biodiesel Production

The use of straight vegetable oils in diesel engines has caused some problems due to their high viscosity and low volatility. The high viscosity causes some pumping difficulties, reduces spray penetration and hence increased engine deposit and lubricating oil thickening in diesel engines (Sangha et al, 2004; Alamu, et al, 2007). Efforts have been made to chemically modify the molecular structure of the oils. The modification is usually aimed at reducing the viscosity and increasing the volatility so that their combustion related properties are brought closer to those of petrodiesel [Krishnakumar, et al, 2008; Venkateswara, et al, 2008]. Different methods of altering the molecular structure of the vegetable oils include, catalytic cracking, blending, thermal decomposition, micro emulsion and transesterification.

Transesterification has been widely acknowledged as one of the best methods of producing biodiesel from vegetable oils and animal fats because the fatty acids esters formed have physical properties close to those of diesel and can be used pure or as a blend with diesel in engines without hardware modification or engine failure [Venkateswara, et al,2008; Ulfschuchardt, et al, 1998; Tewari et al., 1984].

Trasesterification is a chemical reaction in which the triglycerides of the oils or fats react with trihydric alcohol in the presence of catalyst to form esters of fatty acids and glycerol as the by-product. (Morrison,et al, 2005). The process consists essentially of three consecutive reversible reactions and in each stage, triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol accomplished by the release of ester at each step. Transesterification can be base catalyzed, enzym catalyzed or acid catalyzed. It can also be catalyst- free like the supercritical transesterification which uses supercritical methanol at high temperatures and pressures in a continuous process. In the supercritical state, the oil and methanol are in a single phase and reaction occurs spontaneously and rapidly (Bunkyakiat, et al., 2006).The catalyst is usually used to improve the reaction rate and biodiesel yield.

2.5.2 Chemistry of Transesterification

Biodiesel is produced from triglyceride sources such as vegetable oils, animal fats and waste greases like yellow and brown greases. Oils and fats belong to a family of chemicals called lipids and they compose mainly of triglyceride molecules. A triglyceride molecule is basically a triester of glyceride and three fatty acids (long alkyl chain carbonic acids). Mono and di glycerides can be obtained from triglycerides by substituting 2 and 1fatty acids moieties with hydroxyl groups respectively. Lipid feed stock used in biodiesel production may contain a mixture of all these glycerides species plus free fatty acids. The chemical transformation of lipid feedstock to biodiesel involves the transesterification of glyceride species with alcohol to alkyl esters. The major active species in the transesterification process are the alkoxides (methoxide ions) which are formed by the reaction of alcohol with hydroxyl ions from the alkaline hydroxide. The reaction produces protonated catalyst in addition to the methoxide ions as shown below.

$$CH_3OH + B \rightleftharpoons CH_3O^- + BH^+$$

Where B is the catalyst like sodium or potassium hydroxide. The methoxide ions are strong nucleoplules which attack the carbonyl moiety in triglyceride molecules to produce a tetrahedral intermediate from which the alkyl ester and corresponding anion of glyceride are formed

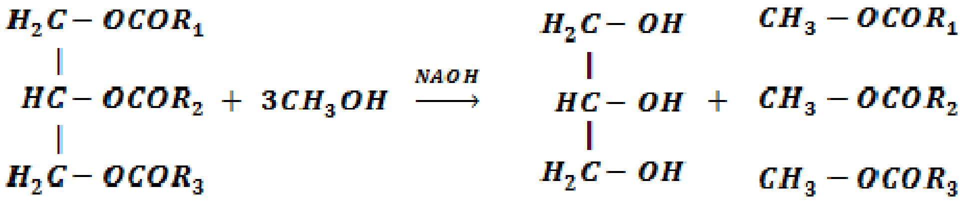
The nucleophile attack of the alkoxides at the carbonyl moiety in triglyceride molecules produces a tetrahedral intermediate from which ~~the~~ alkyl ester and corresponding anion of diglyceride are formed.

This latter deprotonates the catalyst, thus regenerating the active species which is now ready to react with a second molecule of the alcohol, thus starting another catalytic cycle till the triglyceride are Transesterified to glycerol and alkyl esters (biodiesel).In the main, 3 consecutive reactions are required to complete the transesterification of a triglyceride molecule.

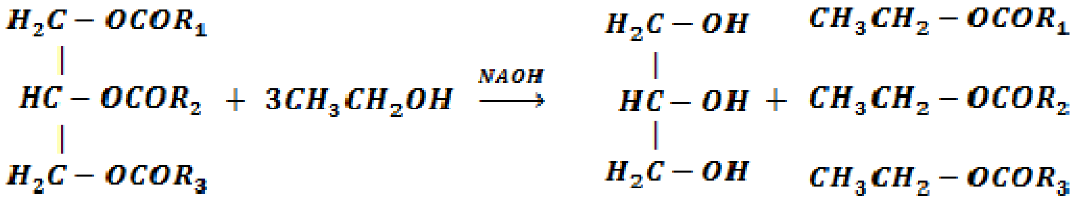
The net reaction produces 3 moles of alkyl esters and 1 mole of glycerol for each mole of triglyceride transformed.

The overall reaction is therefore a sequence of 3 consecutive and revisable reactions.

$$RCOOR' + R''OH \overset{catalyst}{\Longleftrightarrow} R'OH + RCOOR''$$



$$\begin{array}{l} H_2C-OCOR_1 \\ \quad | \\ HC-OCOR_2 \\ \quad | \\ H_2C-OCOR_3 \end{array} + 3CH_3OH \xrightarrow{NAOH} \begin{array}{l} H_2C-OH \\ \quad | \\ HC-OH \\ \quad | \\ H_2C-OH \end{array} + \begin{array}{l} CH_3-OCOR_1 \\ \\ CH_3-OCOR_2 \\ \\ CH_3-OCOR_3 \end{array}$$



$$\begin{array}{l} H_2C-OCOR_1 \\ \quad | \\ HC-OCOR_2 \\ \quad | \\ H_2C-OCOR_3 \end{array} + 3CH_3CH_2OH \xrightarrow{NAOH} \begin{array}{l} H_2C-OH \\ \quad | \\ HC-OH \\ \quad | \\ H_2C-OH \end{array} + \begin{array}{l} CH_3CH_2-OCOR_1 \\ \\ CH_3CH_2-OCOR_2 \\ \\ CH_3CH_2-OCOR_3 \end{array}$$

The stoichiometric reaction requires 1 mole of a triglyceride and 3 mole of the alcohol. An excess alcohol is however added to shift the reaction equilibrium to the right side in order to increase the yield of alkyl esters and to allow its phase separation from the formed glyceride. The R_1, R_2 and R_3 are long hydrocarbon chains sometimes called fatty acid chains.

There are about five types of chains that are common in most vegetable oils and animal fats (others are present in small amounts). The relative amount of the five methyl esters determines the physical properties of the fuel such as the cetane number, cold flow, and oxidative stability.

These chains are designated by two numbers separated by a colon. The first number designates the number of carbons atoms in the chains and the second number designates the number of double bonds. The number of carbon atoms includes the carbon that is double bonded to the oxygen atom at one of the fatty acid (the carboxylic carbon). The common types of long hydrocarbon chains are:

Palmitic: R = $(CH_{2)\,l4}$ –CH_3 16 carbons, 0 double bonds (16:0)

Stearic: R = $(CH_2)_{16}$ – CH_3 18 carbons, 0 double bonds (18:0)

Oleic: R = $(CH_2)_7$CH-CH $(CH_2)_7$-CH_3 18 carbons, 1 double bonds (18:1)

Linoleic: R = $(CH_2)_7$ CH=CH-CH_2-CH=CH $(CH_2)_4$-CH_3 18 carbons 2double bonds (18:2)

Linolenic: R =$(CH_2)_7$CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH3 18 carbons 3 double bonds (18:3)

One important issue during the production of biodiesel is the completeness of the transesterification reaction. Where the reaction is incomplete, there will be triglycerides, di-glycerides and mono-glycerides left in the reaction mixture. Each of these compounds contains a glycerol molecule that has not been released. The glycerol portion of these compounds is referred to as bound glycerol. When the bound glycerol is added to the free glycerol, the sum is known as the total glycerol. The ASTM specification requires that the total glycerol be less than 0.24% of the final biodiesel product as measured using a gas chromatographic method described in ASTM D 6584.Since the glycerol portion of the original oil is usually about 10.5%, this level of total glycerol corresponds to 97.7% reaction completion. Most of this glycerol is removed during the water washing process. Water washed fuel is generally very low in free glycerol, especially if hot water is used for washing. Fuel with excess free glycerol will usually have a problem with glycerol setting out in storage tanks, creating a very viscous mixture that can plug fuel filters and cause combustion problems in the engine. The residual alcohol level in the biodiesel should be very low and a specific value for the allowable alcohol level is specified in European biodiesel standards (0.2% in EN14214). The ASTM standard limits the amount of alcohol to the very low level (<0.1%). Both the alcohol and catalysts are removed by water washing.

2.5.2.1 Base Catalyzed Transesterification

The base catalyzed transesterication employs a strong base capable of deprotonating the alcohol (either sodium or potassium hydroxide) as catalyst while the alcohol can be ethanol or methanol. The base is dissolved in the alcohol to make a convenient method of dispersing the otherwise solid catalyst into the oil. The base-catalyzed transesterification technique is usually preferred because it is the most economical process requiring only low temperatures and pressures and produces about 98 percent conversion yield. Besides, the base catalyzed transesterifiction proceeds faster than acid catalyzed reaction.

Some studies on transesterification have concentrated on optimizing the reaction variables. The results of these studies showed that the base catalyzed transesterification of vegetable oils can be affected by factors like, Reaction temperature, Catalyst concentration, Catalyst type, Reaction time and Reactant molar ratio. [Krishnakumar et al 2008; Lalita et al, 2004; Nye and Smithwell, 1983]. Production yield was found in some cases to decrease with increase in the reaction temperature and mass ratio probably, due to increase in solubility which reduces separation of glycerol.

Lalita et al (2004) suggested that the optimum conditions for a biodiesel yield of about 99.27percent are room temperature (30 degrees), 1% catalyst concentration, 120 minutes reaction time. Molar ratio range of 3:1 to 6:1 has also been suggested. Freedman et al [1984], suggested that for maximum yield of methyl esters, a molar ratio of 6:1 should be used. They opined that molar ratios greater than 6:1 do not enhance yield due to complication in the recovery of the methyl esters and glycerol. Lalita et al [2004] found that catalyst concentration was the most important factor that affect methyl ester yield in the transesterification of palm kernel oil at room temperature.

2.5.2.2 Transesterification Procedure

The basic steps involved in transesterification process are essentially determined by the type and quality of the feedstock used. The amount FFA existing in the oil is a vital measure of its quality and it affects the processing of biodiesel. Fresh vegetable oils have lower FFA content than used oils and fats. Vegetable oils are usually liquids at room temperature because of the degree of unsaturation and number of carbons in the fatty acid radicals while fats are semi-solid at room temperature because their fatty acid composition is more saturated and it results to a higher melting point.

Generally, when the FFA level is less than 1% and certainly if it is less than 0.5%, the FFAs can be ignored. The common amounts of catalyst needed are:

Sodium hydroxide	1% of triglyceride weight
Potassium hydroxide	1% of triglyceride weight
Sodium methoxide	0.25% of triglycerides weight

When the FFA levels exceed 1%, the pretreatment of the feedstock is required. One approach that is adopted is the use of extra alkali catalyst, a portion of which is devoted to neutralizing the FFAs to form soap while still leaving enough to act as the reaction catalyst. Since it takes one mole of catalyst to neutralize one mole of FFA, the amount of additional catalyst can be determined as thus:

Sodium hydroxide: [%FFA](0.144)/P + 1%
Potassium hydroxide: [%FFA](O.197)/P + 1%
Sodium methoxide [%FFA](0.190) + 0.25%

For potassium, P is the purity factor. A recipe proposed by Charles. (1994) for making biodiesel is

For Methyl Ester Biodiesel

MeOH = 0.225xOil
KOH = Oil/100

Where Oil = desired amount of oil in liters, MeOH = amount of methanol in liters, KOH = amount of potassium hydroxide required in kg.

For Ethyl Ester Biodiesel

EtOH = 0.2738 x Oil
KOH = Oil/85

Where Oil = desired amount of oil in litres, EtOH = Amount of ethanol in liters, K0H = amount of potassium hydroxide required in kg.

Majority of the oils and fats used for biodiesel production compose of about 95% triglycerides which are esters resulting from the union one unit of glycerine with three units of fatty acids, linked with ester linkages. The remaining non-triglyceride percentage contains various amounts of impurities including free fatty acids (FFA), gums, phospholipids, tocopherols, colour pigments, sterols, oxidized materials, waxes, moisture and dirt. These impurities affect the colour, flavor, foaming and smoking stability of the finished products. The primary concerns among these impurities are FFA and phosphatides. Phosphatides consist of polyhydric alcohols combined with fatty acids, phosphoric acid and a nitrogen containing compound. The reduction of FFA and phosphatides content of oil is usually of great concern and can be effected by alkalide treatment. The tocopherols are very vital constituents of oils because they act as natural antioxidant protectors which retard the development of acidity hence effort is made to retain them in the finished oils.

Before the main reaction is carried out, preliminary experiments are usually conducted in order to: determine the specific gravity of the oil so as to ascertain the amount of alcohol (methanol) to use for the oil and; determine through titration the amount of catalyst needed to completely neutralize any free fatty acid present so as to ensure a complete transesterification. With the required amounts of alcohol and catalyst determined, the following steps are adopted.

(i) **Purification;** Oil feedstocks particularly waste oils are usually filtered to remove dirt and other non-oil materials. Water is also removed since its presence causes the triglycerides to hydrolyze to give salts of the fatty acids instead of undergoing transesterification to yield biodiesel.

(ii) **Neutralization;** If the product of acid esterification is used, then extra base catalyst is added to neutralize the acid added at this stage. The quantity of base (in moles) required to neutralize the acid is determined through titration. Most low cost feedstocks available for biodiesel production contain large amount of free fatty acids (FFA).The following ranges of FFA are commonly found in biodiesel feedstocks;

Refined vegetable oils	**<0.06%**
Crude vegetable oils	0.3- 0.7%
Used vegetable oils	2- 7%
Animal fat	5-30%
Tap grease	40-100%

Fatty acids normally react with alkali catalyst to produce soaps. Soaps inhibit the reaction and allow emulsification which causes the separation of the glycerol and ester phases to be less sharp. Soap formation also produces water that can hydrolyze the triglycerides and contribute to the formation of more soap. The presence of free fatty acids beyond the recommended level will enhance saponification reaction as side reaction during the transesterification process. This will reduce the conversion of vegetable oil into biodiesel and also leads to the formation of soap hence causing difficulties in the separation of biodiesel and glycerol.

(iii**) Mixing of Alcohol and Catalyst;** the catalyst is usually a strong base like sodium or potassium hydroxide. The required quantity is dissolved in the alcohol to form a methoxide. The alcohol/catalyst mix is then charged into the reactor. Excess alcohol is normally used to ensure total conversion of the oil to biodiesel.

(iv) Transesterification. The mixture of alcohol and catalyst is introduced to the heated oil in the reactor which is then closed to the atmosphere to prevent the loss of alcohol. The mixture is stirred continuously and kept above the room temperature in order to speed up the reaction and the reaction is allowed on for about 1-8 hours.

(v) **Phase separation.** On completion of the reaction, the biodiesel separates to form an amber yellow layer on top of the glycerol. The glycerol is denser and settles at the bottom. It can be drawn from the bottom of the reactor or settling vessel. The separation can also be done by the use of a centrifuge.

(vi) **Alcohol Recovery:** The alcohol is normally recovered to prevent the reaction reversing itself. The alcohol is usually recovered by the using distillation process and is recycled back to the beginning of the process.

(vii) **Biodiesel Refining.** The decanted biodiesel is taken through a refining process to remove excess alcohol, residual catalyst and soap. This is achieved through washing with clean warm water. Further distillation process can be carried out to produce a colourless and odourless methyl or ethyl esters.

(viii) **Glycerol Refining.** The crude glycerol contains unreacted catalyst and soap that are neutralized with an acid. The purified glycerol can be sold to pharmaceutical and cosmetic industries.

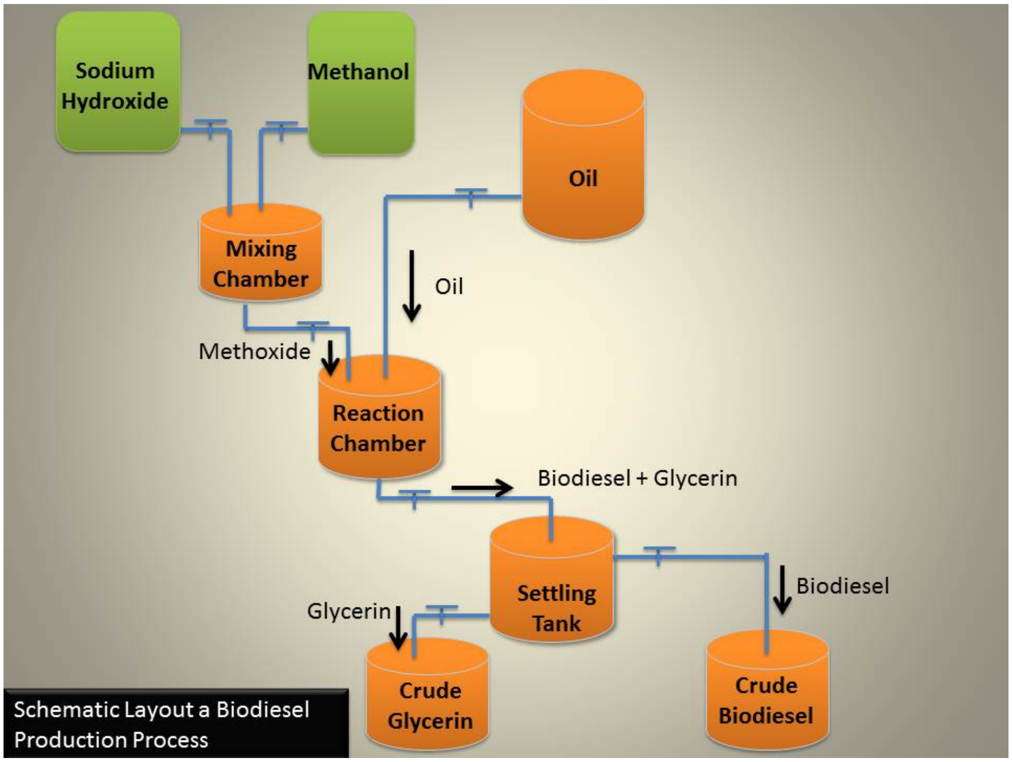


Fig 2.4: Schematic Layout of Biodiesel Production Process

2.5.3 Alternative Methods of Biodiesel Production

There are multiple operating options available for making biodiesel. Many of these technologies can be combined under various conditions and feedstock in an infinite number of ways. The choice of method is influenced by the desired capacity, type and quality of feedstock, alcohol recovery, and catalyst recovery. The other options include,

- ✓ Continuous Process System
- ✓ Supercritical Process (non-catalytic)
- ✓ Ultra Shear & High Shear In-line Reactors
- ✓ Ultrasonic Reactor Method
- ✓ Microwave Method.

i. **The Continuous Process System:** This is a popular alternative to the batch process that uses continuous stirred tank reactors (CSTRs) in series. The system can be varied in volume in order to allow for a longer residence time so as to achieve greater extent of reaction. An essential element in the design of this system is sufficient mixing input to ensure that the composition throughout the reactor is essentially constant. This has the effect of increasing the dispersion of the glycerol product in the ester phase. The result is that the time required for phase separation is extended. There are several processes that use intense mixing, either from pumps or motionless mixers to initiate the esterification reaction. The mixture moves through this type of reactor in a continuous plug, with little mixing in the axial direction. This results in a continuous system that requires rather short residence times, as low as 6 to 8 minutes, for near completion of the reaction. This type of reactor called Plug-Flow Reactor behaves as if it were a series of small CSTRs joined together.

ii. **Supercritical Process:** This is a catalyst free method of transesterification which uses supercritical methanol at high temperature and pressure in a continuous process. When a fluid or gas is subjected to temperatures and pressures in excess of its critical point, there a number of unusual properties exhibited. In the supercritical state, the oil and methanol are in a single phase, and reactions occur spontaneously and rapidly. Under supercritical condition, the reaction is completed in about 4 minutes. The process can tolerate the presence of water in the feedstock and free fatty acids are converted to methyl esters rather than soap, hence a wide range of feed stocks can be used. The catalyst removal step is eliminated but capital and operating cost as well as the energy consumption could be higher.

iii. Ultra-shear & High Shear In-line Reactors: These reactors allow for the continuous production of biodiesel hence the production time is considerably reduced and the output is increased. In ultra- shear, up to three sets of rotors and stator blades are used. These convert mechanical energy to high tip speed, high shear stress, and high shear frequencies. The reaction takes place in the high-energetic shear zone of the mixer by reducing the droplet size of the immiscible liquids such as oil fats and methanol and as a result, the surface area of the reactants is increased and hence a faster reaction.

iv. Ultrasonic Reactor method: The cavitations in the ultrasonic reactor method caused by the ultrasonic waves make the reaction mixture to produce and collapse bubbles instantly. This provides simultaneously the mixing and heating required to carry out the transesterification process. Thus using an ultrasonic reactor for biodiesel production drastically reduces the time of reaction, reaction temperature and energy input. Industrial ultrasonic devices can allow for the industrial scale production of several thousand barrels per day.

v. Microwave Method: This method uses commercial microwave ovens to provide heat needed for transesterication. The microwaves provide intense localized heating that may be higher than the recorded temperatures of the reaction vessel. A continuous flow process producing about 6 liters/minute at 99% conversion rate has been developed.

2.5.4 Biodiesel Characteristics

(i) Physical characteristics

The results of characterization of biodiesel show that it possesses properties that are similar to petrodiesel as shown on Table 2.8. It can be used in a neat state (B100) or blend with petrodiesel in a diesel engine with minimum engine modifications. The most commonly used blend is B20 which is a mixture of 20% biodiesel and 80% petrodiesel by volume. By composition, biodiesel contain less carbon and sulphur than petrodiesel and about 11% oxygen by weight.

Table 2.8 ASTM range of Allowed Values for D2 & D6751

Property	Diesel ASTM D975	Biodiesel ASTM D6751
Standard composition	C 10-C21	C12-C22
Kinematic viscosity@40	1.9 to 4.1	1.9 to 6.0
Specific gravity (g/ml)	0.85	0.90
Flash point (C)	60 to80	100 to 170
Cloud point (C)	-15 to 0.5	-3 to 12
Pour point	-35 to-15	-5 to16
Relative Density @ 15 ^{o}C	0.847	0.878
Oxygen (wt%)	0	11
Carbon (wt%)	87	77
Hydrogen (wt%)	13	12
Cetane number	40 to 55	48 to 60
***B O C L E**	3600	7000

*Ball-on-cylinder lubricity evaluator
Source: National Renewable Energy Laboratory.

The oxygen content ensures more complete combustion and reduces emission of unburnt hydrocarbon and carbon monoxide. The reduced carbon content decreases exhaust emissions of carbon monoxide, carbon dioxide and soot. The lower sulphur content of biodiesel is important for two primary reasons, firstly, as a low sulphur fuel, biodiesel produces little or no emissions of sulphur dioxide which contributes to respiratory illness, aggravates existing heart and lung diseases, contributes to the formation of acid rain and can impair visibility (U.S. EPA, 2008). Secondly, existing regulations in the US and Europe have ensured that the level of sulphur in highway diesel fuel is reduced by 97% and biodiesel is already compliant with the standard (National Biodiesel Board, 2002). Biodiesel has a higher flash point than diesel because of its higher number of FAMEs which are generally not volatile, thus, biodiesel is safer to handle. Biodiesel has higher cetane number than diesel varying from 47 to 67 in contrast to that of diesel that varies between 40 and 45. Cetane number is affected by the differences in the fatty acid composition of the feedstock oil and the saturation level of the fatty acids (Van Gerpen, 2010), and can impact on engines cold starting ability, noise level and exhaust emissions. The pour and cloud points are both higher for biodiesel than for diesel indicating that biodiesel will tend to gel at higher temperature than diesel thereby causing some engine problems. Biodiesel has higher lubricity than diesel and this is an important property that affects the life of the fuel equipment and engine components. Two primary tests that are used to measure lubricity are the Ball on Cylinder Lubricity Evaluator (BOCLE) and the High Frequency Reciprocating Rig (HFRR) test. A BOCLE test involves pressing a ball bearing against a rotating ring immersed in the diesel fuel. Weight is applied on the bearing until the diesel fuel fails leaving a scruff mark on the rotating cylinder (Stanadyne, 2003). The HFRR test consists of a ball that is placed on a flat surface and then rapidly vibrated back and forth with a stroke distance of 1mm while 200g of weight is applied. The vibratory motion closely models engine vibration. After a given time, the flat spot that has been worn into the ball is measured. Biodiesel properties vary according to the feedstock used. There is however, a greater difference between the properties of diesel and biodiesel than between biodiesel from different feedstocks.

(ii) Emission Characteristics

Significant reductions in carbon, CO_2, HC and particulate emissions have been recorded with the use of biodiesel. This could be probably due to lower carbon content and the presence of oxygen in the fuel which gives better combustion characteristics [Kegl et al, 2008. Venkatesware et al,2008 and Prasad et al, 2010].

Biodiesel is said to be the only alternative fuel to have a complete evaluation of emission results and potential health effect submitted to the US, Environmental Protection Agency under the Clean Air Act Section 211(b). The major types of emissions usually considered in the emission characteristics of biodiesel are carbon dioxide, carbon monoxide, nitrogen oxides, particulate matter and unburnt Hydrocarbons.

(a)Carbon dioxide. Carbon dioxide is a naturally occurring gas and is one of the major greenhouse gases that cause global warming. It is also released into the atmosphere by human activity such as the burning of fossil fuels.

Table 2.9 Engine Emissions of Biodiesel Compared to diesel fuel

Emission	Pure Biodiesel (B100)	Blend(B20)

Hydrocarbons	-93%	- 30%
Carbon monoxide	-50%	- 20%
Nitrous oxides	+13.0%	+2. %
Carbon Dioxide (LCA)	-80.0%	- 80%
Particulate matter		
Sulphates	-30.0%	-2.2%
PAH(Polycyclic aromatic Hydrocarbons)	-100%	-20%
	-80%	-13%
Nitrated PAHs	-90%	-50%
Ozone potential of speciated HC	-50%	-10 %

SOURCE; US Environmental Protection Agency

Biodiesel reduces carbon dioxide emissions when used in place of diesel. This conclusion is based on a life cycle analysis of biodiesel and diesel, accounting for resource consumption and emission for all steps in the production and use of the fuel. The US National Renewable Energy Laboratory (NREL) estimates that the use of pure soybean biodiesel (B100) in urban buses reduces net carbon dioxide emissions by 78.45%. The comparison of CO_2 emissions and energy use begins with the cultivation of the crop (soybean) and petroleum extraction, proceeds with all applicable processing and transportation, and ends with combustion in bus engine. The growth of the oil crop (soybean) plant is assumed to absorb as much carbon dioxide as is emitted by decomposition of crop residue after the harvest and by combustion of biodiesel in the engine. The NREL estimates that pure biodiesel (B100) reduces life cycle consumption by 95% relative to diesel, assuming that the quantity of biodiesel is small enough not to affect production.

(b)Carbon monoxide Carbon monoxide is produced from incomplete combustion of fuels. Unlike many gases, CO has no odour, no colour or taste and it does not cause skin irritation but has higher affinity with the red blood cell than oxygen. If there is a large quantity of CO in the air, the red blood cell may replace oxygen with CO leading to possible tissue damage, carbon monoxide poisoning or death. Biodiesel produces about 11% less CO than No. 2-D diesel fuel possibly due to the oxygen content of biodiesel which tends to ensure complete oxidation of the fuel elements. EPA report indicates that CO emission reductions vary according to the feedstock used

©Nitrogen oxides. Nitrogen oxides (NO_x) is the generic term for a group of highly reactive gases containing nitrogen and oxygen in varying amounts such as nitric oxide (NO), nitrous oxide (N_2O), nitrates (NO_3), and nitrogen dioxide (NO_2) and volatile organic compounds which in the presence of hot, stagnant air and sunlight convert to ozone. Nitrogen oxides are classified as hazardous air-bone toxins because of their deterious health and environment effects. The presence of oxygen in biodiesel improves combustion and therefore reduces hydrocarbon, carbon monoxide, and particulate emissions. However, opinions regarding the emissions of nitrogen oxides vary from one study to another. Some studies concluded that NO_x emissions increased with use of all types of biodiesel. The increase in NO_x is partially attributed to biodiesels higher cetane number which causes shorter ignition delay [Walker, 1994]. NO_x is created when an oxygen/ nitrogen mixture is subjected to high temperatures and pressures. At the start of combustion, the combustion chamber of a diesel engine is filled with air. The oxygen and nitrogen mixture is under high pressure and is fairly hot. If there is a delay in the ignition timing, a large amount of NO_x [McCormick et al, 2003]. Marshall et al [1995] suggested that the remedy is by retarding the engine timing to lengthen ignition time. Although the engine timing has the potential of matching the cetane number, there still lies the problem of biodiesels cetane rating varying more than that of diesel.

(d)Particulate Matter. Particulate matter is generic term used for a type of air-bone pollutants which consists of varying mixtures, complexity and sizes of particles. Particulate matter causes respiratory problems like asthma and cardiopulmonary disease. Particulate emissions from conventional diesel engines are generally divided into three components. Each component is present in varying degrees depending on fuel properties, engine design and operating parameters. The component and the one most closely related to the visible smoke often associated with diesel exhaust is the carbon anceous material. This material is composed of sub-micro sized carbon particles which are formed during the diesel combustion process. It is especially prevalent under conditions of very rich fuel-air ratio. The second component is hydrocarbon material which is absorbed on the carbon particles, commonly known as the soluble fraction. A portion of these materials result from incomplete combustion of the fuel and the remainder is derived from engine lubricating oil that passes by the piston oil rings. The third particulate component is comprised of sulphates and bound water. The amount of this directly related to the sulphur content of the fuel. The use of biodiesel decreases the solid carbon fraction of particulate matter (due to the presence of oxygen) and eliminates the sulphur fraction as there is no sulphur in the fuel).

(e)Hydrocarbons. Hydrocarbons are released into the atmosphere from volcanoes, forest fires, internal combustion engine exhaust and automotive fuel systems (Oguntola, et al. 2009). An EPA study in 1999 put the amount of HC emission from on-road vehicles at 29% of the total HC emissions. Hydrocarbons reduce the ozone layer and are found to be carcinogenous.

Biodiesel has the benefit of reducing HC emissions relative to diesel and there is no significant difference in the percentage reduction of HC emissions between different feedstocks (U S EPA, 2002).

(iii) Engine Durability and Material Compatibility

Most studies have shown no significant difference between biodiesel and conventional diesel fuel in terms of engine durability. Clark et al [1984] found that engine wear rates for engines on 200, 500, and 1000 hours tests were well within specified ranges. In one study conducted at the University of Missouri, a Dodge pick-up truck with a Cummins engine was tested after approximately 100,000 miles of operation and the wear rate was found to be normal [Schumacher et al, 1995]. The lubricity benefits of biodiesel especially compared to low sulphur diesel help to reduce wear and prolong engine life.

On the issue of material compatibility, biodiesel is a natural solvent and will usually soften and degrade certain types of elastomers and natural rubber compounds. High density polyethylene (HDPE) is compatible with biodiesel but polyvinyl chloride (PVC) is slowly degraded while polystyrenes are dissolved on contact with biodiesel. On metals, biodiesel is discovered to have effects on copper-based materials like brass and it also affects zinc, tin, lead and cast iron. Stainless steel and aluminum are not affected. In general, problems with gaskets, hoses, and seals are less pronounced as the percentage of biodiesel in the fuel blend decreases [National Biodiesel Board, 2008].

(v)Handling and Storage

Clean biodiesel made from methyl and ethyl esters of soybean and other vegetable oils is not corrosive to the skin. However, blends of biodiesel can cause irritation and a burning sensation to sensitive body parts, so it is advisable to wear rubber gloves while handling biodiesel. Biodiesel is considered essentially non-toxic (Tyson, 2001). Biodiesel gels at lower temperatures and as the fuel gels its properties are affected, inhibiting its ability to flow out of storage tanks and choking fuel filters and hoses. Biodiesel storage temperature generally depends upon the storage environment. Like conventional diesel, biodiesel should be stored in a clean, dry, dark environment. Extremes of temperature should be avoided when possible, since biodiesel has a higher cloud point and pour point than petrodiesel. Acceptable materials for biodiesel storage include black, mild steel, stainless steel, fluorinated polyethylene, and fluorinated polypropylene. Concrete and concrete lined tanks should be avoided since biodiesel tends to degrade concrete over time.

(v)Solvency

Since biodiesel is a mild solvent, it may help to remove engine deposits that settle in the storage tanks of vehicles as well as systems. As a result, fuel filters in vehicles may become plugged giving the false impression that biodiesel plugs filters, while it actually helps to clear out sediments deposited in storage tanks. If biodiesel or biodiesel blend is used in an engine where No 2 diesel was previously used, fuel filters will initially get clogged as the biodiesel cleans out deposits left behind by the petrodiesel.

(iv)Legislation

The production and use of biodiesel have been greatly influenced by some legislation in different countries. In Europe for instance due to legislation between the years of 1992 and 1994, the European parliament help to increase the production capacity of biodiesel to over 1.1 million tonnes annually. The increase in crop production and the resulting increase in biodiesel production are partially attributable to incentives created by two legislative factors. First, the reform of the Common Agricultural Policy in 1992 helped biodiesel obtain a higher potential for market entrance. The reform added substantial subsidies for noon-food production. Secondly, a tax break for non-imported fuels was instituted in February, 1994; this was another major step for biodiesel entrance into the marketplace. Prior to this legislation, 50 percent of the pump price of diesel in Europe was due to taxes. The legislation created a 90 percent tax exemption for biodiesel, which provided monetary incentives for customers to use biodiesel over its counterpart, petrodiesel [National Biodiesel Board, 2003]. Currently, there are no known legislations in favour of biodiesel production in Nigeria. It is hoped that the situation will change as further breakthrough are made in the biodiesel research works being carried out in this country.

An additional factor that could affect policy decision regarding biodiesel implementation in any country is cost. Perhaps the most significant reason why biodiesel has not gained wider acceptance in Nigeria is the cost of biodiesel relative to diesel.

The cost of biodiesel may be reduced by using alternative feedstocks. For example, currently research work is being directed toward the possibility of using algae as a feedstock for biodiesel. The prospects are quite high and utilization of algae will ensure that food is conserved since algae is inedible. Lower quality feedstocks may help as well.

2.5.5 Biodiesel Feedstocks

The primary raw materials for the production of biodiesel are vegetable oils, animal fats and recycled greases. These materials contain mainly triglycerides, free fatty acids and other contaminants depending on the degree of pretreatment done before delivery. The feedstock composition affects some properties of biodiesel like pour point, cloud point and cold filter plugging points [Tyson, 2001]. Animal fats are worst of all in cold weathers. When biodiesel is produced from vegetable oils, it mainly contains esters of oleic and linoleic acids which have unsaturated alkyl esters. In general, the unsaturated degree of the alkyl chains correlates well with the cold flow performance of biodiesel [Edgar et al, 2005]. This means that the more double bonds on the alkyl chain, the lower the lower the melting point of the esters obtained and therefore the colder it can get without exhibiting undesirable high viscosity solidification. This limits the use of biodiesel prepared from animal fats.

The choice of the fats and oils for making biodiesel is influence by both process chemistry and economic decisions. In the case of process chemistry, the primary factor is the amount of the free fatty acids that are associated with the triglycerides. Most vegetable oils have low free fatty content but are more expensive. Examples of vegetable oils for biodiesel production are those from soybean, canola, palm, cottonseed, sunflower, jatropha, castor, rubber seed, rapeseed, algea, mustard, coconut and hemp. Animal fats include beef tallow, lard, poultry fat and fish oils. Other useable and cheap feedstocks are yellow (recycled) grease, brown grease and soap stock. Animal tallows and yellow grease contain high levels of free fatty acids. The free fatty acid content affects the type of biodisesl production process that can be used, and the yield of fuel from the process.

The composition of the feedstock also affects the properties of the fuel like the pour point, the cloud point and the cold filter plugging point [Tyson, 2001]. Animal fats are worst of all in cold weather. When biodiesel is produced from vegetable oil, it mainly contains esters of oleic and linoleic acids which have unsaturated alkyl esters. In general, the unsaturated degree of the alkyl chains correlates well with the cold flow performance of the biodiesel [Edgar, et al.2005]. This means that the more double bonds on the alkyl chains, the lower the melting point of the esters obtained and therefore the colder it can get without exhibiting undesirable high viscosity. Table 2.10 shows the common biodiesel feedstocks and the countries where they mostly used.

Table 2.10 Biodiesel Feedstock and Countries of Applications

Feedstock	Countries
Soybean Oil	U S A, Brazil
Rapeseed Oil	Europe
Palm Oil	Indonesia, Malaysia,Thailand
Linseed And Olive Oil	Spain
Sunflower	Italy And France
Cotton Seed Oil	Greece
Jatropha Carcus	Nicragua, India
Beef Tallow	Ireland
Used Frying Oil	Australia

Nigeria as a country in the tropical region produces Palm oil, rubber seed oil, jatropha oil and groundnut oils in large quantities and this assures the availability of feedstock for biodiesel production in Nigeria. Besides, these oil seeds are among the high oil yielding oil seeds.

2.5.6 **Biodiesel Blends**

Biodiesel has a lot of advantages as fuel for diesel engines including low emission of toxic and greenhouse gases. On the other hand diesel has higher heating value and hence superior power out and engine torque. In other to harness the potentials of the fuels, they are usually blended. Experimental investigations have been carried out to examine the properties, performance and emissions of different blends of biodiesel with diesel. A blend of biodiesel and diesel is usually designated as BXX, with XX representing the percentage by volume of the biodiesel in the blend. Experimental results of the characterization of biodiesel and blends by the Department of Agricultural Engineering, University of Missouri show that the major properties vary with the blend. Properties like density, viscosity, specific gravity, cloud point, flash point, and cetane number increase as the amount of biodiesel in the blend increases while heat of combustion and API gravity decrease as the proportion of the biodiesel increases in the blend shown on Table 2.11.

2.5.7 ASTM Specifications for Biodiesel

The ASTM International specification for biodiesel is ASTM D6751. This specification applies to biodiesel for use as a blend component in diesel. ASTM has not yet developed a specification for blends such as B5 and B20. ASTM D6751 includes limits on several of the same properties that ASTM D975 requires for No. 2 diesel fuel. However, there are additional property requirements for biodiesel. These additional requirements include,

Table 2.11 Physical Properties of Diesel/ Biodiesel Blends

PHYSICAL PROPERTIES	ASTM NO.	DIESEL D975	BIODESIEL BLENDS				PURE BIODESEL
			B20	B30	B50	B70	B100
Density	D1298	0.8393	0.8478	0.8509	0.8586	0.8675	0.8799
Specific Gravity	D1298	0.8399	0.8485	0.8515	0.8592	0.8682	0.8805
API Gravity	D287	36.9	35.3	34.7	33.2	31.5	29.2
Cloud Point ^{0}c	D2500	-12.2	-10	-7.7	-5.5	-3.3	1.1
Pour Point ^{0}c	D97	-16.1	-13.3	-11.6	-8.3	-6.7	0
Cold filter Plug pt.	D4539	-2	4	6	10	12	24
Flash point ^{0}c	D93	165	170	175	180	190	270
Viscosity at 40^{0}c	D445	2.9	2.99	3.11	3.39	3.69	4.3
Heat of combustion	D3338	19672	18981	18681	18368	17850	17041
Cetane Number	D613	47.1	51.9	47.8	49.1	50.9	55.0

Source: University of Missouri, Department of Agric. Engineering

(i) A maximum limit 5ppm for calcium and magnesium. Calcium and magnesium may be present as abrasive solids or soluble metallic soaps, so their presence must be limited, because abrasive solids would contribute to injector and pump wear as well as piston and ring wear.

(ii) Alcohol content is limited in one of two manners. Either the alcohol content must not exceed 0.2 mass percent or the flash point must be 130°C minimum. This is done to ensure that the alcohol used in the transesterification process is properly removed from the fuel.

(iii) The ASTM D6751 specifies a “sulphated ash” maximum of 0.02 mass percent. In addition to limiting abrasive solids and soluble soaps, this specification limits any unremoved catalysts from the biodiesel production process.

(iv) Carbon residue is limited to 0.05 mass percent, but a different test method is used from that for No.2 diesel fuel.

(v) An acid number specification limit of 0.05 maximum mg is placed on biodiesel to control the level free fatty acids or processing acids. High acidity can increase fuel system deposits. It may also increase fuel system corrosion. High acid values may also be an indication of fuel degradation from oxidation.

(vi)Free glycerin is limited to 0.02 mass percent and total glycerin is limited to 0.24 mass percent. High levels of free glycerin can contribute to injector deposits and clogging of fuel system. Free glycerin can also build up in the bottom of storage tanks. The total glycerin includes free glycerin plus any glycerin content of any unreacted oils or incompletely reacted oils or fats. Low levels of total glycerin confirm a high conversion rate of oils and fats. High levels of total glycerin contribute to injector deposits and fuel filter plugging and could impact low temperature operability.

(vii) A limit is placed on phosphorus, because it can damage exhaust after-treatment catalysts. The ASTM maximum limit for phosphorus in biodiesel is 0.001 mass percent (10ppm), US biodiesel has routinely been in the 1 to 2ppm range but biodiesel from other feedstock sources could contain higher phosphorus levels.

(viii) Sodium and potassium may be present as abrasive solids or soluble metallic soaps, resulting in problems similar to those described for sulphated ash.

Table 2.12 Fatty Acid Composition of Different Vegetable Oils

Fatty acid	class	Dika nut[d]	Physic nut[a]	Soya bean[b]	Safflower[b]	Castor oil[c]	pko[e]	Sand box[f]	Rubber seed	Sunflower	Rape seed	Cotton seed
Dihydroxy stearic	$C_{18:1}$	33.9	-	-	-	0.70	-	-	-	-	-	-
Eicosanoic	$C_{18:0}$	0.31	-	-	-	0.30	-	-	-	-	-	-
Linolenic	$C_{18:3}$	59.0	-	8.30	0.10	0.30	-	2.571	16.30	0.00	8.23	0.00
Linoleic	$C_{18:2}$	2.2	48.18	54.10	75.50	4.20	2.40	8.266	39.60	73.73	22.30	57.51
Myristic	$C_{14:0}$	-	-	0.1	-	-	16.3	-	-	-	-	-
Oleic	$C_{18:1}$	-	28.46	22.50	14.40	3.00	15.4	6.141	24.60	16.93	64.40	13.27
Palmitic	$C_{16:0}$	0.18	18.22	10.30	-	1.00	8.40	0.390	10.20	6.80	3.49	11.67
Stearic	$C_{18:0}$	4.20	5.14	4.70	3.30	1.00	2.40	2.440	8.70	3.26	0.85	0.89
Ricinoleic	$C_{18:1}$	-	-	-	-	89.50	-	-	-	-	-	-
Lauric	$C_{12:0}$	-	-	-	-	-	47.8	1.325	-	-	-	-
Palmitoleic	$C_{16:1}$	-	-	-	-	-	-	1.224	-	-	-	-
Capric	$C_{10:0}$	-	-	-	-	-	3.5	-	-	-	-	-
Caprylic	$C_{8:0}$	-	-	-	-	-	3.3	-	-	-	-	-
Caproic	$C_{6:0}$	-	-	-	-	-	0.2	-	-	-	-	-

(ix) a:(El-Diwani et al, 2009); b (Allen et al, 1999); c (Conceicao et al, 2007); d (Bello et al, 2011); e (Edom D. O, 2002); f (Oyeleke et al, 2012).

CHAPTER THREE

RESEARCH METHODOLOGY

Biofuels are seen widely as a promising alternative fuel made from renewable biological resources such as vegetable oils, animal fats and starch bearing feedstock. It is gaining significant attention as a good substitute or blend of conventional fuels due to its sustainability and environmental friendliness.

This experimental research work involves two major stages.

The first stage of this work involves the production of bioethanol from sugar bearing feedstock (sugar cane, palm wine and raffia trunk) and the production of methyl esters (biodiesel) from vegetable oils using base-catalyzed transesterification process with methanol as the alcohol while sodium hydroxide (NaOH) is used as the catalyst.

The second stage involves characterization of the produced biodiesel and bio-ethanol and its blend with petrol fuels, so as to determine the physical properties such as the Specific gravity (relative gravity), cloud point, flash point, kinematic viscosity, pour point, cetane number, octane number and heating value.

The number is limited by the availability of test equipment and cost. The determined properties are checked against the American Society of Testing and Materials standards for biodiesel, bioethanol and conventional fuels.

3.1 MATERIALS

3.1.1 Bioethanol Production

3.1.1.1 Substrate and Production of Ethanol

The materials sourced for the production of bioethanol are sugar cane *(Saccharum L),* wine obtained from palm tree (Elaeis Guineensis) and Raffia (Raphia Vinifera) trunk.

a. Sugar cane: The stems of the cane were cut into pieces of length 25 cm each. This was to make sure that they would go into the hydraulic press used in the extraction of the juice. The pieces were weighed on a balance of sensitivity 5g. Pressure applied on the cane was of the order of 17 MPa until all the mechanically extractible juice was expelled from the cane. The juice was collected and the volume measured in a graduated cylinder.

The juice obtained was diluted with double the volume of water and one litre of the mixture put inside a 1.5 L plastic bottle, sealed air tight and left for fermentation. These bottles were left for 12 days under ambient temperatures between 18 to 22°C.

b. Palm wine: Five litres of palm wine obtained from local palm wine tapers in Eziobodo, Owerri west Local Government Area of Imo state was sealed tight in cans and left for fermentation. The wine is usually sweet but becomes very alcoholic as days go by. Fermentation was done at ambient temperature (20°C – 27°C) for sixteen days so that alcohol production can be maximized (Tangka et al., 2011).

c. Raffia Trunk: The raffia trunks obtained from Eziobodo were cut into pieces of length of about 10cm each. The cut stems were washed with water and packed in buckets, after which the buckets were filled with water, covered and was left for fermentation. The buckets were left for about 21 to 28 days under ambient conditions to allow for maximum alcohol production using natural fermentation. After fermentation has been allowed for about 28 days, the fermented liquid was sediment and filtered for distillation process.

3.1.2 Biodiesel Production

3.1.2.1 Test Materials

The methanol, and sodium hydroxide pellets used were purchased from a standard chemical shop in owerri. Sodium hydroxide pallets of purity of about 97% are chosen because of its availability and low cost (Edgar, et al, 2005). Sodium hydroxide is one of the homogeneous catalysts suitable for the transesterification of fresh vegetable oils with low fatty acid content. Methanol is the preferred alcohol for the transesterification of the vegetable oil. Methanol is cheaper and allows simultaneous separation of esters and glycerol. Methyl esters have shown superior engine performance over ethyl esters of the same parent vegetable oil. Besides, using ethanol is more complicated as it requires a water free alcohol as well as oil with very low water content in order to obtain glycerol separation easily (Schuchard el al, 1998). Sodium hydroxide dissolves more easily in methanol and also methanol reacts more quickly with triglycerides than ethanol.

The transeterification was done with a blender (reactor), thermometer and a heater. One litre high density plastic vessel was used for catalyst/methanol mixing. The characterization was carried out at the industrial chemistry laboratory and the laboratory of the petroleum engineering, both of Federal university of technology owerri, Nigeria.

3.1.2.2 Sample Collection

a. **Physic Nut (Jatropha Curcas) Seed Oil:** The crude jatropha curcas seed oil used in this study was purchased from Kwara state, Nigeria.

b. **Castor (Ricinus Communis) Oil:** Ricinus Communis is a species that belongs to the euphoibiaceae family and it is commonly known as castor oil plant, and palm christi. This plant originates in Africa but it is found in both wild and cultivated states in all the tropical and subtropical countries of the world (Carmen L. B 2005). Castor seeds were harvested from wild within Uke metropolis in Idemili North local government area of Anambra state. The seeds were sun dried and were grinded. Castor oil was extracted from the seeds using traditional method. The extracted oil was filtered and heated to remove moisture.

c. Dika Nut (Irvingia Gabonensis) Oil: The African bush mango or dika nut, the yielding tree has a conical shape and grows mostly in the tropical rain forest. The nuts were harvested from the wild, dried in the sun and the kernel removed by splitting the nut into two halves using a sharp cutlass. The kernels were dried in the sun to reduce moisture content. The oil was extracted using traditional method. The extracted oil which is solid at room temperature was heated to 100^oC for about one hour to remove any water content and then allowed to cool.

d. Sand Box (Hura Crepitans) Seed Oil: Hura crepitans is a large forest tree often found in the tropical rain forest and savanna regions of Nigeria. The seeds are enclosed in hard protective coat which usually and suddenly splash open and scatter when the seed are well dried. The tree has broad leaves with thorns all over its trunk. The seeds were collected from FUTO metropolis during dry season and sun dried to remove moisture after which it was sun dried, crushed and oil extracted. The extracted oil was filtered and heated to remove moisture content.

3.2 METHODS

3.2.1 BIOETHANOL PRODUCTION

3.2.1.1 Distillation Process

The prepared substrates were distilled one after the other in a “Liebig Condenser” while heating the liquid in a three litre round bottom flask and the temperature of the water in the heating jacket was set at 80^{o}C. The temperature was first adjusted until the boiling point of methanol (53^{o}C) in order to separate possible methanol from the final product. The distillate made of water and ethanol was collected at temperature range of 60 to 65^{o}C and this temperature was maintained until there was no more alcohol condensing in the system. This lower temperature was due to the presence of impurities which reduces the boiling point of ethanol in the mixture. The distillate, a mixture of water and ethanol also known as *“azeotrope”* was collected in a cylinder and then purified in a rotavapour to obtain about 95% pure ethanol.

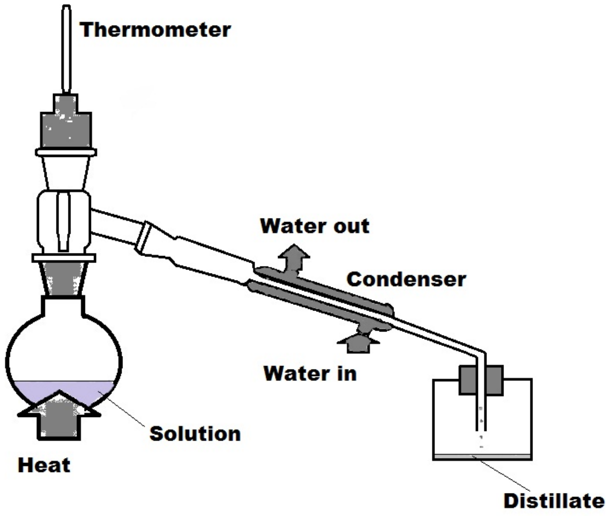


Fig. 3.1: Schematic Laboratory Distillation Equipment.

Nine blends of ethanol petrol mixtures were used. The blends are usually referred to as E_{XX}, where E represents bioethanol and X represents the percentage of the bioethanol in the blend. For instance, E_{20} means a blend composition in which bioethanol is 20% and petrol is 80%. The various compositions are shown in table 3.1.

Table 3.1 : Compositions of bioethanol/petrol blended samples used for analysis.

Sample Code	% Ethanol	% Petrol
E_{10}	10	90
E_{20}	20	80
E_{30}	30	70
E_{40}	40	60
E_{50}	50	50
E_{60}	60	40
E_{70}	70	30
E_{80}	80	20
E_{90}	90	10

The distillation and the analysis of the bioethanol and its blends with petrol were done at the Industrial Chemistry Laboratory of the department of Industrial Chemistry and Petroleum Engineering Laboratory of the Department of Petroleum Engineering, Federal University of Technology Owerri.

3.2.1.2 Measurement of Physical Properties

The flash points of the blends were measured using the Pensky-Martens closed cup method as detailed in ASTM D93 as described by Ajav and Akingbehin (2002). The octane number of the various blends was measured using a portable cetane/octane meter adapted to ASTM D 2699-86 and D 2700-86 methods while the heating values of the different petrol ethanol blends were determined by burning a known amount of blend in a Gallenkemp ballistic bomb calorimeter. The density of the various bioethanol/ petrol blends was determined using the Hydrometer as described by Ajav and Akingbehin (2004). The vapor pressure of the blends was determined using the ASTM test method D4953-99a standard test method for vapour pressure of petrol and petrol oxygenated blends (dry method). The auto ignition point was measured according to the procedure described in ASTM E659.

3.2.2 BIODIESEL PRODUCTION

3.2.2.1 Degumming of Crude Oils

The oils were degummed to remove phospholipids, calcium and magnesium salts of phosphatidic and lysophasidic acids which are strong emulsifiers that inhibit the separation of glycerol which lowers the yield of neutral oil (Igbum et al, 2012). In degumming, the crude oil was mixed with about 3% of warm water and the mixture was agitated mechanically for 30minutes at 70^{o}C. This hydrates the phospholipids and gums, thus making them insoluble in oil. They were thereafter separated by sedimentation (settling).

3.2.2.2 Physical Analysis of Crude Vegetable Oil

Determination of iodine value, kinematic viscosity, specific gravity, flash point, heating value and cetane number were carried out according to the ASTM testing methods.

3.2.2.3 Determination of Amount of Catalyst

The amount of catalyst to be used for successful transesterification is usually dictated by the amount of Free Fatty Acids contained in the oil. For fresh vegetable oils with FFA less than 1%, the amount of NaOH needed is usually 1% of the weight of the oil. However, when the level of FFA in the oil is not certain or above 1%, titration process is usually adopted to determine the amount of catalyst needed.

3.2.2.4 Preparation of Methoxide

Sodium hydroxide catalyst was weighed (1% weight of oil) and was added to appropriate volume of methanol that corresponds to the molar ratio of 6:1 methanol to oil. The mixture was stirred in a mixer at 500rpm until it completely dissolved to form sodium methoxide. The amount of catalyst required for the transesterification process for optimum biodiesel yield for jatropha curcas seed oil, castor oil, dika nut oil and sand box seed oil are 8.75g of NaOH in 200ml of methanol, 0.54g of NaOH in 15ml of methanol, 1g of NaOH in 100ml of methanol and 0.75g of NaOH in 50ml of methanol respectively.

The molar ratio for optimum biodiesel yield by transesterification was 6:1 methanol to oil (Bello et al, 2011). This means that, usually a 100% alcohol excess is used in practice, i:e 6mol of alcohol per mol of oil. This corresponds to a 1:4 alcohol-to-oil volume ratio.

3.2.2.5 Transesterification Process

This process chemically modified the properties of vegetable oils such as their viscosity, cetane number and volatility of the oils to levels that make them suitable for use in internal combustion engines.

500ml of pretreated oil was measured and poured into a large beaker. The pretreatment by heating the oil to a temperature of $70^{o}C$ using a heater removes the remains of solvent or moisture content. The heated oil was allowed to cool down to $50^{o}C$ and then poured into a blender, with the blender still switched off, and the prepared methoxide was emptied into the oil in the blender and properly covered to prevent air from entering into the mixture. The blender was switched on and the mixture was blended for the required time of mixing after which the blender was switched off and the mixture was immediately transferred into a separator can and closed tightly. The mixture was allowed to settle for 24hours and after which a dark colour glycerin settled at the bottom while a pale yellow liquid layer which is the methyl ester separated at the top (Addison, 1999). Upon completion of reaction, two products were formed, glycerin and biodiesel. The clear liquid (methyl ester) found at the top layer was decanted into a beaker.

3.2.2.6 Biodiesel Washing/Purification Process

The biodiesel was washed with warm water (50^oC) to remove impurities such as diglycerine, monoglycerine, catalyst, soap and excess methanol. The washing was done by mixing with 20% volume of warm water and stirred gently for 30minutes. It was allowed to settle and gave a two phase mixture from which the biodiesel was separated. The procedure was repeated three times (Wu et al, 1998; Doranto et al, 2002) to obtain a clear biodiesel. After washing, the methyl ester was finally dried by heating.

3.2.2.7 Measurement of Properties

The main properties of the oil and its biodiesel were measured using mainly the American Society for Testing and Materials (ASTM) protocols for biodiesel fuels.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Results of characterization of bio-ethanol and its blends with Petrol

The measured properties of Bioethanol fuel compared to that of Petrol and the measured properties of the various blends are shown in Tables 4.1 and 4.2 respectively (Appendix A and B). Heating values decrease as ethanol concentration increases therefore more fuel should be consumed per kilometer as the ethanol fraction in the blend increases. The density of blends increased from 747.4 Kg/m^3 for E_0 to 789 Kg/m^3 with E_{100}. This was expected especially as bio-ethanol is heavier than petrol. This shows that addition of ethanol to petrol produces a fuel blend denser than petrol. The specific gravity of a fuel is the weight of the fuel compared to the weight of the same volume of distilled water at a given temperature. It gives an indication of the purity of a fuel. When fuel is contaminated with another liquid, the specific gravity will either increase or decrease depending on the specific gravity of the contaminant.

The flash point increases from -65 at E_0 to 12.6°C with E_{100}. The flash point indicates the temperature at which the fuel can vapourise to produce an ignitable mixture with air. At the flash point an applied flame gives momentary flash instead of some steady combustion. Therefore the flash point gives some indication on the flammability of the liquid. This shows that with the addition of ethanol fractions to petrol the burning characteristics of the mixture reduces. It is important to note that the higher the flash point of a fuel the more difficult it is to start the engine. For example, the flash point of E_{100} was found to be 12.6°C meaning that starting will be very difficult at temperatures of about 9°C. Therefore a petrol engine converted to an E_{100} engine would need to use pre heater plugs in the temperate region.

4.1.1 Effect of Blend on Vapour Pressure

The vapour pressure of the blends decreases from 39 KPa for E10 to 9.5 KPa for E100 as shown in figure 4.1. The vapour pressure of a liquid is very important because it affects the starting and warm up of spark ignition engines.

At high altitudes and during high operational temperatures the cause of vapour lock in fuel pumps depends on the vapour pressure of the fuels. Therefore blending ethanol with petrol will negatively affect the ease of starting the engine.

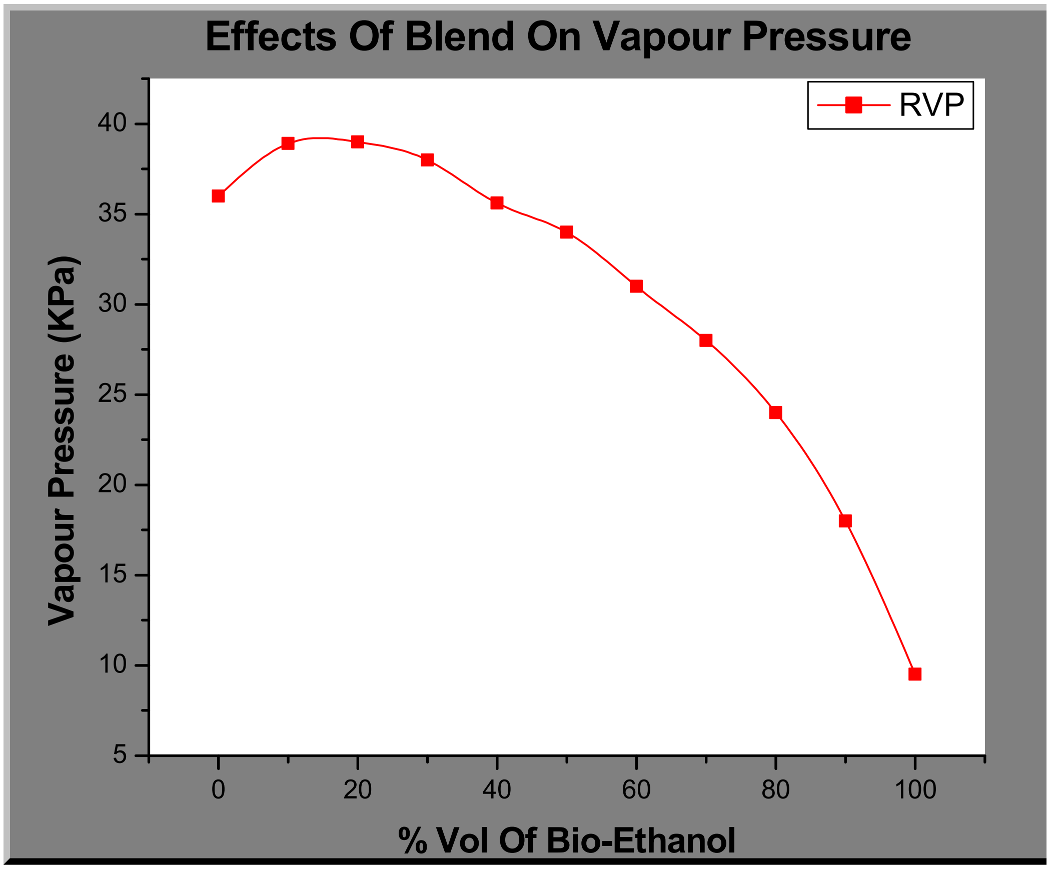


Figure 4.1 Effects of Blend on Vapour Pressure

4.1.2 Effect of Blend on Octane Rating

The Research Octane number (RON) increases from 91 at E0 (100% petrol) to 110 at E90 as shown in figure 4.2. Octane number of a fuel indicates its ability to resist pre-ignition and burn evenly. The Octane number of pure bio-ethanol is 114. This shows that the addition of bio-ethanol to petrol improves considerably, the Octane number consequently increasing the activation energy of the fuel or the energy necessary to start a reaction.

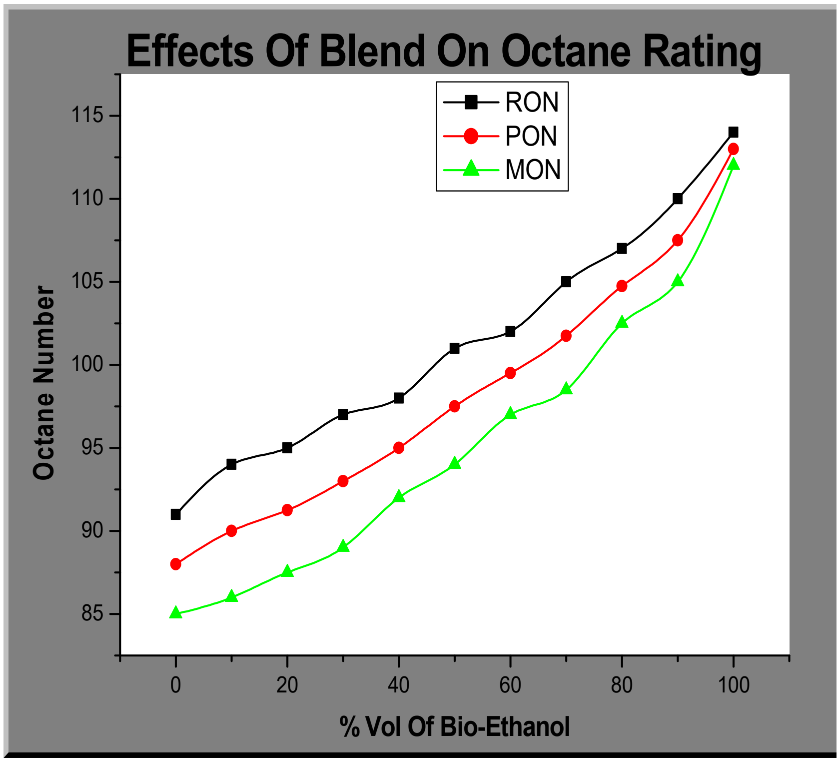


Figure 4.2 Effects of blend on Octane rating

The research octane number RON is a measure of the fuel's tendency to burn in a controlled manner or a measure of its tendency to knock in an SI engine. As far as ignition only is concerned, the best blend would be E50 that gives approximately the same performance like isooctane, that is, with an octane number of 100.

Also, the sensitivity of the blended fuel decreases significantly as the percentage volume of ethanol increases. This shows that the knock properties of the fuel with high percentage composition of bioethanol are less likely to be affected by the changes in operating conditions of the engine. High compression ratios can be used.

4.1.3 Effect of Blends on Lower Heating Value

The lower heating value decreases as ethanol concentration increases as shown in figure 4.3. Therefore more fuel will be consumed per kilometer as the ethanol fraction in the blend increases.

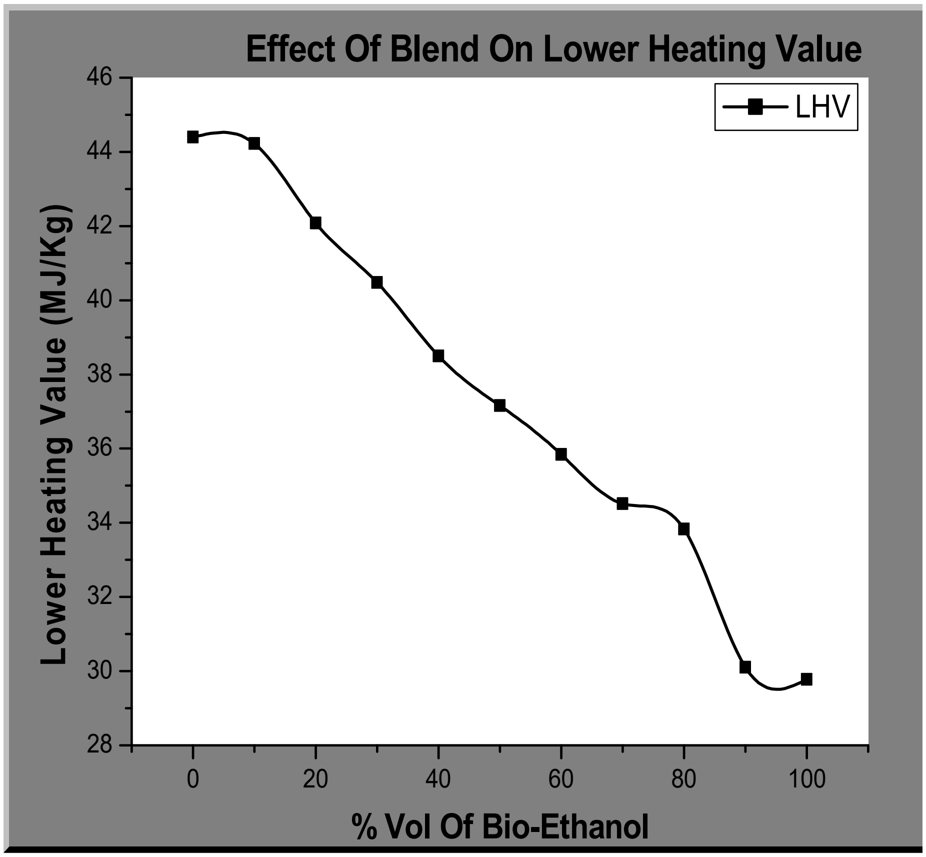


Figure 4.3 Effects of blend on Lower Heating Value

However, higher thermal efficiency and loss of fuel economy are expected with blended ratios bioethanol and petrol because of the lower energy value of bioethanol compared to petrol. The high latent heat of vapourisation of alcohol in combustion process increases the charge density thus higher power output.

4.1.4 Effect of Blend on Air/Fuel Ratio

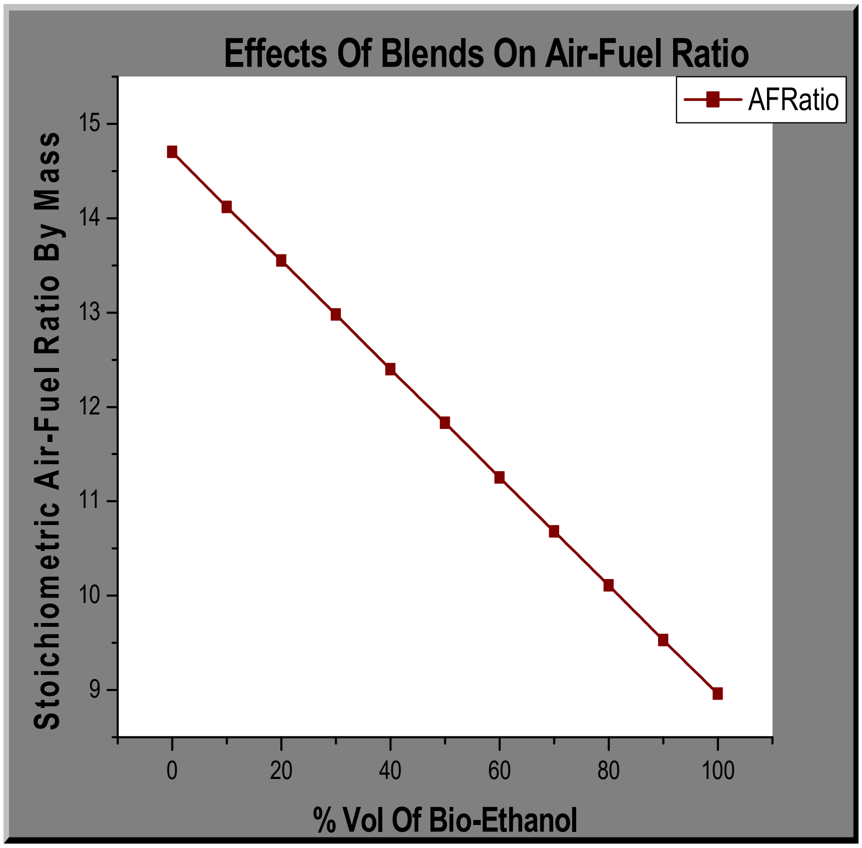


Figure 4.4 Effects of blend on Stoichiometric Air/Fuel Ratio

The air/fuel ratio decreases linearly as the percentage volume of bioethanol increases as shown in figure 4.4. There is only one air/fuel ratio that gives the best engine performance for a given engine load or speed. The ratio is determined by dividing the mass of the air by the mass of fuel.

4.1.5 Effect of Blend on Specific Gravity

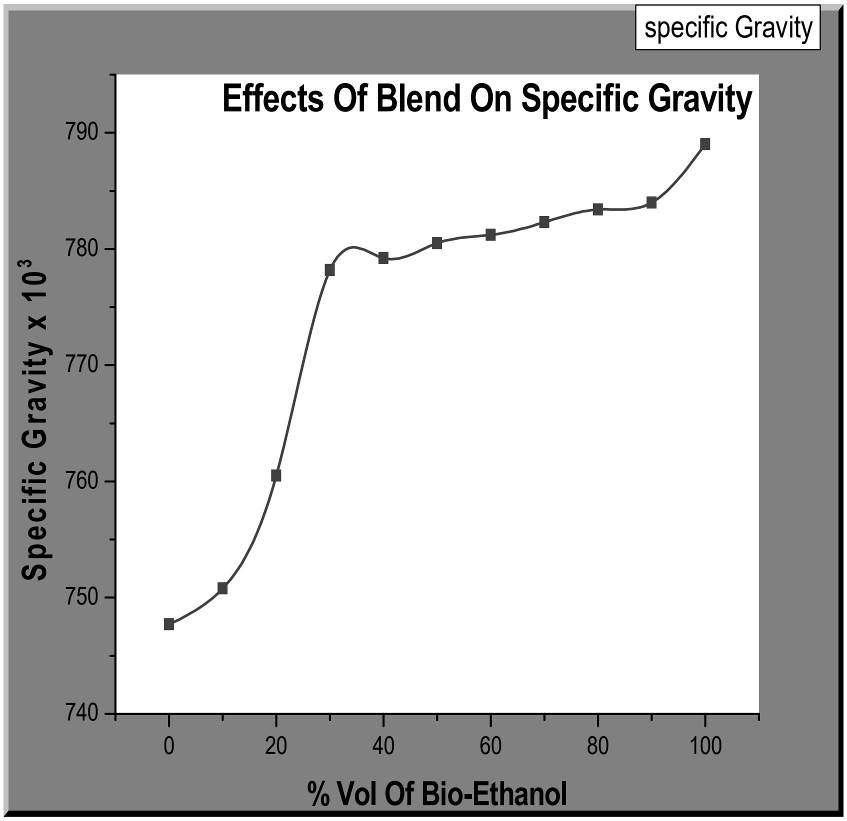


Figure 4.5 Effects of Blend on Specific Gravity

The specific gravity increases as the percentage volume of ethanol increases as shown in figure 4.5. This shows that addition of ethanol to petrol produces a fuel blend denser than petrol. Thus the injection jet will have to be modified every time the specific gravity changes as it affects the air/fuel ratio. This is because the droplet size increases with increase in the percentage volume of bioethanol.

4.1.6 Effect of Blend on Auto Ignition Temperature

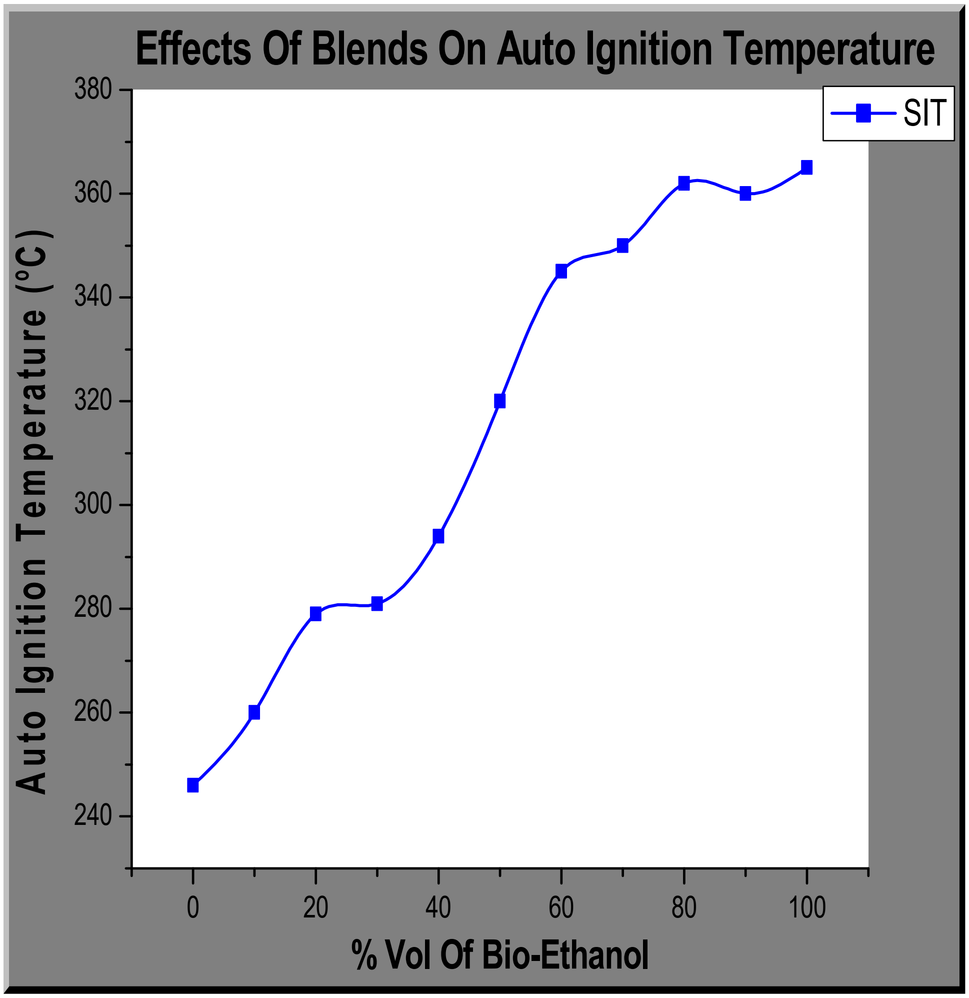


Figure 4.6 Effects of blend on Auto Ignition Temperature

The auto ignition temperature increases as the percentage volume of ethanol increases as shown in figure 4.6. This implies that the fire hazard potential of the blended fuel reduces as the concentration of ethanol increases.

It also implies reduced tendency of engine knock as the blended fuel is less likely to auto ignite during combustion.

4.2. Results of Characterization of Crude Vegetable Oils and Produced Biodiesel.

The properties of the oil and the biodiesel fuel were measured and the results are shown in table 4.3 and table 4.4 respectively. Table 4.5 also show percentage yield of biodiesel from the crude oils by transeterification.

From table 4.3 and table 4.4, it was discovered that the kinematic viscosity of the biodiesel decreases significantly compared to the viscosity of the crude oils. The values obtained from the biodiesels were within the range of ASTM specification which is 3.5 to 5.5 mm^2/s at 40^oC, except for castor biodiesel viscosity (10.75 mm^2/s) which is still out of the range of the specified biodiesel standards.

Table 4.3 Physical properties of Crude Vegetable Oils

Properties	ASTM Testing Method	Castor Oil	Dika Nut Oil	Physic Nut Oil (Jatropha Carcus)	Sand Box Seed Oil
Relative Density	D1298	0.958	0.93	0.9073	0.92
Kinematic Viscosity (40^oC) mm^2/s	D445	228.93	45	35.78	6.44
Flash Point (oC)	D93	310	300	293	288
Pour Point (oC)	D2500	22	28	12	18
Cloud Point (oC)	D2500	15	23	2	12
Lower Heating Value (MJ/Kg)	D240	39.4	28	42.47	26.28
Cetane Number	D613	43	44	51	42

High viscosity in biodiesel is sometimes associated with unreacted triglycerides in the fuel. Modern diesel engines use high tech injection pumps, which does not tolerates very viscous fluids. This is because viscous fluid clog fuel filters and it is also very risky at low temperature as the engines may experience cold starting.

Table 4.4 Physical Properties of biodiesel from Crude Vegetable oils

Properties	ASTM Method	ASTM Standard		Castor Biodiesel	Dika Nut Biodiesel	Jatropha Biodiesel	Sand Box Biodiesel
		Diesel	Biodiesel				
Relative Density	D1298	0.8/0.84	0.86-0.90	0.9268	0.910	0.8749	0.870
Kinematic Viscosity (40^oC) mm^2/s	D445	2-5	3.5-5.0	10.75	3.2	4.2	4.2
Flash Point (^oC)	D93	65	>120	190.7	140	167.5	156
Pour Point (^oC)	D2500	-15	<15	-45	-6	-1	6
Cloud Point (^oC)	D2500	-12	<20	-23	-14	-5	0
Lower Heating Value (MJ/Kg)	D240	42.7	-	30.5	39	43.45	37
Cetane Number	D613	40-55	48-65	50	52	59	50
Iodine Value g(I2)/100g	-	60-135	<120	85	90	95	127.5

The cetane values of biodiesel from jatropha oil, Dika nut Oil, Castor Oil and Sandbox oil are 59.4, 52, 50 and 50 respectively. These cetane values were found to be within the ASTM specified limit. The cetane value of the crude jatropha oils also fall within the ASTM specified limit. The cetane values of the crude oils which were found to be low, shows that transesterification increases the cetane value. The higher cetane value of the biodiesels compared to diesel fuel was an indication that they will be the high potential for engine performance.

Heating value of jatropha and castor oils was found to be high (42.47 MJ/Kg and 39.4 MJ/Kg respectively) while that of Dika nut and Sandbox oils were found to be low (28 MJ/Kg and 26.28 MJ/Kg respectively). From table 4.4, the calorific value of biodiesel from jatropha oil was found to be high (43.45 MJ/Kg). Biodiesel from jatropha oil had a higher heating value than biodiesels from dika nut oil, sandbox oil and castor oil (39 MJ/Kg, 37 MJ/Kg and 30.5 MJ/Kg respectively). However, based on the values obtained in this study, castor biodiesel has a lower calorific value than sandbox, dika nut and jatropha biodiesels. The lower calorific value of castor biodiesel is attributed to the structural differences in the constituent fatty acids of castor oil.

Cloud point of these oils are generally high making the oils unsuited for making biodiesel, especially for use in cold countries (table4.3). Biodiesel from these oils would not be usable in cold countries without the use of additives to improve their cold filter plugging points (CFPP). However, cloud points were generally lowered in biodiesel from these oils. Castor biodiesel and Dika nut biodiesel have lower cloud point than jatropha and sandbox biodiesel, making castor and dika nut biodiesel more suited for use in cold countries (Table 4.4). Jatropha and sandbox biodiesel may require the use of additives to improve its cold weather property desirable in cold countries.

Flash points of the crude oils were high making them better suited for biodiesel production with respect to safety during storage and transportation.

The pour point of biodiesel from these oils reduced significantly after transesterification. These results were found to be within the specified limit and the biodiesel from these oils were suitable not only for the tropical region but also for the moderate temperate region. However, castor biodiesel properties indicated a very low pour and cloud points which make this biofuel a good alternative in winter conditions. It also indicates that castor biodiesel could be used as petroleum diesel additive improving both environmental and flow behavior of the mineral fuel.

The relative density of the products was found to be within the range of ASTM specification as shown in the table of values. It was also discovered from the results that relative densities of the crude oils were found to be higher than those of the biodiesel.

Table 4.5 Percentage Biodiesel Yield from Crude Vegetable Oils

Crude Oil	% Biodiesel Yield
Castor (Ricinus Communis) Oil	56
Dika nut (Irvingia Gabonensis) Oil	68.5
Physic Nut (Jatropha Curcas) Oil	67
Sand Box (Hura Crepitans) Oil	69.32

Biodiesel yields from crude jatropha oil, dika nut oil, sandbox oil and castor oil were found to be 67%, 68.5%, 69.32% and 56% respectively (Table 4.5). Castor biodiesel yields were low; this was attributed to the formation of soap from crude castor oil during transesterification.

CHAPTER FIVE

CONLUSIONS AND RECOMMENDATIONS

5.1 CONLUSIONS

Bioethanol and biodiesel production from the chosen crops were feasible. Bioethanol was produced by fermentation and distillation processes while biodiesel was produced by alkaline based transesterification process using methanol and sodium hydroxide as the alcohol and catalyst respectively. Transesterification process of the vegetable oils was carried out with a basic catalyst and a single step is required because of their favourable acidity level. Therefore in a large-scale process, it would be less costly than chemical processes with other oils with a higher acidity level.

Addition of ethanol to petrol increases the octane number but on the other hand reduces the calorific value.

Biodiesel derived from jatropha oil is suited for use in diesel engine given that its kinematic viscosity, flash point, cloud point and calorific value conform to the recommended international standard. It also has superior cetane value and calorific value which indicate higher potential for engine performance than diesel fuel. On the other hand biodiesel from castor oil is not suitable for use in diesel engines due to the high viscosity and low calorific value. Alternative methods of reducing viscosity like blending castor biodiesel with diesel should be tried. However, castor biodiesel indicates a very low pour and cloud points which make this biofuel a good alternative in cold conditions. It also indicates that castor biodiesel could be used as petroleum diesel additive improving both environmental and flow behavior of the mineral fuel.

African Mango nut oil biodiesel has similar properties to diesel fuel and superior flow properties. The flash point is also much higher than that of diesel fuel which makes it a suitable alternative fuel for diesel engines. Sandbox oil biodiesel, have similar properties to other biodiesel produced except that its iodine value is higher than the specified range for biodiesel. This limits the use of sandbox oil for the production of biodiesel. However, sandbox biodiesel can be utilized by mixing with other biodiesel or other diesel fuel.

All the vegetable oils are liquid at ambient temperature except for Dika oil which is solid at ambient temperature (25°C). Their sources are wild and the crops are non edible, they have high oil content and high conversion rate would make them competitive fuel to diesel and other biodiesel fuels.

Generally, the results of the characterization of the biodiesel and bioethanol showed that the produced fuels are alternative fuels that can be used on modern diesel and petrol engines with little or no engine modifications.

5.2 CONTRIBUTIONS TO KNOWLEDGE

One of the primary reasons for carrying out scientific research is to contribute to knowledge for the advancement of humanity. In line with this, the following contributions to knowledge are believed to have been humbly made.

(i) The base catalyzed transesterification of Nigerian jatropha, castor, dika nut and sandbox oils gives high yield of quality biodiesel fuels that meet international standards specified by American Society for Testing and Materials for diesel engine fuels.

(ii)The produced fuels are expected to give higher thermal efficiencies than the diesel and petrol fuels because of their lower heating values.

(iii)The produced biodiesel fuels can be safely used to run modern diesel engines with little or no engine modifications.

(iv)The produced bioethanol fuel and its blends with petrol fuel can also be safely used to run modern spark ignition engines with little or no engine modifications.

(v) Bioethanol can be used as a doping agent (i:e as an alternative to tetra ethyl lead (TEL)).

5.3 RECOMMENDATIONS

Blended fuels are not yet a good option for less developed countries, which are not manufacturing resistant parts. Bioethanol blended fuels may however call for some adjustments such as advancing of ignition timing, increasing the compression ratio and roughening the piston head.

Based on the result from table 4.2, the optimal blend ratio of E_{20} (20% vol. of bioethanol and 80% vol. of Petrol) are hereby recommended for Nigerian vehicles and automotives running on spark Ignition engines. This will help minimize knock and unwanted emissions.

Finally, further research on the performance evaluation of the operational and behavioral parameters on internal combustion engines using the produced biofuels (Bioethanol and Biodiesels) and their blends with fossil fuels (Petrol and Diesel) are recommended.

REFERENCES

Abreu, F. (2008) "Alternative By-products from Jatropha, In: International Consultation on Pro-poor Jatropha Development"; 10–11 April 2008, Rome. IFAD. Available at: http://www.ifad.org/events/jatropha.

Achten, W.M.J., Verchot, L., Franken, Y.J., Mathijs, E., Singh, V.P., Aerts, R. & Muys, B. (2008) "Jatropha bio-diesel production and use. Biomass and Bioenergy, 32: 1063–1084.

Addison, K. (1999) "Make Your Own Biodiesel", Http://Journeytoforever.org/market/home/default.asp

Al-Hasan M (2003). "Effect of ethanol unleaded gasoline blends on engine performance and exhaust emissions". Energy Conversion Manage. 44: 1547-1561.

Ajav EA, Akingbehin OA (2002). "A study of some fuel properties of ethanol blended with diesel". Agric. Eng. Int. CIGR J. Sci. Res. Dev. Manuscript EE 01 003 Vol. (4).

ARIC Atmosphere, Climate & Environment Information Programme Website; http://www.ace.mmu.ac.uk/eae/Sustainability/Older/Brundtland_Report.html.

Arthur D. Little (1999) Analysis and integral evaluation of potential CO_2 - neutral fuel chains, GAVE reports 9908-9910 (Management Summary, Sheet presentation and Appendices), Netherlands agency for energy and the environment Novem, Utrecht, the Netherlands.

Barman, S. C., Kumar, R., Singh, G. C., Kisku, A. H., Khan, M. M., Kidwai, R. C., Murthy, M. P. S., Negi, P., Randay, A. K., Verma, G. Y. and Bhargava, S.S. (2010) Assessment of Urban air pollution and its possible Health impact. Journal of Environmental Biology.31, 913-920.

Bello, E.I. and Otu, F (2012) “Effects of Blending on Properties of Biodiesel Fuels”; Journal of Engineering Trends in Engineering and Applied Sciences, Vol. 3(3): PP 556-562

Bello, E. I., Fade-Aluko, A.O., Anjonn, S. A. and Mogaji, T. S. (2011), “Characterisation and Evaluation of African Bush Mango Nut (Dika Nut)(Irvingia Gabonensis) oil Biodiesel as Alternative Fuel for Diesel Engine”; Journal of Petroleum Technology anmd Alternative Fuels; Vol. 2(9): PP. 176-180

Bunkyakiat, K. (2006). Continuous Production of Biodiesel via Transesterification from vegetable Oils in supercritical Methanol. Energy and Fuels Vol.20, American Chemical Society

Carmen, L. B. Forero (2005) “Biodieselfrom Castor Oil: A Promising Fuel for Cold Wheather; Poster Presentation 2(7); Francisco de Paula Santander University , Colombia

CGIAR. (2008) Biofuels Research in the CGIAR: A Perspective from the Science Council. A CGIAR Science Council Policy Statement on Biofuels Production. April 2008. Rome, SC Secretariat.

Chiasson, A.,(2007) Geo-Heat Center, “Geothermal Energy Utilization in Ethanol Production,”.

Cloin, J. (2007) Liquid Biofuels in Pacific Island Countries. SOPAC Miscellaneous Report 628. Suva, Fiji Islands, SOPAC Secretariat

Conceicao, M. M., Candeia, R. A., Silva, F. C., Bezerra, A. F., Fernandes, Jr. V. J and Souza, A. G. (2007) “Thermoanalytical Characterisation of Castor Oil Biodiesel”. Ren. Sustain.En. Rev., 11: 964-975.

Conceicao, M. M., Fernandes, Jr. V. J, Bezerra, A. F., Silva, M. C. D., Santos I. M. G., Silva, F. C., and Souza, A. G. (2007) “Dynamic kinetic Calculation of Castor Oil Biodiesel”. Journal of Thermal Anal. Cal., 87:865-869.

Cox, P. M., Richard, A. B., Chis, D. J., Steven, A.S. and Ian, J. T. (2000) Acceleration of Global warming due to carbon cycle Feedbacks in a coupled climate model. Nature 408 (184)

Crews, T.E., and Peoples, M.B., (2004) Legume versus fertilizer sources of nitrogen: ecological tradeoffs and human needs. Agr. Ecosyst. Environ. http://linkinghub.elsevier.com/retrieve/pii/S0167880903003402.

De Jongh, J. & Adriaans, T. 2007. Jatropha oil quality related to use in diesel engines and refining methods. Technical Note. Eindhoven, The Netherlands, Fuels From Agriculture in Communal Technology (FACT).

Edgar, L., Yiyan, L., Lopez, D. E., Suwannakaran, K., Bruce, D. A., James, G. G. Jn. (2005) Synthesis of Biodiesel via Acid Catalysis. Industrial Engineering Chemical Resources. 44.

Eloka-Eboka, A.C. (2010) “Production and Testing of Biodiesel from Prosopis Africana Seed Oil Using Pyrolysis”. An M.Eng Thesis, Department of Mechanical Engineering, University of Agriculture, Markurdi, Nigeria.

EPA (2007) “Recent Climate Change: Atmosphere Changes” Climate Change Science Programme, United States Environmental Protection Agency.

FAO (2003) http://www.fao.org

Fichera, J., and Kueter, J., “Considering Brazil’s Energy Independence,” 2006. www.marshall.org/pdf/materials/455.pdf.

Freedman, B., Pryde, E. H. (1984) Variables Affceting the yields of fatty esters from transesterified Vegetable oils. Journal of American Oil Chemists Society. 61.

Giri, N. (2004) Automotive Technology. Khanna Pubishers. Nai Sarak, Delhi India.

Hamelinck CN, Faaij APC (2006) Production of advanced biofuels. Intl Sugar J 108 (1287): 168-175

Hill, J., Nelson, E., Tilman, D., Polasky, S. and Tiffany, D. (2006) "Environmental, economic and energetic costs and benefits of biodiesel and ethanol biofuels"; Proc Natl Acad Sci, USA 103 : 11206-11210

IEA (International Energy Agency), "Biofuels for Transport—An International Perspective," 2004, http://www.iea.org/textbase/nppdf/free/2004/biofuels2004.pdf.

IEA, (2007) "IEA Bioenergy: Potential Contribution of Bioenergy to the World's Future Energy Demand,".

Igbum, O. G., Eloka-Eboka, A.C. and Nwadinigwe, C.A (2012) "Effects of Transesterification Variables on Yield and Properties of Biodiesel Fuels Produced from Four Virgin Tropical Seed Oils"; International Journal of Environmental and Bioenergy, Vol.1 (2): PP. 119-130

IPCC (2001) Summary for Policy makers (PDF), Climate Change 2001, The Scientific Basis Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change (IPCC).

Jeuland., N., Montagne, X. and Gautrot, X. (2004); "Potentiality of Ethanol as a Fuel for Dedicated Engine"; Journal of Oil and Gas Science Technology Vol. 59(6) pp. 559-570

Jorg, P. A. (2008) Promoting Biofuels: Implication for Developing Countries. Ruhr Economic Papers No. 38.

Katofsky, R.E. (1993) “The production of fluid fuels from biomass”; Report no 279, Princeton University Center for Energy and Environmental Studies, Princeton NJ, USA

Kim, S., and Dale, B. E. (2004) “Global potential of bioethanol production from wasted crops and crop residues”; Biomass and Bioen 26 : 361-375

Knothe Gerhard, Gerpen Jon Van and Krahl Jingen (2005) “The Biodiesel Handbook, Champaign”, Illinois: AOCS Press

Korres, D. M., Anastropoulos, G., Lois, E., Alexandrisdis, A., Sarimveis, H., Bafas, G. (2002). A Neural Network approach to the Prediction of Diesel Fuel Lubricity. Fuel 81.

Krishnakumar, J., Venkatachalapathy., V. S. K. and Elancheliyan, S.(2008). Techanical Aspects of Biodiesel Production from Vegetable Oils. Thermal Science. Vol. 12 No 2 pp 159-169.

Kristensen, J.B.,(2007) ”Ignocellulosic bioethanol—close to commercial reality,” n.d. www.siliconvalley.um.dk/.../A61D6D1C-67E2-4226-8CD0-C5E28A15237B/0/JanBachKristensen_013007_BiofuelTech.pdf.

Kywe, Tint Tint and Myaoo Mya (2009) “Production of Biodiesel from Jatropha Oil in Pilot Plant”; Proceedings of World Academy of Science, Engineering and Technology, Vol. 3(8): PP. 481-487

Lal, R. (2006) Soil and environmental implications of using crop residues as biofuel feedstock. Intl Sugar J 108 : 161-167

Lalita, A., Sukunya, M. and Peesamal, J. (2004) Factors Affecting the synthesis of Biodiesel from crude palm kernel oils. The Joint International Conference on Sustainable Energy and Environment (SEE) Hua, Hin, Thailand.

Larsen, H., and Petersen,L.S.,(2007) ”Risoe Energy Report 6,”.

Lu, J. V., Gabriel, A., Reichler, T. (2007) Expansion of Hadley cell under global warming; Geophysical Research Letters http://www.atmos.berkely.edu.

McMicheal, A. J., Campell-Lendrum, D. H., Corvalan, C. F., Ebi, K. L., Githeko, A., Scherage, J. O. and Woodward, A. (2003) Climate Change and Human Health- Risk and Responses. WHO. Geneva.

Mohammed, H., Chakrabarti and Rafiq, A (2008) "Transesterification Studies On Castor Oil as a First Step Towards Its Use in Biodiesel Production"; Pak. J. Bot., 40(3): PP 1153-1157

Morrison, R. T., Boyd, R. N., (2005) Organic Chemistry. 6th ed., Prentice Hall of India Pvt Ltd. India.

Nagarhalli, M. V., Nandedkar, V. M. and Mohite K. C. (2010) Emission and Performance characteristics of Karanga Biodiesel and its blends in a C.I. Engine and its Economics. ARPN Journal of Engineering and Applied Science. Vol.5. No 2.

Narasimharao, K., Adanlee, and Kareen, W.(2007) Catalyst in the Production of Biodiesel. A Review. Journal of Biobased Materials and Bioenergy Vol.1. American Scientific Publishers.

Nwafor, O, M. I. (2004) Emission Characteristics of Diesel Engine operating on Rapeseed methyl ester. International Journal of World Renewable Energy. UK Vol.29.

Ocloo, F.C.K and Ayernor, G.S, (2010);" Production of Alcohol from Cassava Flour Hydrolyasate"; Journal of Brewing and Distilling Vol. 1(2) pp. 15-21

Ofor, M. (2009) Food Security and Mitigation of Climate Change through Ecosystem based Agriculture. National Question. Vol. 85 No 60.

Oguntola, J. A., Ezra, A. A. Nurudeen, O. A., Salam, O. I. (2009). Power and Torque characteristics of Diesel Engine Fuelled by Palm- kqernel Oil Boidiesel. Leonardo Journal of Science. Issue 14.

Okullo, A., Temu, A.K., Ogwok, P. and Ntalikwa, J. W (2012) "Physico-Chemical Properties of Biodiesel from Jatropha Oils and Castor Oils"; International Journal of Renewable Energy Research; Vol 2(1)

Oyeleke, G. O., Olayiwola, O. A. and Latona, D. F (2012); "Chemical Examination of Sandbox (Hura Crepitans) seed: Proximate, Elemental and Fatty Acid Profile; Journal of Applied Chemistry, Vol. 1(2). PP 10-13

Parikh J (2005) Growing our own oils. Biofuels India Vol. III (3) : 7

Pearson, P. N. and Palmer, M. R. (2000) "Atmospheric Carbon dioxide Concentrations over the past 60 million years. Nature 406(6797).

Personal interview Professor Birgitte Ahring, The Technical University of Denmark, 2007.

Personal interview with Professor Claus Feld by, Danish Royal Veterinary and Agricultural University, 2007.

Peterson JBD (2006) Ethanol production from agricultural residues. Intl Sugar J 108 : 177-180

Prasad, T. H., Reddy, K. H. C., Rao, M. M. (2010) Performance and Exhaust Emissions Analysis of a Diesel Engine Using Methyl Esters of Oil with Artificial Neural Network Aid IACSIT International Journal of Engineering and Technology Vol. 2 No 1

Quick, G. R.(1989). Oil Seeds as Energy Crops, in Oil Crops of the World. McGraw Hill Publishing Company, New York.

Reed, D.D.,(2007) “Michigan Tech’s Wood to Wheels Initiative,”. www.brdisolutions.com/Site%20Docs/TAC%20Meeting%20September%201011,%202007/W2W%208-30-2007.pdf

RFA (2001). Renewable Fuels Association. http://www.ethanolrfa.org/exchange/2 consulted January 2001.

Richard, B. and NeBambi, L (2010) “Jatropha, A Smallholder Bioenergy Crop; The Potential for Pro-Poor Development: Food and Agricultural Organization of United Nations, Fiat Panis, Integrated Crop Management; Vol. 8; Rome Italy

RISE (Research Institute for Sustainable Energy). http://www.rise.org.au/info/Res/biomass/ethanol002.JPG.

Rogers, D. and Randolph (2004) The Global spread of Malaria in a future warmer world. Science. 289 (5485).

Samson, R.A., and Omielan, J.A.,(2007) ”Switchgrass a Potential Biomass Energy Crop for Ethanol Production,” n.d.

Schuchardt, U., Serchelt, R. and Vargas, R. M. (1998) Transesterification of Vegetable Oils. A Review. Journal of Brazilian Chemical Society. Vol.9 No.1.

Schumacher, L.G., Hires, W. G. and Borgelt, S. C. (1992) Fueling a Diesel Engine with Methyl ester soybean oil. Liquid fuels from Renewable Resources. Proceeding of an Alternative Energy Conference. American Society OF Agricultural Enginers. Nashville, TN .

Schumacher, L. G., Borgelt, S. C., Hires, W.G., Fosseen, and Goetz, W. G. (1994) Fueling Diesel Engies with Blends of methyl ester soybean oil and Diesel fuel. Biodiesel 94, Sioux Falls, SD.

Schmacher, L. G., Hires, W. G., and Krahl, J. G. (1995) Cummins 5.9L Biodiesel Fueled Engines. Second Biodiesel Conference of the Americas. Portland

SOFA. 2008. The State of Food and Agriculture. Biofuels: prospects, risks and opportunities. Rome, FAO.

Somerville, C. (2008) Development of Cellulose Biofuels (PDE) US Department of Agriculture.

Stanadyne, W. (2003) Diesel Fuel. http://www.fiss.com/rm/firm0015.html.

Tangka, J. K., Berinyuy, J. E., Tekounegnin and Okale, A. N. (2011); “Physico-Chemical Properties of Bioethanol/Gasoline Blends and the Qualitative Effect of Different Blends on Gasoline Quality and Engine performance”; Journal of Petroleum Tech. and Alternative Fuels Vol. 2(3), pp. 35-44.

Tewari, K. S., Mehrrota, S. N., Vishnoi, N. K., (1985) Text Book of Organic Chemistry, Vikas Pubishing House Pvt. Ltd., New Delhi.

Thomsen M.H., Nielsen, H., et al.(2007) “Sustainable bioethanol production combining biorefinery principles and intercropping strategies,” http://www.risoe.dk/rispubl/reports/ris-r-1608_94-105.pdf.

Turkenburg WC (2000) Renewable Energy Technologies. In : Goldemberg J (ed) World Energy Assessment, United Nations Development Programme, New York NY, USA : 219-272

Tyson, K. S.(2001) Biodiesel, handling and use Guidelines. NREL Golden Co.

University of Nebraska–Lincoln, “Biofuel: Major Net Energy Gain From Switchgrass-based Ethanol,” Science Daily, Jan. 14, 2008. http://www.sciencedaily.com/releases/2008/01/080109110629.htm.

Wang, L., He, H., Xie, Z., Yang, J and Zhu, S (2007) “Transesterification of the Crude Oils of Rapeseed with NaOH in Supercritical and Subcritical Methanol. Fuel Proc. Tech., 88: 477-481.

Wang, M.(2005) “The Debate on Energy and Greenhouse gas Emission Impacts of Fuel Ethanol,”. www.transportation.anl.gov/pdfs/TA/347.pdf.

Watanebe, Y. Kusdiana, D. and Saka, S. (2004). Reactivity of Triglycerides and Fatty Acids of Rapeseed oil in supercritical Alcohol; Bioresources Technology

Wei-Dong H, Rong-Hong C, Tsung-Lin W, Ta-Hui L (2002). Engine performance and pollutant emission of an SI engine using ethanol– gasoline blended fuels. Atmos. Environ., 36(3): 403-410.

Williams RH, Larson ED, Katofsky RE, Chen J (1995) Methanol and hydrogen from biomass for transportation, with comparisons to methanol and hydrogen from natural gas and coal. PU/CEES Report 292, Princeton University/Center for Energy and Environmental Studies, Princeton NJ, USA

World Bank. (2008) “Agriculture for Development”; World Development Report 2008. Washington, DC.

Wu, W H., Foglia, T. A., Marmer, W. N., and Philips, J. G. (1998) “Optimization Production of Ethyl Esters of Grease Using 95% Ethanol by Response Surface Methodology”. JAOCS, 76: 4-10, 58.

APPENDIX

Table 4.1 Properties of Bioethanol Fuel Compared to that of Petrol.

Properties		ASTM Standard		E100
		Petrol	Ethanol	
Density Kg/m^3		747.4	794	789
Vapour Pressure (KPa)		36	10	9.5
Octane Number	RON	91	111	114
	MON	85	92	112
Flash Point (°C)		-65.0	13.0	12.5
Heating Value (MJ/kg)		44.4	30.0	29.78
Auto Ignition Temperature (K)		519	635	638
Distillation Temperature (°C)		30-190	75-80	55-68
Stoichiometric Air/Fuel Ratio		14.7	8.96	8.96

Table 4.2 Properties of Bioethanol Fuel Blended With Various Percentage of Petrol.

Properties		E90	E80	E70	E60	E50	E40	E30	E20	E10
Density Kg/m^3		784	783.4	782.3	781.2	780.5	779.2	778.2	760.5	750.8
Vapour Pressure (KPa)		18	24	28	31	34	35.6	38	39	38.9
Octane Number	RON	110	107	105	102	101	98	97	95	94
	MON	105	102.5	98.5	97	94	92	89	87.5	86
Flash Point (°C)		8.5	5.0	0.0	-1.0	-5.0	-13.5	-15.0	-20.0	-40.0
Heating Value (MJ/Kg)		30.1	33.83	34.51	35.84	37.16	38.50	40.48	42.08	44.22
Auto Ignition Temperature (K)		633	635	623	618	593	567	554	552	533
Stoichiometric Air/Fuel Ratio		9.53	10.11	10.68	11.25	11.83	12.40	12.98	13.55	14.12

Fig. 1 Reagents used for the preparation of Methoxide

Fig. 2 Measuring instruments used for the preparation of methoxide

Fig. 3 Blender used for transesterification process

Fig. 4 Produced bioethanol

Fig. 5 Produced Biodiesels

Fig. 6 Viscometers

Fig.7 Crude Vegetable Oils from the selected Nigerian Crops

Fig.8 Produced biodiesel compared to the Crude vegetable oil from Jatropha

Fig. 9 Hydrometers