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PREPARATION AND CHARACTERIZATION OF BIODIESEL FROM MELON SEED OIL AND TIGERNUT TUBER OIL

BY

SURMA, NGUAMO
PG/M.Sc/05/39981

DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY
UNIVERSITY OF NIGERIA, NSUKKA

JANUARY, 2008
PREPARATION AND CHARACTERIZATION OF BIODIESEL FROM MELON SEED OIL AND TIGERNUT TUBER OIL

BY

SURMA, NGUAMO
PG/M.Sc/05/39981

A PROJECT SUBMITTED TO THE DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY

UNIVERSITY OF NIGERIA, NSUKKA

JANUARY, 2008
CERTIFICATION

SURMA, NGUAMO, a postgraduate student in the department of Pure and Industrial Chemistry with registration number PG/M.Sc/05/39981 has satisfactorily completed the requirements for course and research work for the degree of M.Sc. in Industrial Chemistry. The work embodied in this project work is original and has not been submitted in part or in full for any diploma or degree of this or any other university.

PROF. C.A. NWADINIGWE
(Supervisor)

DR. C.O.B. OKOYE
(Head of Department)
DEDICATION

This project work is dedicated to God Almighty for His guidance and protection and to the memory of my late mum Mrs. Esther Rumun Surma and also my dad Mr Robert Ityover Surma for the countless sacrifices made for my sake.
ACKNOWLEDGEMENTS

My utmost gratitude goes to God Almighty for His love, mercy, guidance and protection given to me to this stage of my life.

I appreciate the hard work of my Supervisor Prof. C.A. Nwadinigwe in ensuring a critical scrutiny of this work. I am also grateful for his care and concern.

My thanks goes to the Head of Department and all the lecturers of the Department of Pure and Industrial Chemistry for the time and energy used in training me. I also wish to thank Mr. Emmanuel Mbaaji and all the staff in the various Chemistry laboratories for their kind support and co-operation.

The head of Department of Civil Engineering and the Chief technologist of fluid mechanics need special thanks for allowing me use their laboratory equipments. I also wish to thank Mr. Onah and Mr. Obi of the National Institute for Energy Research and Development for allowing me use their laboratory equipment.

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ABSTRACT

Oils were separately solvent extracted from 1000g of dried, powdered tubers of tigernut (Cyperus esculentus) and seeds of melon (Cucumis melo). After striping off the solvent by rotatory evaporation, each oil was dried at 55°C and characterized. Results showed viscosity (centipoise), specific gravity (g/cm³), heat of combustion (kJ/kg), saponification value (mg/g), acid value (mgKOH/g), iodine value (g/100g), peroxide value (mg/g), percentage moisture content (% by vol), percentage yield (% by wt), and colour for melon seed oil to be 20.450, 0.902, 36807.891, 5.049, 107.870, 10.400, 1.000, 47.140, and light yellow respectively. The corresponding values for tigernut tuber oil are: 34.190, 0.908, 39764.191, 185.130, 3.366, 83.750, 3.400, 0.900, 24.800, and golden yellow respectively.

Transesterification of the oils with methanol and potassium hydroxide as catalyst gave their corresponding methylesters (biodiesels) and glycerol which were washed, dried at (55°C) and characterized under the same conditions for viscosity (centipoise), specific gravity (g/cm³) heat of combustion (kJ/kg), saponification value (mg/g), acid value (mgKOH/g), iodine value (g/100g), peroxide value and colour of melon biodiesel: 5.348, 0.861, 36002.665, 178.117, 0.208, 104.058, 49.000, 0.050 and light yellow respectively; tigernut biodiesel: 4.650, 0.865, 38998.702, 185.130, 0.208, 82.167, 43.000, 0.040, and golden yellow respectively. Petrodiesel: 5.260, 0.859, 41714.741, 29.423, 0.208, nil, nil, 1.000, and light brown respectively. Comparison of the four critical parameters (viscosity, specific gravity, heat of combustion, and acid value) in the three diesels show that the two biodiesels have excellent diesel characteristics and can be used in place of the fossil based diesel.
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CHAPTER ONE
INTRODUCTION

1.0.0 BACKGROUND OF THE STUDY

Diesel plays an important role in the Industrial economy of our country. This fuel runs a major part of the transport sector and its demand is increasing steadily requiring an alternative fuel which is technically feasible, economically comparative environmentally acceptable and readily available. Vegetable oils are widely available from various sources, and the triglycerides present in the oils can be considered as a viable alternative for diesel fuel. Biodiesel which is synthesized from bio-oils is a realistic alternative because it provides a fuel from renewable resources and has lower emissions than the petroleum diesel. It is biodegradable and contributes a minimal amount of a net greenhouse gases or sulphur to the atmosphere. More specifically biodiesel cuts down the amount of carbon monoxide, hydrocarbons and particulate matter released to the environment.

The heating value of vegetable oils is similar to that of diesel fuel. However, their use in direct injection diesel is restricted by some unfavorable physical properties particularly the viscosity of vegetable oil which is approximately ten times higher than that of diesel fuel. Therefore, the use of vegetable oil in direct diesel engine creates poor atomization, incomplete combustion, carbon deposition on the injector and fuel building up in the lubricating of engine fouling. This necessitates improvement in the viscosity of bio-oil. The possible treatment includes dilution with a suitable solvent, emulsification pyrolysis and transesterification.

Transesterification of vegetable oils has been used since the mid 1800's. More likely it was originally used to distill out glycerine used for making soaps. The “by products” of this process are methyl and ethyl esters. Any source of complex fatty acid can be used to create biodiesel. Earlier on, peanut oil, hemp oil, corn oil and tallow were used as sources of complex fatty acids used in the separation process. Currently soyabeans, rape seed, corn, recycled fryer oil and tallow are common sources of the complex fatty acids and their
by-products biofuels. Biodiesel can be obtained from vegetable oil or animal fat (bio-fat) using transesterification\textsuperscript{10}.

Transesterification is a process of displacement of an alcohol group from an ester by another alcohol. In vegetable oil, almost 90 – 95\% is glycerides, which are basically esters of glycerol and fatty acids\textsuperscript{11}. In the process of transesterification of the glyceride in the bio-oil, a low molecular weight alcohol is used to displace glycerine to obtain esters of fatty acids. The process can be represented as follows:

\[
\text{Glyceride (G) + nROH + nR'CO}_2R \rightarrow \text{Rglycerine}
\]

Where, \(R\) and \(R'\) are hydrocarbon chains of the fatty acid group and alcohol respectively. The number of moles of alcohol is represented by \(n\), which can be 1, 2, or 3 depending upon the nature of the glyceride, that is, whether the glyceride is mono, di or tri. The glycerine produced in this process is a valuable by-product due to its numerous application in various industrial processes\textsuperscript{11}.

Biodiesel is a safer alternative to diesel fuel because it is environmentally safe and has no known side effects on humans. Diesel is used in some vehicles today and consumers do not like them due to the sound and smell. The smell is eliminated with biodiesel because it is made from different materials. It is against this background that this work seeks to investigate the biodiesel characteristics of oils from \textit{Cyperus esculentus} oil and \textit{Cucumis melo} oil in order to determine which biodiesel made from these vegetable oils would be the best replacement for diesel in the future.

1.1.0 STATEMENT OF PROBLEM

Biodiesel is a cleaner burning fuel that is renewable and can be substituted for petroleum diesel fuel and so the study of biodiesel cannot be over emphasized. Diesel made from fossil fuels has serious effects to human health. The National Institute for Occupational Safety and Health wanted diesel to be regarded as a “potential carcinogen”. A carcinogen is something that causes cancer and people can get cancer when they breathe the polluted air
that the car exhaust from diesel engines are creating. The pollution is likely to cause global warming which will also damage our planet later on. On the other hand biodiesel is 50% more likely to harm ozone layer if used in an engine rather than the petrodiesel fuel due to fact that it cuts down the amount of carbon monoxide hydrocarbons and particulate matter released to the environment\textsuperscript{12}.

Information about biodiesel needs to be distributed to the consumer in order to fully popularize their benefits and therefore increase the use of biodiesel throughout the planet. It has also necessitated the governments, research communities and private organizations around the world to look for alternative and renewable source of energy demands due to unpredictability of fossil fuels oil production and increased concerns of rising green house gas emissions\textsuperscript{12}.

If the use of biodiesel is ignored, the amount of unburnt hydrocarbons in the atmosphere will increase as well as carbon monoxide and other matter that is dispersed into the environment through car exhaust. This pollution is likely causing global warming which will also damage our planet\textsuperscript{12}.

1.2.0 AIMS/OBJECTIVES OF STUDY

a) To extract vegetable oils from \textit{Cyperus} esculentus tuber and \textit{Cucumis} melo seed.

b) To investigate some of the physiochemical properties of the extracted crude fat.

c) To carryout transesterification of the vegetable oils in order to obtain their methyl esters (biodiesels); separate the methyl esters from crude glycerol, purify and characterize the methylester.

d) To compare some of the characteristics of the methyl ester with fossil diesel and determine which methyl ester (biodiesel) will be the better replacement for the fossil diesel fuel.
1.3.0 SIGNIFICANCE OF STUDY

The following are important factors that make this research work very important. They are

1) Sustainable reduction of greenhouse gasses by use of biodiesel instead petroleum based diesel.
2) Less reliance on potentially unstable fossil fuel
3) Less reliance on important imported fossil fuel for instance Nigeria
4) Significant increased in opportunities for agricultural diversification and research
5) Increase research on oil plants and seeds
6) Significant development and creation of more job opportunities
7) Significant environmental gains due to biodiesel being biodegradable

1.4.0 SCOPE OF STUDY

This work covers the following areas

1. Seed and tuber collection
2. Oil extraction and Physiochemical characterization
3. Transesterification of the extracted oil to obtain methyl esters (biodiesel)
4. Characterization of the methyl esters (biodiesel) produced and comparison with fossil based diesel.
CHAPTER TWO

LITERATURE REVIEW

2.0.0 WHAT IS BIODIESEL?

The American Society for Testing and Materials (ASTM) defines biodiesel fuel as monoalkyl esters of long chain fatty acids derived from renewable lipid feed stock, such as vegetable oil or animal fat. “Bio” represents its renewable and biological source in contrast to traditional petroleum based diesel fuel. “Diesel” refers to its use in the diesel engines. As an alternative fuel, biodiesel can be used in neat form or blends with petroleum based diesel.

Biodiesel is a light to dark yellow liquid. It is practically immisible with water, has a high boiling point and low vapour pressure. Typically, methyl ester biodiesel has a flash point of 150°C (302°F), making it rather non flammable. Biodiesel has a density of 0.86 g/cm³ that is, less than the density of water. Biodiesel uncontaminated with starting material can be regarded as non toxic.

Biodiesel has a viscosity similar to petrodiesel, the industrial term for diesel produced from petroleum. It can be used as an additive in formulations of diesels to increase the lubricity of pure Ultra-Low Sulphur Diesel (ULSD) fuel, although care must be taken to ensure that biodiesel doesn’t increase the sulphur content of the mixture above 15ppm. Much of the world uses a system known as “B” factor to state the amount of biodiesel in any fuel mix, in contrast to the “B.A” or “E” system used for ethanol mixes for example. Fuel containing 20% diesel is labeled B20 and pure biodiesel referred to as B100.

Chemically most biodiesel consist of alkyl (usually methyl) esters instead of the alkanes and aromatic hydrocarbons of petroleum derived diesel. However, biodiesel has combustion properties very similar to petrodiesel including combustion energy and cetane ratings. Paraffin biodiesel, do not exist. Due to high purity of the source, it has a higher quality than petrodiesel.
Biodiesel is a cleaner burning fuel that is renewable and can be substituted for diesel fuel thereby relieving reliance on petroleum. It is biodegradable and non-toxic compared to petroleum based diesel. Biodiesel has more favourable combustion emission profile such as low emission of carbon monoxide, particulate matter, and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis thereby minimizing the impact of biodiesel combustion on the greenhouse effect. The relatively high flash point (150°C) of biodiesel makes it less volatile and safer to transport or handle than petroleum diesel. It provides lubricating properties that can reduce engine wear and extend engine life. In brief, these merits of biodiesel make it a good alternative to petroleum fuel and have led to its use in many countries especially environmentally sensitive areas.

Biodiesel must however, share common properties with diesel fuel so that they can be injected properly into the diesel engine as well as the energy that is given off by the fuel.

Biodiesel can be distributed using today's infrastructure and its use and production are increasing rapidly.

2.1.0 A HISTORICAL BACKGROUND OF BIODIESEL

Concurrent histories of biodiesel engine and biofuels are necessary to understand the foundation for today's perception of biofuels in general and biodiesel in particular. The history of biofuel is more political and economical than technological. The process for making fuel from biomass feedstock used in the 1800's is basically the same one used today. It was the influences of the industrial magnates during the 1920's and 1930's on both politics and economics of those times that created the foundation for our perception today.

Transesterification of vegetable oils has been in use since the mid-1800's. It was first conducted as early as 1853 by scientist E. Duffy and J. Patrick, many years before the first diesel became functional. More than
likely, it was originally used to distill glycerine, or vice versa. Any source of complex fatty acid can be used to create biodiesel and glycerine. Earlier on, peanut oil, hemp oil, corn oil and tallow were used in the separation process. Currently, soya beans rapeseed, (or the cousin canola oil) corn, recycled fryer oil are common sources for the complex fatty acids and their by-product, biofuel.

Ethanol and methanol are two familiar biofuels. Distillation of grain or weed resulting in an ethyl or methyl alcohol is the process by which these two biofuels are created. The viscosity of the 'original' biodiesel is lowered by approximately 10% methanol or ethanol of biodiesel esters. Methanol is preferred because there is reliable and predictable biodiesel in line with the viscosity requirement of today's diesel engines making it a major competitor of petroleum based diesel fuel.

Research into the use of trans-esterified sunflower oil and refining it to diesel fuel was initiated in South Africa in 1979. By 1983, the process to produce fuel quality engine tested biodiesel was completed and published Internationally (SAE Technical paper series no. 831356. SAE International off High way meeting Milwaukee, Wisconsin, USA, 1983). An Austrian Company Caskoks, obtained the technology from South African Engineers, put up the first pilot plant for biodiesel in November 1987 and the erection of the first industrial biodiesel plant on 12 April, 1989, with a capacity of 30,000 tons of rapeseed per annum. Throughout the 1990's plants were opened in many European countries including the Czech Republic; France, Germany, Sweden. At the same time, nations in other parts of the world also saw local production of biodiesel starting up and by 1998 the Austrian Biofuels institute identified 21 countries with commercial biodiesel project.

In 1990's France launched the local production of biodiesel fuel (known locally as diester) obtained by the transesterification of rapeseed oil. It is mixed to the proportion of 50% into regular diesel fuel and to the proportion of 30% into the diesel fuel used by some captive fleets (public transportation)
Renault, Peugeot and other manufacturers have certified trucks engines for use to this partial biodiesel\textsuperscript{14}.

In September 2005, Minnesota in USA became the first state to require that all diesel fuel sold should contain part of biodiesel. The Minnesota law requires at least 2\% biodiesel in all diesel fuel sold.

2.2.0 SOURCE/PRODUCTION OF BIODIESEL

A variety of oils can be used to produce biodiesel. These include:

1. Virgin oil feed stock, rapeseed and soybean oils are the most commonly used though other crops such as mustard, palm oil, hemp, jatropha peanut and even algae can be used.

2. Waste vegetable oil (WVO).

3. Animal fats including tallow, lard, yellow grease by products of the production of Omega-3-fatty acid from fish oil can be used\textsuperscript{14}.

Biodiesel can be made from vegetable oil or animal fats through transesterification or alcoholysis, enzymatic or lipases conversion and thermal cracking or pyrolysis. In pyrolysis method, fatty oils molecules were thermally or catalytically converted into hydrocarbon mainly alkane and alkenes, which are further fractionated to produce biogasoline or biodiesel. The equipment and operating cost for pyrolysis is expensive. The most commonly used method is trans-esterification of vegetable oils or fat with methanol or ethanol in the presence of a catalyst\textsuperscript{15}.

The reaction is shown in the figure below

Fig. 1:

\[
\begin{align*}
\text{Seed Oil Triglyceride} & \quad \text{CH}_2-OOC-R_1 \\
\text{CH}_2-OOC-\text{CH} & + 3\text{R}_4\text{OH} \quad \text{HO-CH} + \text{R}_4\text{COOR}_4 \\
\text{CH}_2-OOC-R_2 & \quad \text{CH}_2-OH + \text{R}_2\text{COOR}_4 \\
\end{align*}
\]

Glycerol

Esters
Transesterification of seed oils to produce fatty acid esters\textsuperscript{15}.

Because the reaction is reversible, excess of alcohol is used to shift the equilibrium to the product side. The completion of the transesterification reaction involves multiple parameters including molar ratio of the oil-to-alcohol, catalyst, reaction temperature, reaction time, free fatty acids and water contents of oils and fats. The mechanism and kinetics of biodiesel production has been studied by many researchers\textsuperscript{16,17}. These studies show that, the transesterification consists of a number of consecutive reversible reactions. Triglycerides are first reduced to diglycerides. The diglycerides are subsequently reduced to monoglycerides. Lastly, the monoglycerides are reduced to esters and glycerol the order of reactions changes with the reaction conditions\textsuperscript{15}.

The most common way to produce biodiesel is therefore by transesterification which refers to a catalysed chemical reaction involving vegetable oil and alcohol to yield fatty acid ester (the biodiesel) and glycerol\textsuperscript{13}. Triglycerides are the main components of vegetable oil, consist of three long chain fatty acids esterified to a glycerol backbone. When triglycerides react with an alcohol (e.g., methanol), the three fatty acids and chains are released from the glycerol skeleton and combine with the alcohol to yield fatty alkyl esters, fatty acid methyl esters or FAME\textsuperscript{13}. Methanol is the most commonly used alcohol because of its low cost and is the alcohol of choice in the process development. In general, a large excess of methanol is used to shift the equilibrium to the right\textsuperscript{13}.

A number of approaches are available for ensuring that transesterification reactions occur quickly enough to be practical. These options can be classified into the following groups.

1) Base catalyst such as NaOH, KOH and NaMeO
2. Acid catalyst such as H\textsubscript{2}SO\textsubscript{4}, H\textsubscript{3}PO\textsubscript{4}, and CaCO\textsubscript{3}.
3. Lipase enzymes (activity depends on source)
4. Non-catalyst options such as super critical processes and co-solvent systems\textsuperscript{18}.
Base catalysts are used for essentially all vegetable oil biodiesel production. The initial free fatty acid content is generally low and the water content is also generally low, tallow and greases with a free fatty content greater than 1% must be pre-heated to either remove the free fatty acid, (FFA) or to convert the FFA to esters before beginning. The base catalyst will react with the free fatty acids, to form soap and water. The soap formation reaction is very fast, with residence time from about 5 minutes to about 1 hour, depending on temperature, concentration, mixing and alcohol triglyceride ratio.\(^\text{19}\)

Acid catalysed systems are characterized by slow reaction rates and high alcohol. Generally, acid catalyzed reactions are used to convert free fatty acids (FFA) to esters and soaps, to esters as pretreatment step for high FFA feed stocks. Residence times from about 10 minutes to about 2 hours are reported.\(^\text{18}\).

Lipase catalyzed reactions have the advantage of producing only esters and pure glycerol. The enzyme reactions are highly specific and chemically clean. The reactions are very slow with a three step sequence requiring from 4 to 40 hours, or more. The reaction conditions are modest, from 35 - 40°C.

The non-catalyst options are designed to overcome the reaction initiation lagtime caused by extremely low solubility of the alcohol in the T.G. Phase. One approach that is nearing commercialization is the use of a co-solvent, tetrahydrofuran, to solubilize the methanol. The result is a fast reaction, on the order of 5 to 10 minutes and no catalyst residues in either the ester or the glycerol phase. The THF co-solvent is chosen, in part because it has a boiling point very close to that of methanol. This system requires a rather low operating temperature 30°C.\(^\text{18}\)

The first two types have received greatest attention. As for the enzyme-catalysed system, it requires a much longer reaction time than the other two systems, (1920). To date it has only been carried out on the laboratory scale and therefore will not be discussed herein.
Most current biodiesel research concentrate on the alkali catalyzed technology carried out on a bench scale and no detailed technological information is available on overall continuous industrial processes in both reactor and down stream separation units which are continually operated. Information on industrial process stimulation and design is also unavailable. Apart from transesterification reaction, the actual process of biodiesel production includes many process steps from raw material refining to product separation and purification.

2.2.1 ALKALI CATALYZED SYSTEM

Many studies on alkali-catalyzed transesterification on the laboratory scale have been carried out. A reaction temperature near the boiling point of the alcohol (eg. 60°C for methanol was used) and 6:1 molar ratio of alcohol to soybean were recommended. The Kinetics of the alkali-catalyzed system was also studied by Freedman. et. al., 1984 and Noureddini and Zhu (1997). Based on their results, approximately 90 – 98% oil conversion to methyl esters was observed within 90 min. In order to speed up the reaction Boocock et. al (1998) suggested the addition of tetrahydrofuran (THF) as a co-solvent to minimize mass transfer resistance. After the reaction, different techniques to purify the biodiesel product from the other products were investigated by Karaosmonoglu et. al. (1996). In terms of purity and high yield of biodiesel product, they concluded that the use of hot water washing at 50°C was the best way to obtain purity (99%) and yield of the production biodiesel.

The batch methods for biodiesel production are slow, tedious, labour intensive and low in productivity. A commercial continuous alkali-transesterification process to produce methyl esters on the industrial scale under high pressure (90 bars) and at higher temperature (240°C) was demonstrated by Kreutzer (1984) was applied industrially apart from the bench scale research. However, higher energy consumption, a significant increase in equipment cost and process safety issues related to for example,
high pressure and high temperature, could make this process prohibitive. Krawezyk (1996) presented a flow diagram for producing biodiesel via transesterification on the industrial scale. The process mainly consisted of a transesterification reactor, a methanol/glycerol distillation column. A continuous deglycerolization process to produce biodiesel from refined rapeseed oil by alkali catalyzed transesterification at ambient pressure and temperature (65 – 70°C) was introduced by Connermann and Fisher (1998). They noted successful applications of this process; a distillation column was also used to separate methanol from bio-diesel and glycerol. The methanol was recycled to the transesterification reactor and multistage washing was employed to purify the biodiesel product.

One limitation of the alkali-catalyzed process is the sensitivity to the purity of reactants; the alkali catalyzed system is very sensitive to both water and free fatty acids. The presence of water may cause ester saponification under alkali conditions. Also, free fatty acids can react with an alkali catalyst to produce soaps and water. Saponification not only consumes the alkali catalyst, but also the resulting soaps can cause the formation of emulsions. Emulsion formations create difficulties in downstream recovery and purification of biodiesel. Thus, dehydrated vegetable oil with (less than 0.5wt %) free fatty acids, an anhydrous alkali catalyst and anhydrous alcohol are necessary for commercially viable alkali catalyzed system.

2.2.2 ACID-CATALYZED SYSTEM

Despite its insensitivity to free fatty acids, in the feed stock, acid catalyzed transesterification has been largely ignored mainly because of its relatively slower reaction rate. Freemann et. al (1984), investigated the transesterification of soyabean oil, with methanol using 1% wt concentrated sulphuric acid. They found that at 65°C and a molar ratio of 30:1 methanol to oil it took 69 hours to obtain more than 90% oil conversation to methyl esters. Canakei and Gerpen (1999), studied the effects of the molar ratio of alcohol to soybean oil, the reaction temperature, the amount of catalyst and reaction...
time on the ester conversion by acid catalyzed transesterification. Each effect was studied independently on their effects. They found that increased ester conversion could be obtained at increased molar ratios of alcohol to oil, increased reaction temperatures, increased concentration of sulphur acid, and a longer reaction time. However, possible interaction of these variables was not investigated and optimal conditions for the acid-catalyzed reaction were not recommended.

Studies on the acid catalyzed system have been very limited in number. No commercial biodiesel plants to date have been reported to use the acid catalyzed process. Despite its relatively slow reactions rate, the acid catalyzed process offers benefits with respect to its independence from free fatty acid content and the subsequent absence of pretreatment step. These advantages favour the use of acid catalyzed process when using waste cooking oil as a raw material.

2.3.0 HOW TO MAKE BIODIESEL

Making biodiesel can be experimentally and technically challenging. To power our vehicles, we need to reduce the viscosity of the vegetable oil. Basically the vegetable oil needs to be mixed with alcohol, given time to settle, then drained. There are literally millions of different ways this can be done.

Vegetable oil is a triglyceride, that is three vegetable oil fatty acid radicals attached to glycerine through ester linkage. Glycerine is what makes vegetable oil thick. To make biodiesel, we want to remove glycerine and replace it with an alcohol. This is the process already referred to as transesterification.

To initiate the biodiesel reaction we need a catalyst. Vegetable oil is an ester, so to break the vegetable oil molecule, a strong base is added. For this, sodium hydroxide (NaOH) or potassium hydroxide (KOH) also known as lye are used. The amount of lye is constant with new vegetable oil. Details of the proportion of catalyst to be used is given in (Make your own biodiesel).
The amount of lye is however not constant with used vegetable oil, the amount varies due to the amount of free fatty acids (FFA's) from heating the oil. To determine the amounts of FFA's, a titration is performed.

The base catalyzed production of biodiesel generally occurs using the following steps:

2.3.1 Mixing of alcohol and Catalyst:

The catalyst is typical sodium hydroxide (caustic soda) or potassium hydroxide (potash). It is dissolved in the alcohol using a standard agitator or mixer.

2.3.2. Separation:

Once the reaction is complete two major products exist glycerine and biodiesel. Each has a substantial amount of excess alcohol (methanol) that was used in the reaction. The reaction mixture some times neutralized at this step is needed. The glycerine phase is much more denser than the biodiesel phase and the two can be gravity separated with glycerine settling down and run off the bottom of the settling vessel in some cases, a centrifuge or separatory funnel is used to separate the two material.

2.3.3 Alcohol Removal:

Once the glycerine and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. In other systems, the alcohol is removed and the mixture neutralized before the glycerine and esters have been separated. In either cases, the alcohol is recovered using distillation equipment and is re-used. Care must be taken to ensure no water accumulates in the recovered alcohol stream.

2.3.4 Methyl ester wash (washing biodiesel)

There are a number of water insoluble impurities left in biodiesel after the reaction and initial settling is complete. The contaminants include...
(primarily) soaps, a small amount of left over lye and some free glycerine. Washing the fuel with water removes these nasties. Washing also has two additional advantages; it stops very slow remaining reaction that sometimes occur (in unwashed fuel, sometimes glycerine is seen setting over a period of weeks or months, and washing and removing methanol or lye will stop this) and it provides one with some quality feed back control.

When biodiesel is first made, it is quite caustic with a pH of between 8.0 and 9.0. Washing with plain water is sufficient to wash out all remaining catalyst, bringing the pH down to near territory (neutral).

2.3.4.1. Bubble Washing

Bubble washing involves gently adding 1/3 water to 2/3 biodiesel adding a cheap aquarium air stone and air pump set up to the water portion (water sinks to the bottom and biodiesel will float on top) and air bubbling through the water. The air bubbles allow a sort of indirect agitation of the two fluids — they pick up a tiny amount of the water and gently carry it through the biodiesel picking up soaps and other contaminants, when the bubble bursts at the surface it drops the water which it picks up more of the soaps and contaminants on its way back down. After about 6 hours of this (low-wattage) washing, the air is stopped, then the water is drained more fresh water is added and the process repeats. These wash water changes are repeated about 3 times on average until the water measures the same pH of your tap water, and is perfectly clear. The wash water can be reused a number of times to wash succeeding batches.

Advantages are that bubbles washing use less water than others and that it uses very cheap equipment. The disadvantage is that if the biodiesel produced is of poor quality, or and in a very small bath, bubble washing can an agitate the water and biodiesel too vigorously, causing emulsification of the two liquids. Emulsification is the quintessential wash problem but it is also a form of quality testing and feed back on your process.
Mist Washing

Mist washing was developed as a way to address emulsification issues. It uses more water and more complicated equipment. It also masks quality problems – a "good wash" can be obtained but will have much less of an idea of what you've made. This system uses a very fine mist head from a garden supply store, suspended over a container of biodiesel, with a way to drain the water falls through the fuel. The mist stirs up the fuel less than in bubble washing, and remove soap gradually. The gentler agitation gives less of an opportunity for the soap and mono and diglycerides to form emulsions. Many mist users also do bubble washing as final step after the soaps are gone and the monoglycerides and diglycerides alone won't usually emulsify the fuel and water as much, so bubbling after misting usually works.

2.3.4.2 Mix washing (Bulk Washing)

Mix washing is usually done with 50% water and 50% biodiesel. The water is in first and then the biodiesel. The water and biodiesel are mixed using whatever mixing device. It is then turned off and allowed to settle to the bottom and the biodiesel will remain on top of the water. As the mix settle out, the water will slowly sink, taking with it any soluble material mainly the remaining alcohol and catalyst. Heat will speed up this reaction nicely.

In the first wash, the water will turn almost totally white; this is because a form of soap is created when water comes in contact with the catalyst in the biodiesel. It should clear up as the soap washes out with sub-sequential washings. The water is drained after each washing and the wash is repeated three times or more until the drained water wash is totally clear, if the biodiesel is allowed to cool and filtered through a 10-micron filter while cold.

2.3.4.5 Acid Washing

The university of Idaho and many published instruction about washing used to recommend using acid to help washing easier. People use it routinely in
their first wash. Which acid to use doesn't matter very much, and household vineyard or citric acid was routinely used.

If an emulsion is formed during biodiesel production, an acid is used to see if it might break the emulsion. However, it isn't the best method to use as it compromise the quality of the finished fuel.

Acidifying a wash or an emulsion works by breaking up the soaps into their constituent parts for minor a salt and free fatty aid. The FFA will end up in the biodiesel and is indistinguishable from it. FFA content is of concern to the ASTM and other specifications for biodiesel. FFA promotes some corrosion of metals raising the FFA doesn't seem to be a good thing to do.

2.3.4.6 Drying

When biodiesel is clear (not colourless but translucent) it is dry. Drying the biodiesel requires a little more than heating up the final biodiesel at 55°C (130°F), but also holding it there for 15 – 20 minutes any remaining water should evaporate out or drop out easily where it an be drained out.

Based on past experiments, water washing was found to be inefficient method, because of the amounts of water used, and the soap emulsions were difficult to remove. Therefore, a cleaner easier method is used which involves washing the biodiesel with silica gel. The ester should be free from alcohol before silica gel treatment. The methyl ester is transferred to an Erlenmeyer flask into which silica gel is added. The mixture is stirred to remove the silica gel from methyl ester. Biodiesel is filtered through a layer of sodium sulphate to remove any traces of water present.

It is generally accepted to filter – biodiesel through a 10-micron filter before suspended component that solidify at cooler temperatures.

2.4.0 VEGETABLE OIL, DIESEL BLENDS AS POTENTIAL FUEL SOURCES

During World War II, experiments were carried out using several vegetable oils in a Perkins diesel engine with great success. The result of this
experiment showed that vegetable oil could be used to power a vehicle under normal operating conditions. However, it was noted that much more work was needed before vegetable oils could be used as a reliable substitute for diesel fuel.35

The southwest Research Institute evaluated the Chemical and physical properties of 14 vegetable oils. These injection studies pointed out that the oils behave very differently from petroleum-based fuels. This change in behaviour was attributed to the vegetable oils high viscosity. Engine tests showed that carbon deposits in the engine were reduced if the oil was heated prior to combustion. It was also noted that carbon levels differed for oils with similar viscosities indicating that the oil compositions was an important factor.36

Studies on the characteristic properties of eleven vegetable oils to determine which oils would be the best suited for use as an alternative fuel source was carried out of the eleven oils tested. Corn, rapeseed, sesame, cotton seed oil and soybean oils had the most favourable fuel properties.37

Sunflower oil was tested as a replacement of diesel in agricultural tractors. Sunflower oil viscosity was 14% higher than diesel fuel at 37°C. Engine performance using the sunflower oil was similar to that of diesel fuel, but with slight decrease in full economy. Oxidation of sunflower oil left heavy gum and wax deposits on test equipment which could lead to engine failure.38

The use of several vegetable oils as potential fuel sources was evaluated. Initial engine performance test using vegetable oils were found to be acceptable, while noting that the use of these oils caused carbon build up in combustion chamber. Continuous running of a diesel engine at part-load and mid-speeds was found to cause rapid carbon depositions rates on the injector tips. Short - 2 – hour test were used to visually compare the effects of using different vegetable oils in place of diesel fuel. Although short-term engine test results were promising long term engine testing to determine the overall effects of using vegetable oils as a fuel in diesel engines was recommended.39

Rapeseed oil was used as a diesel fuel replacement in Germany with mixed results. Short-term engine tests indicated rapeseed oil had similar
energy output when compared to diesel fuel. Initial long-term engine tests showed that difficulties arose in engine operation after 100 hours due to deposits on piston rings, valves, and injectors. The investigators indicated that further long-term testing was needed to determine if these difficulties could be averted.40

Short term and long term test performance test using 100% soybean oil in a small diesel engine was conducted. Short-term result indicated that soybean performance was equivalent to that of diesel fuel. However, long-term engine testing was aborted due to power loss and carbons build up on the injector.41

A reviewed report for successes and shortcomings for alternative fuel research was carried out. This article stated that short-term engine test using vegetable oil as fuel source was very promising. However, long-term engine test results showed that durability problems were encountered with vegetable oils because of carbon build up and lubricating oil contamination. Thus it was concluded that vegetable oils must either be chemically, altered or blended with diesel fuel to prevent premature failure.42

Studies involving the use of raw vegetable oils as a replacement fuel for diesel fuel replacement indicate that a diesel engine can be successfully used with 100% vegetable oil on short-term basis. However, long-term engine durability studies show that fueling diesel engines with 100% vegetable oil causes engine failure due to engine oil contamination, stock piston rings, and excessive carbon build-up on internal engine components. Therefore, 100% unmodified vegetable oils are not reasonable diesel fuel replacements.43

A data for 10% to 50% soyabean oil fuel blends used in diesel was performed. The initial results were encouraging. They reported at the conclusion of a 50-hour test that carbon build-up on the combustion chamber was minimal. For the fuel blends studied, it was originally observed that vegetable oils could be used as fuel source in low concentrations. Power, measurements for the fuel blend only differed slightly from 100% diesel fuel. Fuel blends containing 60% or higher concentration of vegetable oils caused the engine to sputter. Engine sputtering was attributed to fuel filter plugging.
They concluded that waste soyabean oil could be used as diesel fuel extender with no engine modifications.46

Studies in New Zealand indicated that vegetable oils, particularly rapeseed oil could be used as a replacement for diesel fuel. Their initial short-term engine tests showed that a 50% vegetable oil fuel blend had no adverse effects. While in long term tests, they encountered injector pump failure and cold starting problems. Carbon deposits on combustion chamber components was found to be approximately the same as that found in engines operated on 100% diesel fuel. These researchers concluded that rapeseed oil had grant potential as a fuel substitute but that further testing was required.45

The long-term effects of using sunflower oil as a diesel fuel replacement in direct and indirect injected diesel engine was examined. Indirect injected diesel engines were run for over 2000 hours using de-gummed, filtered sunflower oil with no adverse effects. The direct injected engines were not able to complete even 400 hours of operation on the 20% sunflower oil to 80% diesel fuel mixture without a power loss. Further analysis of the power loss was due to severely coked injectors, carbon build up in the combustion chamber, and the stuck piston rings. Lubricating oil analysis showed high piston liner, and bearing wear.46

A characterization of injection and combustion properties of vegetable oils was carried out. The atomization and injection characteristics of vegetable oil were significantly different from that of diesel fuel due to higher viscosity of the vegetable oils. Engine performance tests showed that power output slightly decreased when using vegetable oil blends. Injector coking and lubricating oil contamination appeared to be a more dominant problem of oil based fuel having higher viscosities.47

Due to engine durability problems encountered using raw vegetable oils as a fuel in the early 1980's most researchers opted to use chemically modified vegetable fuels more commonly known as biodiesel in place of unrefined vegetable oils as a fuel additive.43
2. COMPOSITION OF VEGETABLE OIL

Vegetable oils and fats are obtained from seeds or fruits rich in the oils. They have mostly yellow colour or light green colour and have a slight smell and a taste of seed or fruit from which they are obtained. They are suitable after extraction as table oils, others are used in the preparation of products such as margarine. Vegetable oil can also be used in the production of biodiesel. It is also suitable for the production of paints and varnishes.

Chemically, vegetable oil consists of glycerol molecule completely esterified with fatty acid to form triglycerides (three fatty acids). They consist mostly of unsaturated acids, which have a deficiency of hydrogen atoms so that the link between the unsatisfied carbon atoms becomes a double bond. They also consist of saturated acid as shown in stearic and palmitic acids.

A very high proposition of vegetable oil is composed of a group of closely related component the triglycerides which are fatty and esters of trihydric alcohol glycerol. Minor components which are non-glyceride together rarely compose more than 5% of the total material and are frequent in even lower concentrations. These include phospholipids glycolipids, steroids, several tocopherols vitamin A and vitamin D among others. Only the major component of vegetable oils will be further discussed.

Triglyceride

These components are formed by a reaction of trihydric alcohol glycerol (commonly known as glycerine) and fatty acid. Triglycerides that are solid at room temperature are often referred to as 'fats' whereas those that are liquids are called unsaturated fatty acids and are referred to as oils.

It is a combination of different acids and glycerols which gives the wide range of triglycerides and influences the physical characteristics of the various oils which occur in nature. The structures of triglycerides are named according to the nature of acids present.
Fatty Acids: Fatty acids are the simplest lipids. A fatty acid is a long chain of carbon and hydrogen atoms with a carboxylic group at the end. If the hydrocarbons contain one or more double bonds, it is unsaturated and has room for more hydrogen atoms. Those with one double bond are mono unsaturated while those with two or more bonds are polyunsaturated. On the other hand, if the hydrocarbon contains no double bond, it is said to be saturated as it is in palmitic acid.

The structure of the fatty acid is relatively simple and follows that of the simplest organic compounds, the normal paraffin. The molecule of a saturated acid consists of a chain of carbons carrying a carbon oxide, the organic acid grouping. This is shown in palmitic, lauric and stearic acid common saturated acids are shown in table. (1.1)

The unsaturated acids have a deficiency of hydrogen atoms so that the link between the two carbon atoms becomes a double bond as shown in oleic and palmitoleic acids which are unsaturated.

Poly unsaturated fatty acids which have a special arrangement of double bonds known as conjugated systems \(-\text{CH}=-\text{CH}-\text{CH}=\text{CH}-\) is possible. This gives some special strong drying properties. They are usually referred to as essential fatty acids (EFA) because of their necessity for growth and occurrence of syndromes attributed to their deficiency, some polyunsaturated fatty acids are listed in table. Fatty acids seldom occur free but are usually combined with other molecules to form substances (Triglycerides).
Free fatty acids (FFA)

Fatty acids can be bound or attached to other molecules like triglycerides, phospholipids. When they are not attached to other molecules, they are known as "free fatty acids". The uncombined fatty acids or free fatty acid may come from the breakdown of a higher triglyceride into its component (fatty acid and glycerol). When the fatty acid chains are broken from the glycerol and then re-esterified to methyl or ethyl groups, those fatty acids still have their double bonds; they lower the cloud point because they resist solidifying at lower temperatures. So, for instance, if one uses lard or tallow, the biodiesel will solidify at a higher temperature because the fat it was formed from also solidified at a higher temperature.

Table 1.1 Some common saturated and unsaturated fatty acids.

<table>
<thead>
<tr>
<th>Common name</th>
<th>Chain length C-atom</th>
<th>No. of double bonds</th>
<th>Abbreviated structural formula</th>
<th>Melting point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric acid</td>
<td>12</td>
<td>0</td>
<td>CH₃(CH₂)₁₂-COOH</td>
<td>44.2</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>14</td>
<td>0</td>
<td>CH₃(CH₂)₁₄-COOH</td>
<td>54.2</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>16</td>
<td>0</td>
<td>CH₃(CH₂)₁₆-COOH</td>
<td>62.9</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>18</td>
<td>0</td>
<td>CH₃(CH₂)₂₀-COOH</td>
<td>69.6</td>
</tr>
<tr>
<td>Palmitoleic acid</td>
<td>16</td>
<td>1</td>
<td>CH₃(CH₂)₁₄-CH=CH(CH₂)₂-COOH</td>
<td>0.5</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>18</td>
<td>1</td>
<td>CH₃(CH₂)₁₆-CH=CH(CH₂)₂-COOH</td>
<td>16.0</td>
</tr>
<tr>
<td>Erucic acid</td>
<td>22</td>
<td>1</td>
<td>CH₃(CH₂)₁₈-CH=CH(CH₂)₂₀-COOH</td>
<td>34.0</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>18</td>
<td>2</td>
<td>CH₃(CH₂)₁₄-CH=CH(CH₂)₇-COOH</td>
<td>-7</td>
</tr>
<tr>
<td>Linolenic acid</td>
<td>18</td>
<td>3</td>
<td>CH₃(CH₂)CH=CH(CH₂)₇-COOH</td>
<td>-11</td>
</tr>
</tbody>
</table>

Since oils and fats contain glycerol, the differences between them must be due to the differences in their fatty acid components. Also, the physical and chemical properties of oils are due to the dominant fatty acid component present.
2.6.0 Methods of extracting vegetable oil

Fats may be recovered from oil-bearing tissues by three general methods with varying degrees of mechanical simplicity\(^4\). The seeds or nuts must first be crushed or flaked before oil extraction. These methods include rendering, pressing, and solvent extraction. Depending on the particular seed and extraction method, the moisture content must be adjusted to an optimum level by exposing the seeds to a temperature of 40 – 60°C in the oven for about 24 hours depending on the nature of seeds.

2.6.1 Rendering

This process is used in the preparation of palm oil, the fresh palm fruits are boiled in water and the oil is skimmed from the surface. Such processes can be used only with seeds or fruits (such as olive and palm) that contain large quantities of easily released fatty matter. The rendering process is applied on a large scale to production of animal fats such as tallow, lard, bone fat and whale oil. It consists of cutting or chopping the fatty tissue into small pieces that are boiled in open vats or cooked in steam digesters. The fat gradually liberated from the cells, floats to the surface of the water, where it is collected by skimming\(^5\).

2.6.2 Pressing

With many oil bearing seeds and nuts rendering will not liberate the oil from the cellular structures in which it is held. These cases the cell walls are broken by grinding, flaking, rolling or pressing under high pressures to liberate the oil.

The general sequence of modern operations in pressing oil seeds and nuts are as follows:

1) The seeds are passed over magnetic separator to remove any stray bits of metal
2) If necessary the shells or hulls are removed
3) The kernels or meats are converted to coarse meal by grinding between grooved rollers or special types of hammer mills.

4) They are pressed in hydraulic or screw passes with or without preliminary heating depending on the type of oil-bearing material and the quality of oil desired\textsuperscript{16}. This can be done cold or hot\textsuperscript{17}.

Oil expressed without heating contains least amount of impurities and it is often of edible quality without refining or further processing. Such oils are known as cold-drawn, cold pressed, cold-drawn or virgin oils. Cold pressing is done at room temperature yielding a lesser amount of oil, and substances such as vitamins and phytosterols, which give it the flavour and many of its medicinal properties\textsuperscript{18}.

Pressing the coarse meal while it is heated removes more oil and also greater quantities of non-triglycerides impurities such as phospholipids, coloured bodies and unsaponified matter. Such oil is more highly coloured than the cold-pressed oil\textsuperscript{19}.

2.6.3 Solvent extractions

A more complete extraction is carried out using solvent extraction. Modern commercial methods of solvent extraction use volatile purified hydrocarbons especially the various grades of petroleum, commonly referred to as petroleum ether, commercial hexane, or heptanes, benzene and carbon tetrachloride. In a large scale production, solvent extraction is a more economical means of recovering oil than is mechanical pressing. A pre-processing process performed in seeds or nuts, is done to remove a portion of the oil before extraction. A typical extracting system consists of the following processes.

i) Cleaning to remove iron, dirt, foreign weeds, seeds and stones,

ii) Removing hulls or shells in cracking aspirating or screening operations;

iii) Cracking or rough grading the kernels meats or pre-pressed cake

iv) Steaming of the meats

v) Flaking the small pieces between smooth flaking rolls;
Extracting the oil with the solvent;
Separating the meat or marc from the oil solvent solution called miscella
Removing the solvent from both the miscella and the marc. The marc may be toasted or pelletize or both for use in animal feeds.

Most extracted meats contain less than 100% of residual oil. The amounts vary depending on the degree of pre-pressing the type of material being extracted and the efficiency of the extracting system.

Extractability of the oil has been found to depend on the nature of the solvent, flake thickness and the pre-treatment conditions of the seeds. Different factors determine the choice of solvents seed-oil properties, process safety, solvent volatility, stability and economic factor. The colour intensity or the absorbance of the extracted oil and the variation in the non-fatty materials extracted along with the oil depend on the differences in solvent capacity. These therefore lead to the differences in the quality of the oil obtained.

The properties of a suitable solvent for use in a simple extraction procedure is that, it should readily dissolve the substance to be extracted, should be immiscible with any other liquid used, should not lead to any undesirable side reactions and should be volatile so that it can readily be removed after extraction. Other considerable factors include the flammability of the solvent, cost, toxicity, and ease of manipulation of the solvent. The table below shows the boiling points (ranges) of the different common extractable solvents.
Table 1: Extractible solvents in order of decreasing polarity

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Molecular formula</th>
<th>Boiling point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>100</td>
</tr>
<tr>
<td>Acetone Acid</td>
<td>CH₃COOH</td>
<td>118</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>CH₃CN</td>
<td>82</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
<td>65</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>78</td>
</tr>
<tr>
<td>Acetate</td>
<td>CH₃COOCH₃</td>
<td>56</td>
</tr>
<tr>
<td>Ether</td>
<td>C₂H₅OC₂H₅</td>
<td>35</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>CH₃COOC₂H₅</td>
<td>77</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>CH₂Cl₂</td>
<td>44</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CHCl₃</td>
<td>61</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>CCl₄</td>
<td>76</td>
</tr>
<tr>
<td>Toluene</td>
<td>C₆H₅CH₃</td>
<td>111</td>
</tr>
<tr>
<td>Ligolin (mixture)</td>
<td>C₆H₅CH</td>
<td>90 – 100</td>
</tr>
<tr>
<td>Petroleum ether</td>
<td>–</td>
<td>35 – 60</td>
</tr>
<tr>
<td>N-Pentane</td>
<td>–</td>
<td>36</td>
</tr>
<tr>
<td>N-Hexane</td>
<td>C₆H₁₂</td>
<td>69</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>C₆H₁₂</td>
<td>81</td>
</tr>
<tr>
<td>N-heptane</td>
<td>C₂H₁₆</td>
<td>94</td>
</tr>
</tbody>
</table>

2.7.0 PHYSICAL AND CHEMICAL PROPERTIES OF VEGETABLE OILS

2.7.1 PHYSICAL PROPERTIES

Vegetable oils may either be liquid or noncrystalline solids at room temperature. Contrary to the popular belief, pure fats and oils are colourless and tasteless. The characteristic colour, odour and flavour associated with them is by foreign substances that have been absorbed by oils and soluble in them. The viscosity increases with a slight increase in the degree of saturation and increasing chain length. Prolonged heating tends to reduce the viscosity of the oil.
They are lighter than water and immiscible with it but freely soluble in organic solvents such as benzene, petroleum ether and others\textsuperscript{61}. The density of the oils decreases with decreasing molecular mass, degree of unsaturation and free fatty acid content\textsuperscript{62}. The Melting points of fatty acid of oils decreases with increases in the degree of unsaturation and decreases with increases in the molecular mass on the other hand, the boiling point of oils increases with decrease in unsaturation\textsuperscript{69}.

2.7.2 CHEMICAL PROPERTIES

Drying

Based on the concept of drying, oils can be classified into drying, semi-drying and non-drying oils. This method of classification has its weakness and is more suited to classification for industrial use more than for edibility\textsuperscript{50}.

Drying oils

Certain oils containing glycerides of unsaturated acids with 2-3 double bonds such as linoleic and linolenic have the property of slowly absorbing oxygen and polymerizing to form hard transparent coating. This process is known as drying and the oils that exhibit this characteristic are called drying oils\textsuperscript{61}.

The exact mechanism of this process is not fully understood but it is sufficient for our purpose to accept that cross-linking takes place between two adjacent molecules. The double bonds of the fatty acids are involved in this cross-linking which is of great relevance to the paint industry. In the edible oil field, it can give rise to deterioration of frying fats owing to polymerization. As the rate of oxidation and polymerization is related to the degree of unsaturation, it is this factor that limits the use of highly unsaturated fats. Polymerization is accompanied by a rise in viscosity, a fall in iodine value (a measure of unsaturation) and deterioration of flavour\textsuperscript{68}. 
If oils contain a conjugated system of double bond for example, eleostearic acid and licanic acids, present in tung and oiticica oils, drying takes place faster.

Rancidification

On long storage in contact with air, vegetable oils undergo slow decomposition and develop unpleasant smell. This process is known as rancidification. The following chemical changes have been reported to take place. They include:

- Aerial oxidation of unsaturated acid produced during hydrolysis, followed by decarboxylation forming ketones possessing unpleasant flavour.

Rancidity is a major concern to food industry and chemist involved in this area are continually seeking new better substances that act as antioxidants which can be added in very small amounts (0.01-0.001)% to suppress rancidity.

Hydrolysis

Oils and fats can be hydrolyzed to glycerol and fatty acid by dilute acid, alkaline and superheated steam. Hydrolysis is brought about by enzymes (for example lipases). Fig 3 Hydrolysis of oil

\[
\begin{align*}
\text{CH}_2\text{OOC}_{15}\text{H}_{31} + 3\text{H}_2\text{O} & \rightleftharpoons \text{CHOH + 3C}_{18}\text{H}_{31}\text{COOH} \\
\text{CH}_2\text{OOC}_{15}\text{H}_{31} & \rightarrow \text{CH}_2\text{OH}
\end{align*}
\]

Hydrolysis of oil

Alkaline hydrolysis is termed saponification because one of the products of the hydrolysis is soap generally, sodium of potassium salts of fatty acids.

Fig 4.
Vegetable oils which contain more unsaturated glycerides than unsaturated glyceride are liquids at room temperature. When liquid hydrogen is passed through them under high pressure and in the presence of a suitable catalyst, usually, finely divided nickel or Raney nickel, the unsaturated glyceride and the oil assume a solid form. This is known as margarine or vegetable ghee.

Another chemical property of vegetable oil is hydrogenolysis which is the splitting of a component by means of hydrogen.
Hydrogenated oils and shortenings can be used to make biodiesel. Margarine is more problematic, and should be avoided, unless one is an expert. When oils are hydrogenated, hydrogen atoms are added to the carbon double bonds in unsaturated fatty acids, which then become saturated. This result in higher melting points. Hydrogenation also lowers the iodine value (iv) of the oil. So biodiesel made from hydrogenated oils is less likely to oxidize and polymerize but will have a higher melting point than if it were made from unhydrogenated oil of the same kind. It increases the risk of filter plugging in cold weather or even just cool weather and is best used as summer fuel6).
2.8.0 VEGETABLE OIL
SOME ANALYTICAL CHARACTERISTICS OF VEGETABLE OIL

2.8.1 ACID VALUE

Acid value is the measure of free fatty acids present in a fat/oil. Some of
the deterioration that takes place during storage of either the raw material from
which the fat is obtained or in the fat itself, after isolations results in the
hydrolysis of triglycerides to yield free fatty acids.\(^5\)

Acid value of fat or oil is the number of milligrams of potassium hydroxide required to neutralize the free organic acid present in 1gm of fat or
oil.\(^5\)

A high acid value is indicative of stale oil or fat stored under improper
conditions. The acid value is the direct measure of FFAs in BIOO. The free
fatty acids can lead to corrosion and may be a high symptom of water in fuel.\(^6\)

2.8.3 IODINE VALUE

Iodine value is a measure of the proportion of unsaturated acids present.
There is no iodine present in oils and fats, but the test measures the amount of
iodine which can be absorbed by unsaturated organic compounds in the
reactivity of the double bonds, especially their ability to form addition
compounds with halogens. As addition takes place at the double bonds,
measurement of the quantity absorbed is a measure of the number of double
bonds present. As the concentration and types of unsaturated acids present in
the fat are fairly constant the iodine value will give a figure for the percentage
of iodine absorbed by the fat.\(^5\)

Iodine value is defined as the number of grams of iodine taken up by
100gm of fat or oil.\(^6\) Generally, the higher an oil’s iodine value, the lower the
mixture's cloud point (CP), and pour point (PP) in practice they all mean the same
matter with both systems using straight vegetable oil as fuel and with
biodiesel, but more so with straight vegetable oil (SVO).\(^6\)
Low iodine value oils have higher cetane values and are more efficient fuels than high iodine value oils, but they also have higher melting points and are usually solids at room temperature. Biodiesel made from low iodine value oils have a higher melting point and might be suitable for use in summer.

High iodine value oils have lower melting points and make better cold-weather biodiesel, but with high iodine value oils there is more risk of biodiesel oxidizing and polymerizing (drying) into a tough, insoluble plastic-like solid. Biodiesel made from high iodine value oils should be stored carefully and used quickly. Semi drying oils like Soyabean and sunflower are also prone to polymerization, though not as quickly as the drying oils.

Iodine value tells us the type of oil that we have whether it is drying oil or non-drying oil. When the iodine value is high about 150, the oil is a drying oil. When the iodine value is below 150, it is a non-drying oil (85 – 105). For semi drying oils the iodine value ranges from (105 – 130).

Table 1.4 Classes of oil and their iodine number.

<table>
<thead>
<tr>
<th>Iodine number</th>
<th>Classes of oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>Drying oil</td>
</tr>
<tr>
<td>100 – 130</td>
<td>Semi drying oil</td>
</tr>
<tr>
<td>&lt; 100</td>
<td>Non drying oil</td>
</tr>
</tbody>
</table>

2.8.3. SAPONIFICATION VALUE

This is defined as the number of milligrams of potassium hydroxide required to saponify 1gm of oil or fat, that is to neutralize completely, the fatty acid resulting from complete hydrolysis of 1 gram.

The saponification value gives on idea of the molecular weight of the fatty acid. The higher the saponification value, the higher the molecular weight. It is determined by refluxing a weight amount (1 – 2gm) of fat or oil with know excess of standard alcoholic caustic potassium solution and back titrating the excess alkali with a standard acid.
Table 1.5: Saponification value of some oils.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Saponification value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut</td>
<td>246 – 250</td>
</tr>
<tr>
<td>Palm</td>
<td>196 – 210</td>
</tr>
<tr>
<td>Castor</td>
<td>176 – 187</td>
</tr>
<tr>
<td>Olive</td>
<td>185 – 200</td>
</tr>
<tr>
<td>Cotton seed</td>
<td>191 – 196</td>
</tr>
<tr>
<td>Linseed</td>
<td>190 – 196</td>
</tr>
</tbody>
</table>

2.8.4 PEROXIDE VALUE

The peroxide value is usually used as an indication of deterioration of fats. As oxidation takes place the double bond in the unsaturated fatty acid are attacked forming peroxide. These breakdowns to produce secondary oxidation known as rancidity. The peroxide value can therefore be used to estimate oxidation, but as the compound formed is unstable and the oxidation proceeds further, it is not a complete measure of oxidation and if taken in isolation may give rise to misleading conclusion.

When unsaturated oils and the biodiesel made from them are exposed to oxygen the oxygen attaches to a carbon that is immediately adjacent to those involved in the double bond (a beta carbon). This forms a hydroperoxide molecule. The presence of these compounds is a measure of peroxide value, which is an indicator of early steps in the oxidation process, and this gives an idea of the fuel stability.

A fuel is considered unstable when it undergoes chemical changes that produce undesirable consequence such as deposits, acidity or a bad smell. There are three different types of stability commonly described in the technical literature; thermal stability, oxidative stability and storage stability.
Thermal stability addresses fuel changes that occur due to elevated temperature. These changes may occur at conditions commonly found in diesel fuel injection system (66 – 100°C) and particularly at conditions found at the fuel injector temperature (300°C).

Oxidative stability refers to the tendency of fuels to react with oxygen at temperatures near ambient. These reactions are much slower than those that would occur at combustion temperature, and they produce varnish deposits and sediments.

Storage stability is also frequently used to refer to the stability of the fuel while it is in long-term storage. These terms are not necessarily exclusive terms. For example, oxidative attack is probably one of primary concerns of storage stability but storage stability might also involve issues of water contamination and microbial growth. For this reason, we won’t focus on the use of these terms but will describe the actual processes that cause the chemical changes in the fuel.

Vegetable oils are generally susceptible to oxidative attack because they are less saturated, that is, they contain more carbon – carbon double bonds. Depending on the physical conditions of the oil, the hydroperoxides can either break apart to form short chain aldehyde and acids or they can attach together to form dimers and polymers. The short chain acids can be volatile and cause a foul smell, and lowering of the flash point. Polymerization can cause an increase in viscosity and the formation of insoluble sediments and varnish deposit.

As mentioned earlier, unsaturated molecules are more susceptible to oxidation than saturated molecules. Oils with high iodine values (unsaturated) such as soybean oil are very susceptible to oxidation while animal fats with low iodine values such as tallow are much less susceptible.
There is numerous test procedures for characterizing fuel stability. ASTM D2274 is a commonly used method for diesel fuels. The method consists of accelerated oxidation of the fuel by bubbling oxygen through it at elevated temperature and filtering the fuel to measure the amount of insoluble sediment that was found. Unfortunately, the method described in the ASTM standard is not suitable for use with biodiesel, the filters absorb and this is falsely indicated as excessive sediment. Alternative materials have been proposed but ASTM procedure is suggested. Concerns have also been expressed about whether the solvent used in D2274 can transport all adherent sediments without dissolving them.

2.9.0 THE CHEMISTRY OF BIODIESEL

It is useful to review some of the fundamental chemical principles that are behind biodiesel so that its properties be understood.

All vegetative oils and animal oils consist primarily of triglyceride molecules as shown schematically below.

Fig. 7

\[
\begin{align*}
R_1 & \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{R}_1 \\
\text{H} & \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{R}_2 \\
\text{H} & \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{R}_3 \\
\text{H} & \quad \text{O} \\
\end{align*}
\]

$R_1$, $R_2$ and $R_3$ represent the hydrocarbon chain of the fatty acid elements of the triglycerides. Note that there are three-carbon chains called the glycerol backbone that runs along the left side of the molecule. Extending away from the backbone are the three long fatty acid chains. In their free form, the fatty acids have the configuration below.
Where $R$ is a hydrocarbon chain of greater than 10-carbon atoms.

The properties of the triglycerides and the biodiesel fuel will be determined by the amounts of each fatty acid present in the molecules.

Fatty acids are designated by two numbers of carbon atoms in the acid and the second number of double bonds. For example, 18.1 designates oleic acid, which has 18 carbon atoms and one double bond.

The names of the fatty acids given below as follows.

- 14.0 Myritic acid
- 16.0 Palmitic acid
- 18.0 Stearic acid
- 18.2 Linoleic acid
- 18.3 Linolenic acid
- 20.0 Arachidic acid
- 22.1 Erucic acid

Biodiesel consists of monoesters formed when triglyceride react with alcohols such as methanol.

What are esters and monoesters?

Esters are a type of chemical compounds that contain the following grouping of carbon and oxygen.
Fig 8: Ester Group

\[ O - C - O - \]

One example is methyl palmitate

Here example is methyl palmitate

\[ \text{CH}_3(\text{CH}_2)_{14} - C - O - \]

Here the \( \text{CH}_3 \) represents the palmitic acid and the \( \text{CH}_3 \) designates the ester are part of the molecule

Fig 9: Structure of some fatty acids.

\[ \text{CH}_3 - (\text{CH}_2)_{16} - C - O - \text{CH}_3 \]

Note that they only contain one occurrence of ester functional group, the ester functional group

\[ O - C - O - \]

All these are examples known as monoesters. Other organic molecules can contain more than one occurrence of the ester group such as the triglycerides shown earlier in the fig. 8 above. If a molecule contains the ester group three times, it is said to be a trimester. Sometimes people refer to the reaction that converts oil or fat (triglycerides) to methyl ester (biodiesel) as "esterification" as if the reaction were converting something that is not an ester
to an ester. This is why the reaction is more properly known as "transesterification".

Transesterification is the process of reacting a triglycerides molecule with an excess of alcohol in the presence of a catalyst (KOH, NaOH etc) to produce glycerine and fatty acid.

2.10 BIODIESEL CHARACTERIZATION

2.10.1 FUEL/PHYSICAL PROPERTIES

Biodiesel is a simple fuel consisting of a few specific naturally derived fatty acid esters. Each fatty acid source has a fairly constituent fatty acid profile and composition. Most physical properties of organic compounds can be empirically correlated using methods based on law of corresponding states.

These properties include specific gravity, kinematic viscosity, flashpoint, cetane number and flash point.

1. Density

Specific gravity is relative to density of the substance \( \rho \) to a reference density \( \rho_{ref} \). The equation for specific gravity (SG) = \( \rho / \rho_{ref} \). The most common reference density used in the measurement of specific gravity is the density of water at 4°C, which corresponds to a reference density of 1g/cc. The specific gravity of conventional No 2 diesel is 0.85 while a typical density of biodiesel is 0.88, which means that biodiesel is more dense than conventional diesel.

API = The API gravity is a widely used measure of fuels density. It is related to the specific gravity of the fuel by the following equation.

\[
API = 141.5 \left[ \text{sp gr @ 60°F/60°F} \right] - 131.5
\]
Kinematic Viscosity

To define kinematic viscosity, it is useful to begin with the definition of viscosity. Simply stated, viscosity, which is also called dynamic viscosity ($\eta$), is the ease with which a fluid will flow. There is a hydrodynamic definition of viscosity as well. Technically, it is the ratio of the shear stress to the ratio of a fluid. In contrast, the kinematic viscosity ($\nu$) is the resistance to flow of a fluid under gravity. Therefore, the kinematic viscosity of a fluid is related to the dynamic viscosity through the density ($\rho$) i.e $\nu = \eta / \rho$. The standard procedure for measuring kinematic viscosity in diesel or biodiesel is ASTM D445.

The greater the viscosity, the less readily the liquid flows. The viscosity of petroleum oils is a strong function of temperature with the decreasing as the temperature increases. ASTM D445 as a standard test procedure provides a measure of time required for a volume of liquid to flow under gravity through a calibrated glass capillary tube. The kinematic viscosity is then equal to the product of this time and a calibration constant for the tube. The dynamic viscosity is then equal to the product of this time and a calibration constant for the tube, the dynamic viscosity can be obtained by multiplying the kinematic viscosity by the density of the fluid.

Biodiesel is more viscous than no 2 diesel fuel, but only by a small amount. Depending on the feedstock and amount of oxidation, biodiesel is viscosity will vary between 4.0 and 6.2 while No. 2 diesel fuels tend to fall in a narrow range of 2.4 – 2.6.
Table 1.7: Specification for biodiesel ((B100) – ASTM D6751 – 02 requirements\(^\text{64}\).

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM method</th>
<th>Limits</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash point closed cup</td>
<td>D93</td>
<td>130min</td>
<td>°C</td>
</tr>
<tr>
<td>Water and sediment</td>
<td>D2709</td>
<td>0.050</td>
<td>% vol</td>
</tr>
<tr>
<td>Kinematic viscosity at 40°C</td>
<td>D445</td>
<td>1.9 – 6.0</td>
<td>mm(^2)/s</td>
</tr>
<tr>
<td>Sulphated ash</td>
<td>D874</td>
<td>0.020</td>
<td>Wt. %</td>
</tr>
<tr>
<td>Total Sulphur</td>
<td>D5453</td>
<td>0.05(_{\text{max}})</td>
<td>Wt. %</td>
</tr>
<tr>
<td>Copper strip corrosion</td>
<td>D130</td>
<td>No 3(_{\text{max}})</td>
<td></td>
</tr>
<tr>
<td>Cetane number</td>
<td>D613</td>
<td>47min</td>
<td></td>
</tr>
<tr>
<td>Cloud point</td>
<td>D2500</td>
<td>Report to customer</td>
<td>°C</td>
</tr>
<tr>
<td>Carbon residue</td>
<td>D4530</td>
<td>0.050</td>
<td>Wt %</td>
</tr>
<tr>
<td>Acid number</td>
<td>D664</td>
<td>0.80(_{\text{max}})</td>
<td>mgKOH/g</td>
</tr>
<tr>
<td>Free glycerine</td>
<td>D6584</td>
<td>0.020</td>
<td>Wt %</td>
</tr>
<tr>
<td>Total glycerine</td>
<td>D6584</td>
<td>0.240</td>
<td>Wt %</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>D4951</td>
<td>0.0010</td>
<td>Wt %</td>
</tr>
<tr>
<td>Vacuum distillation end point</td>
<td>D1160</td>
<td>360°C(_{\text{max}}) at T-90</td>
<td>% distilled</td>
</tr>
<tr>
<td>Storage stability</td>
<td>To be determined</td>
<td>To be determined</td>
<td>To be determined</td>
</tr>
</tbody>
</table>

Cloud Point

The cloud point is the temperature at which components in the biodiesel begin to solidity out of solution, that is the temperature at which it cloud of wax crystal first appears in a fuel sample that is cooled as described by ASTM D 2500\(^\text{68}\). The cloud point is a critical factor in cold weather performance for all diesel fuels\(^\text{68}\).
Flash Point

A key property determining the flammability of fuel is the flash point. The flash point is the lowest temperature at which an applied ignition source will cause the vapours of a sample to ignite. Therefore, it is a measure of the tendency of a sample to form flammable mixture with air. As a side note, the value of flash point is used for the classification of flammable and combustible materials needed for safety and shipping regulations. The standard for measuring flash point for diesel and biodiesel fuels is ASTM D 93, the flash of the fuel in a stirred container and passing a flame over the surface of the liquid. If the temperature is at or above the flash, the vapours will ignite and an easily detectable flash can be observed. The flash need not correspond to a sustained flame. The fire point is sometimes used to designate the fuel temperature that will produce sufficient vapour to maintain a continuous flame.

Cetane Number

Perhaps the most important measure of ignition characteristics of diesel and or biodiesel fuels is cetane number. Since it pertains to ignition within compression ignition engines. The analog of cetane number in gasoline is the octane number. The cetane number is a measure of diesel fuel's engine performance, compared to a standard fuel. ASTM D-6751 requires a minimum cetane number of 47 for B100. The primary reference fuels are n-cetane (n-hexadecane), which has a cetane number of 100 and heptamethylnonane (HMN), which has a cetane number of 15, when the ignition delay is restored to 13 degrees the cetane number is computed from the following relationships

\[
\text{Cetane number} = \% \text{n-cetane} + 0.15 (\% \text{HMN})^69
\]

Since the price of the primary reference fuel is quite high, most commercial cetane ratings is done with secondary reference fuel that have been calibrated to known cetane values.
It is important to note that if a 50/50 blend is made of fuels with cetane number of 40 and 50, respectively, the blended fuel will likely not have a cetane number of 45, this phenomenon is due to the fact that cetane numbers of the blend is not directly proportional to the cetane number of the constituents. The cetane number of biodiesel is typically higher than standard diesel fuel and its addition to standard diesel fuel will generally increase the cetane number of the subsequent fuel.

Cetane index (ASTM D979 or D4737) the cetane index is a calculated quantity intended to approximate the cetane number. It is much cheaper to determine than engine based cetane number but its accuracy is limited to the type of fuel on which the equation is based.

Table 1.8: Petroleum diesel properties vs, biodiesel

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Petroleum diesel</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>Kg/m³</td>
<td>810 – 850</td>
<td>860 – 900</td>
</tr>
<tr>
<td>Cetane</td>
<td></td>
<td>45</td>
<td>52 – 56</td>
</tr>
<tr>
<td>Viscosity</td>
<td>mm²/s</td>
<td>23 – 50</td>
<td>6.3 – 8.1</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>60</td>
<td>130</td>
</tr>
<tr>
<td>Content of sulphur</td>
<td>%mass</td>
<td>0.15</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Content of water</td>
<td>%mass</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>Ashes</td>
<td>%mass</td>
<td>0.01</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>Carbon residue</td>
<td>%mass</td>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>Calorific value</td>
<td>KJ/kg</td>
<td>42,500</td>
<td>37,250</td>
</tr>
</tbody>
</table>

Table 1.9: Comparism of properties of diesel canola oil and commercial use biodiesel.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Petrol diesel</th>
<th>Canola oil</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density kg/l @ 15.5 deg C</td>
<td>0.84</td>
<td>0.92</td>
<td>0.88</td>
</tr>
<tr>
<td>Calorific value MJ/kg</td>
<td>38.3</td>
<td>36.9</td>
<td>33 – 40</td>
</tr>
<tr>
<td>Viscosity mm²S⁻¹ @ 20 deg C</td>
<td>4 – 5</td>
<td>70</td>
<td>4 – 6</td>
</tr>
<tr>
<td>Viscosity mm²S⁻¹ @ 40 deg C</td>
<td>4 – 5</td>
<td>37</td>
<td>4 – 6</td>
</tr>
<tr>
<td>Viscosity mm²S⁻¹ @ 70 deg C</td>
<td>-</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Cetane number</td>
<td>45</td>
<td>40 – 50</td>
<td>45 – 65</td>
</tr>
</tbody>
</table>
### Table 1.10: Fuel related properties and iodine value of various fats and oils

<table>
<thead>
<tr>
<th>Oil or fat</th>
<th>Iodine value</th>
<th>Cetane number</th>
<th>Heat of combustion KJ/kg</th>
<th>Viscosity mm²/S</th>
<th>Cloud point deg C</th>
<th>Pour point deg C</th>
<th>Flash point deg C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Babassu</td>
<td>10 – 18</td>
<td>38</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Castor</td>
<td>82 – 88</td>
<td>7</td>
<td>39500</td>
<td>297(38°C)</td>
<td>-</td>
<td>31.7</td>
<td>260</td>
</tr>
<tr>
<td>Coconut</td>
<td>6 – 12</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Corn</td>
<td>130 – 140</td>
<td>37.6</td>
<td>39500</td>
<td>34.9(38°C)</td>
<td>-1.1</td>
<td>400</td>
<td>277</td>
</tr>
<tr>
<td>Cotton seed</td>
<td>90 – 119</td>
<td>41.8</td>
<td>39468</td>
<td>33.5(38°C)</td>
<td>1.7</td>
<td>10.0</td>
<td>234</td>
</tr>
<tr>
<td>Crambe</td>
<td>93</td>
<td>44.6</td>
<td>40482</td>
<td>53.6(38°C)</td>
<td>10.0</td>
<td>12.2</td>
<td>274</td>
</tr>
<tr>
<td>Linseed</td>
<td>168 – 204</td>
<td>36.6</td>
<td>39307</td>
<td>27.2(38°C)</td>
<td>1.7</td>
<td>15.0</td>
<td>241</td>
</tr>
<tr>
<td>Olive oil</td>
<td>75 – 94</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Palm</td>
<td>35 – 61</td>
<td>42</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Peanut</td>
<td>80 – 106</td>
<td>41.8</td>
<td>-</td>
<td>39.6(38°C)</td>
<td>12.8</td>
<td>-6.7</td>
<td>271</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>94 – 120</td>
<td>37.6 &lt; TD width</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Heating Value**

The heating value is a measure of the energy content available upon combustion. Individual methyl esters all have values of about 39.8(MJL⁻¹). This value is slightly higher than the value given by Prof. Jiri, (1998) which is 37.250kJ/kg. 
2.10.2 Chemical properties

Sulphated ash

"The residue remaining after a sample has been carbonized and the residue subsequently treated with sulphuric acid and treated to a constant weight" this monitors the mineral as residual when a fuel is burned. For biodiesel, this test is an important indicator of the quantity of residual metals in the fuel that came from the catalyst used in the esterification process\textsuperscript{64}.

Total Sulphur

"This method cover the determination of total sulphur in liquid hydrocarbons, boiling in the range from approximately 0.2 and 20cst (mm\textsuperscript{2}/s) at room temperature". Vegetable oil feedstock typically have very little sulphur, but this test is an indicator of the contamination of protein material and/or carry over catalyst material or neutralization material from production processes\textsuperscript{64}.

Copper Strip Corrosion

Many of the compounds in diesel fuel can be corrosive. The corrosiveness of a fuel is measured using the copper strip corrosion test which is ASTM D130. This test monitors the presence of acids in the fuel. For B100, the most likely source of a test failure would be excessive free fatty acids, which are determined in accordance with an additional specification\textsuperscript{67}.

The corrositivity of fuel has implications on storage and use of the fuel. As an indicator of the tendency of a fuel to cause corrosion, polished copper strips are placed in the fuel for 3 hours at 50\degree C, then the strips are washed in a solvent and compared to the description in the Table below. The test results are given as a number followed by a letter. For example, a strip that was slightly tarnished with a dark orange colour would be designated as "lb"\textsuperscript{67}.
Copper strip classifications

<table>
<thead>
<tr>
<th>Classification</th>
<th>Designation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Slight Tarnish</td>
<td>a) Light orange, almost the same as freshly polished strip</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b) Dark orange</td>
</tr>
<tr>
<td>2</td>
<td>Moderate Tarnish</td>
<td>a) Claret red</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b) Lavender</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c) Multi coloured with lavender or silver or both, overlaid or claret red</td>
</tr>
<tr>
<td>3</td>
<td>Dark Tarnish</td>
<td>a) Magenta cover cast on brassy strip</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b) Multi coloured with red and green showing (Peacock) but no grey</td>
</tr>
<tr>
<td>4</td>
<td>Corrosion</td>
<td>a) Transparent black, dark grey or brown with peacock green barely showing</td>
</tr>
</tbody>
</table>

Carbon Residue

“In petroleum products, the sample remaining after it has been subjected to thermal decomposition”. The carbon residue is a measure of how much residual carbon remain after combustion” This is particularly important in diesel engine because of the possibility of residues clogging in the fuel injectors. The most common cause of the excess residue in B100 is an excessive level of total glycerine.64.

Free Glycerine

Glycerine present as molecular glycerine in fuel. Free glycerine results from incomplete separation of the ester and glycerine products after esterification reaction. This can be as a result of incomplete alcohol removal
and a lowered flash point. The free glycerine is a source of carbon deposits in the engine because of incomplete combustion.\textsuperscript{67}

**Total glycerine** — "is the sum of free and bonded glycerine" — "is the glycerine portion of mono-di- and triglyceride molecules" Elevated total glycerine values are indicators of incomplete esterification reactions and predictors of excessive carbon deposits in the engine. The terms "glycerine and glycerol are used interchangeably.\textsuperscript{65}

**Phosphorus** — "This test covers the quantitative determination of barium, calcium, copper, magnesium, phosphorus, sulphur and zinc in unused lubricating oils and additive packages" In the case of B100, phosphorus can come from incomplete refining of the vegetable oil and from bone and proteins encountered in the rendering process.\textsuperscript{64}

**Water and Sediment**

*Water and sediment* is a test that "determines the volume of free water and sediment in middle distillate fuels having viscosities at 40°C in the range of 1.0 to 4.1 mm\(^2\)/S and densities in the range of 700 to 900 kg/m\(^3\)." This test is a measure of cleanliness of the fuel. For B100, it is particularly important because water can react with esters making free fatty acids and can support microbial growth in storage tanks.\textsuperscript{64} Water also reduces the heat of combustion of the bulk fuel. This means more smoke, harder starting, less power.\textsuperscript{4}

**ENVIRONMENTAL AND OTHER BENEFITS OF BIODIESEL IN COMPARISM WITH PETRODIESEL**

Biodiesel is a safer alternative to diesel fuel because it is environmentally safe and has no known side effects to humans. Diesel is a fuel that is made from fossil fuels and has serious side effects to human health. If people continue to use diesel as fuel in transportation, the pollution will cause
serious side effects to wildlife, the environment and human race. Humans can get cancer from breathing the pollution along with other problems in high-populated areas where diesel engine is common. The National Institute for Occupational Safety and Health wanted diesel to be regarded as a “potential occupational carcinogen” biodiesel is safer to the environment and to human health.

Biodiesel reduces the amount of unburned hydrocarbon by 10.50% with biodiesel, there is also reduction in the emission of carbon monoxide by 10 – 50% soot by 40 – 60%, all polycyclic aromatic hydrocarbon and sulphur dioxide by 100%22, biodiesel also reduces emissions of carbon dioxide by 78% on a net lifecycle basis because the carbon in biodiesel emission is recycled from carbon was already in the atmosphere, rather than being new carbon from petroleum that was sequestered in the earth’s crust27. Therefore, there is reduction of matter that is dispersed into the environment through car exhaust. This pollution is likely to cause global warming which will also damage the planet later on Biodiesel is 50% less likely to harm ozone if used in an engine rather than diesel fuel22.

Diesel is used in some vehicle today and many consumers do not like them due to the sound and smell25. Biodiesel replaces the exhaust odour typical of petroleum diesel with the pleasant smell of French fries or donuts31.

Biodiesel can provide farmers with a new source of income. This will create a new major market for farmers and potentially relieve the downward pressures created by the fact that our agricultural capacity of this oil is greater than our demand. Developing this much biofuel would result in a dramatic reinvestment in our agricultural sector. Farmers would provide life blood for our transport system as well as for our dining tables. It is still believed that we can indeed produce much biofuel (biodiesel) without increasing the amount of land devoted to agriculture and while still meeting our food animal feed and textile needs73.
Biodiesel's high lubricity index compared to petrodiesel is an advantage and can contribute to longer fuel injector life. Biodiesel is a better solvent than petrodiesel and has been known to breakdown deposits residue in the fuel lines previously being run on petrodiesel\textsuperscript{14}.

Generally, due to purity of source biodiesel has higher quality than petrodiesel. Petrodiesels non-biodegradable and non-toxic as compared with petrodiesel. The U.S. Department of energy confirms that biodiesel is less toxic than table salt and biodegrades as quickly as sugar. In the United State, biodiesel is the only alternative fuel to have successfully completed the health testing requirements. (Tier I and Tier II) of the Clean Air Act (1990)\textsuperscript{14}

Biodiesel produces 10\% - 25\% more nitrogen oxides. NO\textsubscript{x} tail pipe emissions than petrodiesel. As biodiesel has low sulphur content, NO\textsubscript{x} emissions can be reduced through the use of catalytic converters to less than NO\textsubscript{x} emissions from conventional diesel engines. Nonetheless, the NO\textsubscript{x} pipe tail emissions of biodiesel after the use of a catalytic converter will remain greater than the equivalent emissions from petrodiesel. As biodiesel contains no nitrogen, the increase in NO\textsubscript{x} emissions may be due to the higher cetane ratings of biodiesel and higher oxygen content, which allows it to convert nitrogen from the atmosphere into NO\textsubscript{x} more rapidly. Debate continues over NO\textsubscript{x} emissions. In February 2006 a navy biodiesel expert claimed NO\textsubscript{x} emissions in practice were actually lower than base line, further research is needed\textsuperscript{14}. The problem of increase in NO\textsubscript{x} emissions can also be reduced by a simple engine up grade\textsuperscript{31}.

2. USES/APPLICATION OF BIODIESEL

There are many ways to use alkyl esters, including as many solvents and as chemical intermediate for the formation of detergents. However, the application of most interest to us is as fuel. Fuel applications can be divided into three categories\textsuperscript{68}.
1. Pure fuel (B100).

Biodiesel can be used in its pure form also known as neat diesel, or B100. This is the approach that provides the most reduction in exhaust particles, unburned hydrocarbons, and carbon monoxide. It is also the best way to use biodiesel when its non-toxicity and biodegradability are important. Marine applications may be important for B100. Although neat biodiesel would not be expected to cause any operational problems, its solvent properties will be at their higher intensity and may cause problems with loosening of varnish deposits in fuel tanks and degradation of fuel lines because some elastomers are not compatible with biodiesel (such as BNA rubbers) and paints removal near fuel fill parts. Concrete can also be degraded if it is subjected to chronic exposure to biodiesel. B100 will also have the most severe problems with cold flow properties. Biodiesel will degrade natural rubber gaskets and hoses in vehicles. (Mostly found in vehicles manufactured before 1992), although these tend to wear out naturally and most likely will have already been replaced with vitron which is non reactive to biodiesel.

Blends (typically 20 – 50%)

Biodiesel will blend with petroleum-based diesel fuel in any proportion so it is common to use blends of 20 to 50% biodiesel in 80-50% No. 2 diesel fuel. Blends reduce the cost impact of biodiesel while retaining some of emissions reductions. Most emissions reduction appears to be proportional to the percentage of biodiesel used the cold flow and solvency problems noted with B100 are less of a concern when blends are used. Fuel filters may be clogged with particles if a quick transition to pure biodiesel is made as biodiesel “cleans” the engine process. It is therefore recommended to change the fuel filter with 600 – 800 miles after first switching to biodiesel blend.
As an additive, 1 – 2% (BO2)

Tests for lubricity has shown that biodiesel is very effective lubricity enhancer. Even as little as 0.25% is enough to convert a very poor lubricity fuel into an acceptable fuel. Although these levels are too low to have any impact on the cetane number of the fuel or the emission from the engine. The lubricity provides a significant advantage at modest cost\textsuperscript{66}.

Usage

All the three applications described above relate to diesel engines. In warm climates pure unblended biodiesel can be poured straight into the tank of any diesel vehicle, some older diesel engines will still have natural rubber parts, which will be affected by biodiesel, but in practice these rubber parts should have been replaced long ago. Biodiesel has also been considered for use in spark-ignited engines, but without much success.

Biodiesel is being used in a variety of non engine applications such as solvent for removing adhesive residue from glass, removing grease from engine, cleaning oil stains and also removing paint stains\textsuperscript{66}.

Biodiesel has been noted to be linked to premature injection pump failures. While many vehicles have been using biodiesel for many years without ill effect, the uncanny correlation between several cases of pump failure and biodiesel cannot be dismissed. Pure biodiesel produced "at home" is in use by thousands of drives who have not experienced failure, however, the fact still remains that biodiesel is a very new subject and will carry some risk until it is fully researched\textsuperscript{14}.
CHAPTER THREE
MATERIALS AND METHODS

3.0.0 COLLECTION AND PRESERVATION OF SAMPLES

_Cucumis melo_

The seeds of _Cucumis melo_ were bought in February 2007, from Northbank market in Makurdi Local Government Area of Benue State. The seeds were dehulled manually and dried under the sun and stored in polythene bags. This was exposed to sunlight and air to prevent decay of seeds and also enhance proper loss of moisture. The melon seeds were pulverized and extraction of the oil from seed was done immediately.

_Cyperus esculentus_

The tubers of _Cyperus esculentus_ were bought in February 2007 also from Northbank market in Makurdi Local Government Area of Benue State. The tubers were dried properly under the sun and stored in a polythene bag and were exposed to air and sunlight daily to prevent decay of tubers. Tubers were milled with a milling machine and extraction was done immediately.

_Petrodiesel._

The Petrodiesel (from Shell petroleum) was bought from Conoil Filling Station in Nsukka Enugu State.

3.1.0 INSTRUMENTS/APPARATUS/REAGENTS

3.1.1 APPARATUS/INSTRUMENTS

- Weighing balance
- Water bath
- Retort stand and clamp
Blender
Milling machine
Beaker
Oven
Sample bottles
Conical flask
Separating funnel
Measuring cylinder
Standard volumetric flask
Burette
Pipette
Density bottle
Ferranti portable viscometer
Rotary evaporator
Magnetic stirrer/heater
Thermometer
Heating mantle
Oxygen bomb calorimeter
Plastic wrap and rubber band
Boiling tube
Test tube holder
Reflux condenser
Buckner funnel
Buckner flask
Suction pump
Extraction glass column

3.1.2 SAMPLES/MATERIALS

*Cucumis melo* oil
*Cyperus esculentus* oil

Petrodiesel

3.1.3 REAGENTS/MATERIALS

Petroleum ether
Distilled water
Potassium hydroxide
Methanol
Ethanol (absolute)
Glacial acetic acid
Chloroform
Phenolphthalein
Potassium iodide
Hydrated sodium thiosulphate
Starch
Wij's solution
Carbon tetrachloride
Sodium bicarbonate
Methyl red

3.2.0 EXTRACTION OF VEGETABLE OIL FROM THE SAMPLE MATERIAL USING THE COLD PROCESS

1000g of the powdered material of each of the samples of *Cucumis melo* and *Cyperus esculentus* was weighed in each case and transferred into an extraction column. The extraction column was plugged with cotton wool at the base and the tap was closed. Petroleum ether was poured into the Extraction column with the material in it and covered with a plastic wrapper which was held together firmly with a rubber to prevent evaporation of the petroleum ether. This was allowed to stand for 48 hours at normal temperature. The extraction was repeated for about seven times to obtain enough quantity of sample(s).

The tap at the base of the extraction column was opened after 48 hours and the extracted oil in each case was collected in a 1000ml beaker. The solvent in the oil was removed with the aid of a rotary evaporator. The oils in each case were heated in the oven at 55°C for 2 hours. The dried oil was then characterized.
3.3.0 DETERMINATION OF SAPONIFICATION VALUE

2g of the oil sample in each case of *Cucumis melo* and *Cyperus esculentus* was weighed and transferred into a 250ml conical flask followed by the addition of 25ml of 0.5M ethanolic solution of potassium hydroxide. The reflux condenser was attached and the contents in the flask were heated for 1 hour with frequent swirling. While the solution was added and still hot 1ml of phenolphthalein was added and excess of alkali was titrated with 0.5M hydrochloric acid.

The blank titration was carried out under the same conditions without the samples being examined.

The same procedure was repeated for the methylester (biodiesel) samples of *Cucumis melo* and *Cyperus esculentus*. The same was done for petrodiesel.

The saponification value was obtained by this formula.

\[
\text{Saponification value} = 28.05 \times \frac{\text{blank titration-sample titration}}{\text{Weight of sample}}
\]

28.05 is the number of milligram of potassium hydroxide in 1ml of 0.05m potassium hydroxide.

3.4.0 DETERMINATION OF ACID VALUE

1g of *Cucumis melo* and *Cyperus esculentus* oil in each case was weighed into a 25ml conical flask. 50ml of a mixture of 50% ethanol and 50% petroleum ether was added containing 6ml of phenolphthalein indicator. This was titration against 0.1M potassium hydroxide shaking constantly until a pink colour, which persisted for 15 seconds, was obtained.

The same procedure was repeated for the methyl ester samples of *Cucumis melo* and *Cyperus esculentus*. The same was done for petrodiesel.
The acid value was determined by this formula

\[ \text{Acid value} = V \times 56.1 \]

\[ V = \text{volume of 0.1M potassium hydroxide required for the titration} \]

3.5.0 DETERMINATION OF IODINE VALUE (BSI METHOD)

0.2g of *Cucumis melo* and *Cyperus esculentus* oil in each case was weighed out and placed in a dry flask. The oil was dissolved in 20ml of carbon tetrachloride and 25ml of Wij's solution in each case. The stoppered flask was swirled to mix the contents and stood in a dark cupboard for 1 hour at normal temperature. (Approx. 77°F 25°C). It was removed and 20ml of a 15% potassium iodine solution was added followed by 100ml of distilled water. The liberated iodine was slowly titrated with 0.1M thiosulphate solution until the yellow colour almost disappeared. At this stage 2ml of starch indicator was added and the blue colour which appeared was added discharged by further slow additions of thiosulphate.

The procedure was repeated for the methyl esters of *Cucumis melo* and *Cyperus esculentus*.

The iodine value was obtained by this formula

\[ \text{Iodine value} = \frac{(B - S) \times M \times 12.69}{\text{Weight of sample}} \]

\[ B = \text{blank titration} \]

\[ S = \text{Sample titration} \]

\[ M = \text{Molarity of sodium thiosulphate solution} \]

12.69 = atomic weight of iodine
3.6.0 DETERMINATION OF PEROXIDE VALUE

1g of Cucumis melo and Cyperus esculentus oil was measured in each case into a dry clean boiling tube 1g of powdered potassium iodine and 20ml of solvent mixture (Glacial acetic acid and chloroform) was added in each case and placed in a boiling water bath so that the liquid boiled within 30 seconds and allowed to boil vigorously for not more than 30 seconds. The content was then poured into a titration flask (conical flask) containing 20ml of fleshly prepared 5% potassium iodine solution. The tube was washed twice with 25ml portions of water and added to the titration flask and titrated with 0.002M sodium thiosulphate solution using starch as an indicator.

The same procedure was repeated for the methyl esters (Biodiesel) samples of Cucumis melo and Cyperus esculentus. The same was also done to the Petrodiesel sample.

A blank was carried out but in this case, the mixture in the boiling tube was allowed to boil for 2 minutes in the water bath to enable iodine to be properly liberated. Peroxide value was determined by this formula

\[
\text{Peroxide Value} = \frac{2(a - b)}{\text{weight of Fat/Oil}}
\]

\(A\) = volume of 0.002M sodium thiosulphate used in sample titration

\(B\) = volume of 0.002M sodium thiosulphate used in blank titration determination.25

3.7.0 DETERMINATION OF VISCOSITY BY FERRANTI PORTABLE VISCOMETER.

1. The outer cylinder was fitted ensuring that the location spring laid flat against the side of the shaft.
2. The knurled knob (left of the handle) was rotated clockwise to "lock" the inner spindle. The guard ring was inserted on the outer cylinder.

3. The appropriate inner cylinder was chosen and the spindle was inserted inside the guard ring. The inner cylinder was slowly rotated maintaining a light upward pressure until the ball end engaged the retaining spring.

4. The inner spindle was then unlocked and cylinders were immersed in the fluid to be tested in this case *Cucumis melo* and *Cyperus esculentus* oils and their methyl esters (biodiesel) and also Petrodiesel. The determinations were made with the top of the outer cylinder just covered by the liquid.

5. The speed required was selected and switched on. The mains supply required 200 – 250 volts. 50 cycles.

6. Viscosity in poises, at a given speed and cylinder combination was obtained by multiplying the instrument reading by the appropriate multiplying factor given on the calibration chart and then multiplying with $10^2$ to get centipoises.

$$1 \text{ poises} = 10^2 \text{ centipoise}$$

$$1 \times 100 = 100 \text{ centipoise}$$

3.8.0 DETERMINATION OF SPECIFIC GRAVITY BY DENSITY

BOTTLE METHOD

1. The mass of the density bottle including the stopper was taken as $M_1$.

2. The mass of the density bottle + stopper + sample was taken as $M_2$.

3. The mass of density bottle including stopper + distilled water was taken as $M_3$.

4. Specific gravity was given by this formula
Specific gravity = \( \frac{M_2 - M_1}{M_r - M_1} \)

The procedure was repeated for two times and the average of specific gravities were taken. The specific gravities of *Cucumis melo* and *Cyperus esulentus* oil as well as their methyl esters, were determined. The specific gravity of the Petrodiesel was also determined.

3.9.0 DETERMINATION OF HEAT OF COMBUSTION USING OXYGEN BOMB CALORIMETER

1. The outer canister was filled with water and stirred by the hand stirrer of the equipment to get an average temperature before the experiment was conducted.

2. About 3000g (3 liters) of distilled water was poured into the inner canister. Their combined weights were obtained. Each time the bomb was removed from the inner chamber distilled water was filled to compensate for the loss due to bomb removal.

3. The weight of the sample + Ignition wire (or Ignition thread) + bomb container were measured in grams.

4. The two ends of the Ignition thread were fixed on two electrode poles and made to keep a good touch with the sample to be evaluated.

5. 10 mls of distilled water was filled in the oxygen bomb and the cover was screwed down.

6. Oxygen was filled into the bomb at a pressure of 2.8 – 30 Mpa.

7. The oxygen bomb with its contents was put in the clamp in the inner canister.

8. The necessary wires were connected and the temperature sensor was put in the inner canister.
9. The "POWER" and "STIR" buttons were switched on.

10. The water was allowed to stir for about 2 minutes and the initial temperature was taken as $T_0$.

11. The "FIRE" button was pressed. The instrument automatically measured and saved the data, when the testing time reached 31, the experiment was stopped. The final temperature of the water $T_1$ was noted.

12. Stirring was stopped and the temperature sensor was pulled out. The lid was opened and the bomb was removed and the oxygen set free inside before opening the bomb. The sample was completely burnt for all the samples that were determined.

13. The length/mass of the unburned firing wire was measured.

14. The inner lining of oxygen bomb and crucibles was washed with distilled water, 2 drops of methyl red indicator were added and titration was with 0.0709M sodium carbonate.

15. The volume of the consumed alkali $V_1$ was recorded

The samples determined were Cucumis melo and Cyperus esculentus oil and their methylesters as well as petrodiesel.

The heat of combustion was calculated using the formula

\[ W = \frac{EDT - \phi - V}{M} \]

- $W = \text{heat of combustion}$
- $M = \text{mass of sample to be evaluated}$
- $EDT = T_1 - T_0$
- $\phi = \text{Length of unburned multiplied by } 2.3 \text{cm}$
- $V = \text{vol of alkali used}$
3.10.0 DETERMINATION OF MOISTURE CONTENT

The already washed and cleared silica dishes were dried in an oven and cooled in a dessicator. Five millilitres of each of the sample was put into the appropriate silica dish and weighed accurately. Each dish and its contents was put in an oven at a temperature of 105°C to dry for 1 hour. Each dish was transferred into a dessicator and allowed to cool and was weighed. This was repeated until a constant weight was obtained.

The moisture content was calculated using this relationship

\[
\% \text{ moisture } = \frac{\text{mass of sample after drying}}{\text{mass of sample taken}} \times 100
\]

3.11.0 PREPARATION OF METHYLESTER (BIODIESEL)

REAGENTS/MATERIALS

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>500ml</td>
<td>Crude vegetable oil</td>
</tr>
<tr>
<td>100ml</td>
<td>Methanol 99%</td>
</tr>
<tr>
<td>2.9g</td>
<td>2.9g of 85% KOH</td>
</tr>
</tbody>
</table>

PROCEDURE

500ml vegetable oils of *Cucumis melo* and *Cyperus esculentus* in each case was heated at a temperature of 55°C (130°F) in a 1000 ml beaker. 100ml of methanol was measured using a measuring cylinder and poured into a 500ml flat bottomed flask using a funnel and 2.9g of 85% KOH was carefully added. A bar magnet was placed in the methoxide and the content with the bar in it was placed on a magnetic stirrer. The top of the flat bottomed flask was
covered with a plastic wrap and held in place with a rubber band. This was stirred for about 30 minutes until all the particles were thoroughly mixed.

The methoxide solution was carefully added into the warm preheated vegetable oil and stirred vigorously on the magnetic stirrer for 1 hour. As soon as the process was completed, the mixture was poured into a 1000ml separatory funnel and allowed to settle for 24 hours. The glycerine which settled at the bottom was obtained by slowly turning the tap of the separatory funnel open and the glycerine was collected. The biodiesel which was the top layer was collected in a conical flask. The alcohol (methanol) was removed with the aid of a rotary evaporator.

The biodiesel was then washed. Washing was done using the bulk washing process which involved using 50% water and 50% biodiesel. The distilled water was poured in the separatory funnel first and then the biodiesel. The water and biodiesel were mixed by shaking the separatory funnel up and down until the mixture appeared homogenous. It was then turned off and allowed to settle. The biodiesel remained on top of the water while the water slowly sank to the bottom taking with it soluble materials mainly alcohol and catalyst as well as other impurities. In the first wash the water turned almost totally white but this cleared up as the soap washed out with subsequent washing. The water was drained out after each wash after allowing the mixture to stand for 48 hours. This process was repeated several times until the drained water became totally clear.

The biodiesel obtained after the wash was dried in the oven at 55°C for 1 hour. The remaining water in the biodiesel was out, then it was filtered under vacuum to recover the suspended components that solidity at cooler temperature. The dried biodiesel was then characterized.
## RESULTS AND DISCUSSION

### RESULTS

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>Cucumis melo oil</th>
<th>Cyperus esculentus oil</th>
<th>Cucumis melo biodiesel</th>
<th>Cyperus esculentus biodiesel</th>
<th>Petrodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>Centipoise</td>
<td>20.450</td>
<td>34.190</td>
<td>5.348</td>
<td>4.650</td>
<td>5.260</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>g/cm³</td>
<td>0.902</td>
<td>0.908</td>
<td>0.861</td>
<td>0.865</td>
<td>0.859</td>
</tr>
<tr>
<td>Heat of combustion</td>
<td>KJ/Kg</td>
<td>36807.891</td>
<td>39764.191</td>
<td>36002.665</td>
<td>38998.702</td>
<td>41714.741</td>
</tr>
<tr>
<td>Saponification value</td>
<td>mg/g</td>
<td>178.117</td>
<td>185.130</td>
<td>178.117</td>
<td>185.130</td>
<td>29.423</td>
</tr>
<tr>
<td>Acid value</td>
<td>mgKOH/g</td>
<td>5.049</td>
<td>3.366</td>
<td>0.280</td>
<td>0.280</td>
<td>0.280</td>
</tr>
<tr>
<td>Iodine value</td>
<td>g/100g</td>
<td>107.870</td>
<td>83.750</td>
<td>104.058</td>
<td>82.167</td>
<td>-</td>
</tr>
<tr>
<td>Peroxide value</td>
<td>mg/g</td>
<td>10.400</td>
<td>3.400</td>
<td>49.400</td>
<td>43.000</td>
<td>-</td>
</tr>
<tr>
<td>Percentage moisture</td>
<td>% by vol</td>
<td>1.000</td>
<td>0.900</td>
<td>0.050</td>
<td>0.940</td>
<td>1.000</td>
</tr>
<tr>
<td>Percentage yield</td>
<td>% by wt</td>
<td>47.140</td>
<td>24.800</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Colour</td>
<td></td>
<td>Yellow</td>
<td>Golden yellow</td>
<td>Light yellow</td>
<td>Golden yellow</td>
<td>Light brown</td>
</tr>
</tbody>
</table>
Table 4.2: Absorption characteristics of the samples. Infra red spectrum. \( \text{Cm}^{-1} \).

<table>
<thead>
<tr>
<th>Description</th>
<th>Cyperus esculentus biodiesel</th>
<th>Cucumis melo biodiesel</th>
<th>Cyperus esculentus oil</th>
<th>Cucumis melo oil</th>
<th>Petroleum diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H, N-Stretching</td>
<td>3468.46</td>
<td>3465.36</td>
<td>3474.24</td>
<td>3474.13</td>
<td>3449.86</td>
</tr>
<tr>
<td>C-H stretch of unsaturated compound of aromatic or alkene</td>
<td>3002.82</td>
<td>3007.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H stretch of aliphatic compounds</td>
<td>2923.07</td>
<td>2924.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H stretch of aliphatic compounds</td>
<td>2854.11</td>
<td>2854.99</td>
<td>2854.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=O, C=O=N stretching</td>
<td>2680.02</td>
<td>2681.02</td>
<td>2677.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=O stretch of esters</td>
<td>2317.37</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O=C, O=N stretching</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=O stretch of esters and ethers</td>
<td>1744.29</td>
<td>1744.32</td>
<td>1778.74</td>
<td>1778.74</td>
<td></td>
</tr>
<tr>
<td>C=O (acids, aldehydes Ketones, amides, anhydride stretching</td>
<td>1655.93</td>
<td>1664.48</td>
<td>1664.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=O stretch of esters and ethers</td>
<td>1444.24</td>
<td>1437.08</td>
<td>1461.01</td>
<td>1461.01</td>
<td></td>
</tr>
<tr>
<td>C-O stretch of esters and ethers</td>
<td>1361.82</td>
<td>1376.84</td>
<td>1376.84</td>
<td></td>
<td></td>
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<tr>
<td>C-H deformation of alkyl and aryl groups</td>
<td>1166.86</td>
<td>1166.86</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H deformation of alkyl and aryl groups</td>
<td>1017.57</td>
<td>1017.55</td>
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<tr>
<td>C-H deformation of alkyl and aryl groups</td>
<td>851.59</td>
<td></td>
<td>849.70</td>
<td>849.70</td>
<td></td>
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<tr>
<td>Deformation of methyl groups C-H</td>
<td>721.26</td>
<td>723.27</td>
<td>722.54</td>
<td></td>
<td></td>
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<tr>
<td>Deformation of alkyl groups</td>
<td>589.36</td>
<td>585.84</td>
<td>587.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table (4.3): Results of UV-visible spectral.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavelength(nm)</th>
<th>Absorbance</th>
<th>Possible chromophore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tigernut oil in cecil</td>
<td>213.6</td>
<td>1.158</td>
<td>-C=C-</td>
</tr>
<tr>
<td>Tigernut oil in petroleum ether</td>
<td>290.0</td>
<td>0.069</td>
<td>C=O</td>
</tr>
<tr>
<td>Melon oil in petroleum ether</td>
<td>290.0</td>
<td>0.327</td>
<td>C=O</td>
</tr>
<tr>
<td>Melon oil in petroleum ether</td>
<td>368.0</td>
<td>0.087</td>
<td>-C=C-</td>
</tr>
<tr>
<td>Tigernut biodiesel in petrol ether</td>
<td>254.0</td>
<td>0.301</td>
<td>-C=C=O</td>
</tr>
<tr>
<td>Tigernut biodiesel in petrol ether</td>
<td>290.0</td>
<td>0.084</td>
<td>C=O</td>
</tr>
<tr>
<td>Melon biodiesel in petrol ether</td>
<td>236.0</td>
<td>3.000</td>
<td>-C=C-</td>
</tr>
<tr>
<td>Melon biodiesel in petrol ether</td>
<td>269.0</td>
<td>3.000</td>
<td>C=O</td>
</tr>
<tr>
<td>Melon biodiesel in petrol ether</td>
<td>290.0</td>
<td>3.000</td>
<td>-C=C-</td>
</tr>
<tr>
<td>Petroleum diesel in carbon tetrachloride</td>
<td>248.0</td>
<td>0.477</td>
<td>-C=C-</td>
</tr>
<tr>
<td>Petroleum diesel in carbon tetrachloride</td>
<td>263.0</td>
<td>0.477</td>
<td>-C=C-</td>
</tr>
<tr>
<td>Petroleum diesel in carbon tetrachloride</td>
<td>272.0</td>
<td>0.477</td>
<td>-C=C-</td>
</tr>
<tr>
<td>Petroleum diesel in carbon tetrachloride</td>
<td>314.0</td>
<td>1.021</td>
<td>-C=C-</td>
</tr>
</tbody>
</table>

4.2.0 DISCUSSION

4.2.1 Colour/ Percentage yield per gram.

The oil of *Cyperus esculentus* (tigernut) is golden yellow with a strong and delightful fragrance. That of *Cucumis melo* (melon) is light yellow with its own peculiar fragrance. The methylester (biodiesel of *Cyperus esculentus* was also golden yellow while that of *Cucumis melo* was light yellow with the intensity of colours reducing after the methylesters were thoroughly washed with distilled water to remove the soaps formed and other impurities. The percentage yield per gram of the tuber/seed of *Cyperus esculentus* and *Cucumis melo* gave 47.140% and 24.800% of
These values can be compared with the percentage yield per gram of rapeseed and soybean cultivated in Europe which is 37% and 14% per gram of oil respectively\(^6\).

The physiochemical properties determined in this work are presented in table (4.1). A detailed analysis of the parameters is presented in histograms below.

### 4.2.2 Viscosity

The viscosities of the various samples of *Cyperus esculentus* oil, *Cucumis melo* oil, *Cyperus esculentus* biodiesel, *Cucumis melo* biodiesel and the conventional petrodiesel were determined using a Ferranti portable viscometer at 30°C. The values obtained in centipoises were as follows: 34.190, 20.450, 4.650, 5.348 and 5.260 respectively. The values of the biodiesel samples obtained are in agreement with the values given by the ASTM specification which is (1.9 – 6.0 mm\(^2\)/s at 40°C)\(^6\). These values are also in agreement with the value given in\(^6\) which is (4.0 – 6.2 mm2/s). This shows
that the essence of glycerine removal is to make the methyl ester of the triglyceride less viscous\textsuperscript{11} as the viscosities of the triglycerides of the oils as obtained from the determination was 20.450 for \textit{Cucumis melo} and 34.190 for \textit{Cyperus esculentus}. The removal of glycerine from vegetable oils can be represented by this equation\textsuperscript{18}.

\[
\begin{align*}
\text{CH}_2\text{O} - \text{C} - \text{R} & \quad \text{I I} \\
\text{CH}_2\text{O} - \text{C} - \text{R'} & + 3\text{CH}_2\text{OH} \\
\text{CH}_2\text{O} - \text{C} - \text{R''} & \quad \text{I I} \\
\text{Methanol} & \\
\text{Triglyceride} & \\
\text{CH}_3\text{O} - \text{C} - \text{R} & \quad \text{I I} \\
\text{CH}_3\text{O} - \text{C} - \text{R'} & + \text{CH} - \text{OH} \\
\text{CH}_3\text{O} - \text{C} - \text{R''} & \quad \text{I I} \\
\text{Patty acid} & \\
\text{Methylesters} & \\
\text{CH}_3\text{OH} & \quad \text{I$^\$} \\
\text{Glycerol} & \\
\end{align*}
\]

The specific gravity of the various samples of \textit{Cyperus esculentus} oil, \textit{Cucumis melo} oil, \textit{Cyperus esculentus} biodiesel \textit{Cucumis melo} biodiesel and petrodiesel as determined by the density bottle method at 30°C (g/cm\textsuperscript{3}) yielded
the following results; 0.908, 0.902, 0.865, 0.861 and 0.859 respectively. These values are in agreement with the specification for biodiesel and also the value given by the Conference of fuel chemistry which is \((860 - 900 \text{ Kg/m}^3)\) for biodiesel and \((810 - 860 \text{ kg/m}^3)\) for petrodiesel. Consequently, biodiesel is denser than the conventional petrodiesel. This means that the biodiesel of the two samples have good combustion characteristics because of the greater the density of the diesel fuel, the greater it is heat of combustion per unit volume and therefore, greater its power or fuel economy.

### 4.2.4 Heat of Combustion

![Heat of combustion graph](image)

The heat of combustion of the various samples of *Cyperus esculentus* oil, *Cucumis melo* oil, *Cyperus esculentus* biodiesel, *Cucumis melo* biodiesel and Petrodiesel was determined with an Oxygen bomb colorimeter. The values
obtained (in KJ/Kg) were as follows; 39764.19, 36807.89, 38998.70, 36002.60 and 41714.74 respectively. The values for the heat of combustion of the methylesters were slightly lower than that of their corresponding triglycerides. The values of the two biodiesel samples are however in agreement with the value given in 71. Which is in the range of 33 – 40(MJL⁻¹) This indicates that, the two biodiesel samples will give out substantial heat on combustion in a diesel engine.

4.2.5 Saponification value

The saponification value determinations of all the samples of Cyperus esculentus oil, Cucumis melo oil, Cyperus esculentus biodiesel, Cucumis melo biodiesel and petrodiesel were determined and the value (mg/g) obtained were; 185.130, 178.117, 185.130, 178.117 and 29.423 respectively. This indicates that, the mean molecular weights of the triglycerides of the oils of the two
samples are the same with their methylesters. The triglyceride of the oil of *Cyperus esculentus* is higher than that of *Cucumis melo* with its methylester. The saponification value of the petrodiesel as obtained under the same conditions gave 29.428, which means that petrodiesel is expected to have a lower molecular weight. The triglyceride and methylester of *Cyperus esculentus* has higher saponification value and so will a higher tendency of forming soaps as compared to the triglyceride and methylester of *Cucumis melo*.

### 4.2.6 Acid value

<table>
<thead>
<tr>
<th>Acid Value</th>
<th>Tigernut Oil</th>
<th>Melon Oil</th>
<th>Tigernut biodiesel</th>
<th>Melon biodiesel</th>
<th>Petrol diesel</th>
</tr>
</thead>
</table>

It is observed that the acid value of *Cucumis melo* oil is higher 5.049 mgKOH/g than that of *Cyperus esculentus* oil which is 3.366 mgKOH/g indicating that the *Cucumis melo* oil had a higher amount of free fatty acid compared to *Cyperus esculentus* oil and so will hydrolyse more easily, especially if stored under improper conditions to give a stale oil. The acid values of the methylesters as well as the petrodiesel were also determined under the same condition and the value obtained was 0.208 mgKOH/g for all the
three samples of *Cyperus esculentus, Cucumis melo* biodiesels and Petrodiesel. These values are in agreement with the ASTM specification for biodiesel (B100) which is 0.5 mgKOH/g maximum\(^6\). This makes the methylesters of *Cyperus esculentus* and *Cucumis melo* good for the engine because the presence of free fatty acids in biodiesels more than this amount can lead to corrosion of engine wares and the presence of the free fatty acids could be increased as a result of water in the fuel\(^6\).

### 4.2.7 Iodine value

![Iodine Value Chart]

The iodine value of 107.870 and 104.058 g/100/g for the triglyceride of *Cucumis melo* and its methylester were obtained respectively. This shows that the triglyceride of *Cucumis melo* oil is semidrying as it falls within \((100 - 130)\)\(^6\). The triglycerides of *Cucumis melo* oil has the ability of slowly absorbing atmospheric oxygen to produce a soft film after prolonged exposure to air\(^6\). Higher iodine value oils have lower melting points therefore,
triglycerides of *Cucumis melo* oils will make better cold weather biodiesels, but with high iodine value oils, there is more risk of the biodiesel polymerizing (drying) into a tough insoluble plastic like solid. *Cucumis melo* oil biodiesel is semi-drying so will not polymerize as fast as the drying oils. Biodiesel made from *Cucumis melo* oil should be stored carefully and used quickly.\(^6\)

The value of triglyceride of *Cyperus esculentus* oil and its methylester is non-drying as it falls within \((0 - 100)^6\). With a lower iodine value of 83.750 mg/g, the oil can remain liquid at normal (room) temperature and is capable of forming elastic film after long exposure to air. Biodiesel made from lower iodine value oil like *Cyperus esculentus* oil is more efficient fuel than the higher iodine value oils because they have higher cetane numbers. Therefore, *Cyperus esculentus* biodiesel is not susceptible to oxidation and can be conveniently used if the biodiesel require long term application.\(^6\)

### 4.2.8 Peroxide Value

From the peroxide value determination, triglyceride of *Cucumis melo* oil and its methylester has a higher value of 10.400 mg/g and 49.400 mg/g respectively while the triglyceride of *Cyperus esculentus* oil and its methylester
has a lower value of 3.400 mg/g and 43.000 mg/g respectively. This indicates that *Cyperus esculentus* oil and the biodiesel made from it are more stable to oxidation. Since the *Cyperus esculentus* oil has a lower iodine value. Therefore, *Cyperus esculentus* biodiesel and its oil are less susceptible to oxidation. The biodiesel made from it can be stored for a longer time.

*Cucumis melo* oil and its biodiesel from the result has a higher peroxide value, since *Cucumis melo* oil and its biodiesel is more unsaturated, oxidation can take place more easily at the double bond forming peroxide (as a result of hydrolysis) a condition known as rancidity. Consequently biodiesel made from *Cucumis melo* should be stored carefully to prevent oxidative attack.

**Determination of moisture content**

<table>
<thead>
<tr>
<th>Moisture Content</th>
<th>Tigernut Oil</th>
<th>Melon Oil</th>
<th>Tigernut biodiesel</th>
<th>Melon biodiesel</th>
<th>Petrol diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage</td>
<td>0.8</td>
<td>1.0</td>
<td>0.8</td>
<td>0.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The moisture content of the biodiesel samples of *Cyperus esculentus*, *Cucumis melo* and the triglyceride of their oils; *Cyperus esculentus* and
Cucumis melo as well as the petrodiesel gave the following results; 0.04%, 0.05%, 0.900%, 1.00%, 1.00% respectively. The values of the biodiesel samples are in agreement with the ASTM specification for biodiesel which is 0.05 max. Values higher than this can increase the free fatty acid content which could result in commission of vital fuel system components. These biodiesels can be stored effectively because they will not support microbial growth in storage tanks.

4.2.10 Spectroscopic Analysis

The spectroscopic analysis particularly that of infra red spectrum indicates the presence of the O-H group in all the samples of Cyperus esculentus and Cucumis melo methyl esters and the oils of Cyperus esculentus and Cucumis melo as well as the commercial based petroleum diesel. This could result from the incomplete removal of the catalyst (KOH) or methanol used in the transesterification process. Presence of traces of water in the samples could have also resulted to the presence of the hydroxyl group. Another possibility could be that, the reactions were not 100% complete. This result also indicates the presence of the important ester functional group which peaked at 1744 and 1778. The prominent peaks in the results of UV-visible spectral represented in table (4.3) reveals the possibility of C=O and \(-\text{C=}-\) chromophores in the oil samples.

4.3.0 CONCLUSION

From the result of the extraction and Physiochemical analysis and discussion, it was obvious that both Cucumis melo and Cyperus esculentus methyl esters (biodiesels) are very important sources of fuel for diesel engines. It could be recalled that the high viscosity of the vegetable oils is as a result of glycerine and this could be eliminated by the conversion to form ester. This
has been confirmed in the results. The other three critical parameters of specific gravity, heat of combustion, and acid value, also compared well with the commercial petrodiesel fuel.

The *Cyperus esculentus* oil will make better biodiesel because of its non drying character and can be used on long term basis especially in hot weather\textsuperscript{14}. *Cucumis melo* oil on the other hand produced a biodiesel that is recommended for use on short term basis because of its semi drying character and will be suitable for cold-weather\textsuperscript{14}.

The government should encourage the cultivation of *Cyperus esculentus* tuber and *Cucumis melo* seed and more research should be focused on their utilization. The oils from these tuber/seed could be refined to produce biodiesel that reduces the following emissions: carbon monoxide, Ozone forming hydrocarbons, hazardous diesel particulate and acid rain causing sulphur dioxide.
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