

Production of biodiesel from palm kernel oil through base-catalyzed trans-esterification process

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Abstract

Growing concerns about environmental problems associated with fuels have engineered so much research into biofuels, such as biodiesel. However, continuous and large-scale production of biodiesel from edible oil could result in serious food security problems if cheap and viable alternatives are not made available. To solve this problem, oil was obtained from non-food/ underutilized seeds of palm kernel using Soxhlet apparatus. Physicochemical properties and fatty acids composition of these oils were determined using standard analytical and instrumental methods. Biodiesel was processed from these oils via sequential base (KOH) homogeneous catalysis. Fuel properties of biodiesel from the oil were determined using standard methods and the results obtained were compared with standards. Oil yields were found to be 37.6% for palm kernel seed respectively. Physicochemical properties of palm kernel oil respectively are: saponification value:(115.00)mg KOH/g, acid value(4.488)mgKOH/g, free fatty acid value (2.244)mg/KOH/viscosity:(29)mm²/s, moisture content: (0.46)%, peroxide value:(3.12)meqkg⁻¹,refractive index:(1.455), specific gravity (0.899)g/cm. Fuel properties of biodiesel from palm kernel seed oil respectively are: Kinematic viscosity at 40°C: (nil) mm²/s, smoke point (100°C), flash point(90°C),fire point:(150°C),pour point(nil) and cloud point:(nil).The physicochemical properties of the biodiesel produced showed that the flash point, viscosity, density, ash content, percentage carbon content, specific gravity and the acid value fell within American Society for Testing and Materials (ASTM) specifications for biodiesel. Therefore, the biodiesel produced from the oil significantly met standard quality requirements.

Keywords: Biodiesel; Palm Kernel oil; Trans-esterification; Base catalyst; Yield optimization; Sustainable energy; Alternative fuel; Environmental impact; Fuel properties.

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1. Introduction

Palm oil has been consumed for more than 5000 years and is obtained from the fruit of the palm tree, *Elaeis guineensis*. This tree is native to western Guinea. From the fifteenth century was introduced to other parts of Africa, Southeast Asia and Latin America along the equator. Oil palm was introduced in Malaysia in 1870 as an ornamental plant. The palm was cultivated on an industrial scale after the First World War, drawing on experiences from the plantations of Sumatra (1). Currently, Indonesia, Malaysia, Thailand, Nigeria and Colombia are the world's largest producers of palm oil (2). In Central and South America, the first plantations were established in the forties. In Colombia, in 1957 began the cultivation of palm for ornamental purposes. Then the palm cultivation takes place on an industrial scale. In 2008 there were 350 000 hectares of planted area, with a tendency to increase over the next decade. In November 2009, Colombia is the fifth largest producer of palm oil with a production of 800,000 tons (3). Palm tree takes from 2 to 3 years to start producing fruit. Palm trees can produce fruit for 25 years. Among the oilseed crops palm tree produce more oil per hectare. The fruit contains 50% oil. The palm tree can yield 3 000 to 5 000 kg of pulp oil per hectare and 600 to 1 000 kg of kernel oil per hectare from the kernel (4).

1.1. Classification of the oil palm

The palm is a perennial plant. There are several genera and species in the Arecaceae family, the family of the Palms (5). The classification of the oil palm in varieties is mainly done by the form, colour, composition of fruit and leaf shape. The mesocarp and endocarp vary in thickness. This characteristic is directly related to oil production. The shell and mesocarp contain palm oil. The crude palm oil (CPO) is produced from the mesocarp of the fruit. It is one of the few oils produced from the mesocarp of the fruit. The other is olive oil. The crude palm kernel oil (CPKO) is produced from the inner nut or kernel (figure1). There are three varieties of the oil palm fruit: dura, tenera, and pisifera. The tenera produces fruit with higher oil content.

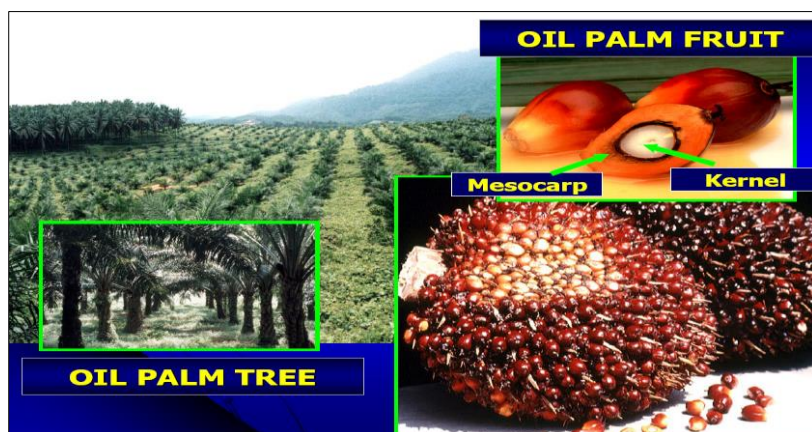


Figure 1 Oil Palm Tree

1.2. Dura (Deli dura)

Dura grew commercially in the world until the late sixties. Its main feature is the presence of a large kernel 2 to 8 mm and a thin mesocarp. This decreases the percentage of pulp in the fruit and therefore its oil content is low. There are still some small plantations

1.3. Pisifera.

The pisifera palm produces a fruit that has no endocarp or shell. This variety produces smaller fruit than the Dura. Because of the size of the fruit and the lack of shell, this variety produces little oil. So it is used only to improve the variety by crossing.

1.4. Tenera (Djongo Tenera).

The kernel of the fruit is thin. The proportion of pulp is considerably higher, so the oil content is significantly abundant. Tenera differs from the Dura variety because their fibers are darker. Tenera variety is the most widely used commercially in the world. However, the Dura variety is also cultivated (Deli dura) (6).

1.5. Morphology

The oil palm is a monocot plant. The primary roots develop from a bulb located below the stem. The horizontal roots predominate in the first 50 cm of the soil. Other roots descend into the soil. Secondary roots develop on the primary roots. The trunk grows 35 to 75 cm in height each year (in Malaysia the growth is about of 45 cm every year). With this growth in height of the palm fruit harvest becomes very difficult after 15 years of age of the plants. The leaves are green, have a length of 6 to 8 m and are arranged in spirals on the trunk. Under normal conditions, the trunk holds between forty and fifty-six leaves. These should be pruned or cut during harvesting and maintenance activities, otherwise the leaves accumulate on the trunk (20 or 30 leaves per year). The oil palm reaches maturity at 10 to 12 years (7).

1.6. Agronomics requirements

The oil palm prefers warm-temperate to tropical climates with regular water in hot weather. Optimally the oil palm requires at least 1 600 to 2 000 mm of annual rainfall and sunlight (approximately 5 hours per day on average during the year). The relative humidity should be above 75%. The soil water loss by direct evaporation and transpiration through the leaves affects the development of palm oil. The relative humidity is influenced by the insulation from the sun, the vapor pressure of the atmosphere, temperature, and wind and soil moisture. It is needed an average maximum temperature of around 29°C and a mean minimum temperature of about 22°C to 24°C. Lower temperatures stop the growth and reduce the yield of adult palms (3). It takes approximately 4 to 5 years to begin to bear fruit and reaches its highest productivity just before 20 years. However, it is a crop that can withstand periods of drought and floods, extreme weather conditions prevalent in countries where it is cultivated (8).

1.7. Composition of the seed.

The palm oil is a natural food that is extracted from the seeds and fruit without chemical solvents, so reducing the risk of contamination. The palm oil contains equal proportions of saturated fatty acids and unsaturated fatty acids. It contains 40% oleic acid (monounsaturated), 10% linoleic acid (polyunsaturated), 44% palmitic acid (saturated) and 5% stearic acid (saturated). The unrefined palm oil is an important source of vitamin A. This oil is also a natural source of vitamin E, tocopherols and tocotrienols. Palm oil has high solid glycerides content, which make it semi-solid. It is normally used in its natural state without hydrogenation. (9).

1.8. Products and by-products of the palm tree

Oil palm is a stable source of the world supply of vegetable oil. It is considered to reach highest oil yield per hectare. The variation in the reached oil yield is related to the type of tree, the different fertilizers and rate of maturation of the plant. The palm fruit produces two different types of oils: palm acid oil from the mesocarp and lauric palm kernel oil from its kernel. The fresh fruit bunches are crushed in a pressing machine to obtain crude palm oil and palm kernel. The palm kernel is further crushed to produce palm kernel oil and protein flour (palm kernel cake) (3). Ideally, the crops can produce up to 20 tons of fruits per hectare and per year. It is possible to extract up to 25% palm oil (five tons) and 5% of palm kernel oil (one ton). This amount is greater than the amount produced by any other source of vegetable oil (7). Only 10% of the palm yields oil (palm oil and palm kernel oil). The remaining 90% of biomass includes empty fruit bunches (EFB), fibers, kernels, fonds and trunks. If this rest of biomass is burn open or left to settle in waste ponds, it will emit carbon dioxide and methane contributing to global warming. By using the oil palm in the mills of the oil palm industry, as fuel for production of heat and power, the emission of greenhouse gas is reduced. The use of the biomass from palm oil for production of heat, electricity and biofuels should continue developing.

1.8.1. Palm kernel cake.

The palm kernel cake is used almost exclusively for animal feed. According to several studies, the use of palm kernel cake in animal feed favors the healthy development of the animals. Additionally, it is estimated that the integration of palm kernel cake with palm oil in animal feed increases the animal's weight gain, ensuring higher returns for farmers (7).

1.8.2. Crude palm oil and palm kernel.

Once extracted, the crude oil is processed into two products: olein (liquid) that is used almost exclusively as food and stearin (solid) whose main use is in cosmetics, soaps and detergents.

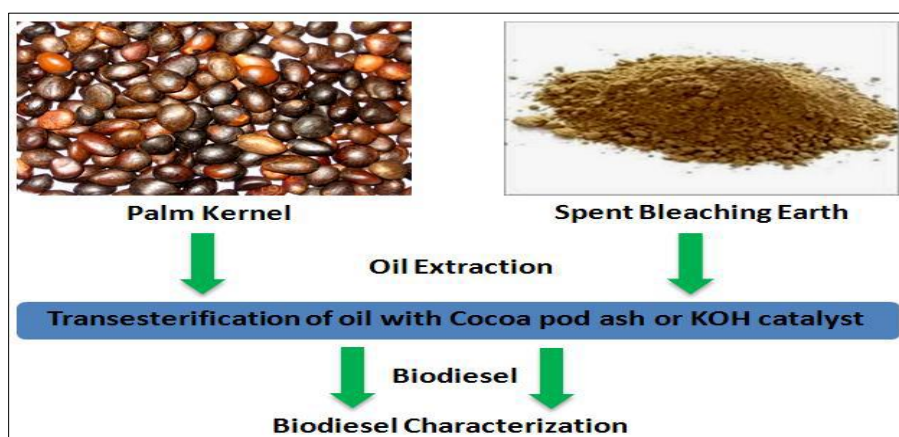
1.8.3. World Production and prices.

World production of palm oil was 45 million tons (2). In March 2012 the price of palm oil was 1100 USD per metric ton (FOB Brazil) (10). Table1 shows the production of palm oil in the world.

Table 1 Palm oil producers

Indonesia	20.75
Malaysia	18.50
Thailand	1.3
Nigeria	0.82
Colombia	0.80
Others	2.85

Figure 2: shows the main producers of palm oil in 2001(FAO).

**Figure 2** Palm kernel seeds

1.8.4. Statement of the Project Problem

The current demand for energy is insatiable. The crisis surrounding the cost and environmental effects of fossil fuels both in the present and nearest future has brought up the need to look for alternative source of energy (11). Biodiesel is one of the promising alternatives to fossil fuels in Nigeria, because the nation has in abundant the resources required for biodiesel production. Embracement of biodiesel in Nigeria will address the issue of recurrent fuel scarcity, poor electricity generation in rural areas and environmental pollution. Converting the huge palm kernel oil around to biodiesel is not enough; producing quality biodiesel at established optimum conditions, through a clean technology with good economic value is of great importance. This project is to provide answers in this direction, so that people in rural areas can successfully embark on biodiesel production. Nigeria, as a developing nation, need not only to make significant impact in global biodiesel production, but also to ensure that the biodiesel technology adopted (which include procedures and feedstocks) meets the international standards, putting into consideration the environmental implication associated with it. The life cycle assessment (LCA) of biodiesel is one science-based tool that can address such tasks.

1.8.5. Aims and Objectives of the Project

The aim of this project work is to establish optimum conditions for the production of high yield and environmental friendly biodiesel from the trans-esterification of palm kernel oil (PKO) and investigate the life cycle assessment of biodiesel produced from the oil.

The objectives of the project study are:

- To determine a more suitable alkali catalyst (between KOH and NaOH) for palm kernel oil through trans-esterification.
- To establish optimum conditions for biodiesel production by considering methanol/oil mole ratio, catalyst concentration, reaction time and reaction temperature.
- To formulate a model suitable for the prediction of biodiesel cetane number.
- To perform the Life Cycle Assessment (LCA) of biodiesels produced from palm kernel oil.
- To predict the environmental impacts of utilizing the biodiesel produced.

1.8.6. Significance of the Study

Many advanced countries (Germany, USA, France, Malaysia etc.) pay a lot of attention to research and development of biodiesel technology and this has resulted into huge profit in these countries. Nigeria, with a population of over 160 million people, ought not to be left out in this development, considering the huge number of oils generated yearly. Converting these less valued oils to biodiesel, at commercial level, is a right and timely step in developing our economy and improving the health of our environment. The research work, among other things, will guide in the choice of suitable feedstocks for the production of biodiesel through the application of LCA of biodiesel (considering the human health and environmental implications). In addition, the LCA will assist in the evaluation of the sustainability of a future biodiesel industry. Some of the benefits the nation stands to derive from biodiesel production and LCA of biodiesel produced include:

- Reduction in total reliance on petroleum and crude oil products,
- Reduction in emissions of greenhouse gases.
- Economic growth in the form of employment in rural areas.
- Reduction or elimination of waste oil pollution.
- Diversification of income and economy in the country.
- Improved knowledge on environmental impact of biodiesel production and utilization.

1.8.7. Scope and Limitations of the Project

The project work was restricted to the trans-esterification of crude palm kernel oil. The determination of the molecular weight of the oil triglycerides was based on the fatty acids profiles obtained from Gas Chromatography system. Methanol was the only alcohol considered during trans-esterification process, and the one catalyst used was KOH laboratory scale batch reactor was simulated and used. Cetane number of biodiesels produced could not be measured because of equipment limitations (an important parameter in the assessment of biodiesel). Life cycle assessment of biodiesel was based on biodiesel purification stages.

2. Literature review

2.1. Background study of biodiesel

Biodiesel (fatty acid methyl esters) is an alternative fuel for diesel engines. It is an alcohol ester product from the trans-esterification of triglycerides in vegetable oils or animals accomplished by reacting lower alcohols such as methanol or ethanol with triglycerides.

The National Biodiesel Board (USA) technically defined biodiesel as a mono-alkyl ester. Blends of biodiesel and conventional hydrocarbon-based diesel are products most distributed for use in the retail diesel fuel marketplace. Biodiesels contain no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. Much of the world uses a system known as the “B” factor to state the amount of biodiesel in any fuel mix:

- 100% biodiesel, 100% Petro-diesel is referred B100.
- 20% biodiesel, 80% Petro-diesel is referred to as B20.
- 5% biodiesel, 95% Petro-diesel is referred to as B5.
- 2% biodiesel, 98% Petro-diesel is referred to as B2.

Blends of less than 20% biodiesel can be used in diesel equipment with no, or only minor modifications. Biodiesel can also be used in its pure form (B100) but may be blended with petroleum diesel at any concentration in most injection pump diesel engines. New extreme high-pressure (29000 psi) common rail engine have strict factory limits of B5 or B20 depending on manufacturers. Biodiesel has different solvent properties than Petro-diesel and will degrade natural rubber gaskets and hoses in vehicles (mostly vehicles manufactured before 1992), although these tend to wear out naturally and most likely will have already been replaced with FKM, which is non- reactive to biodiesel. The first diesel engine was produced by Rudolf in Augsburg and Germany. In remembrance of this event, August 10 has been declared “International Biodiesel Day”. Rudolf diesel demonstrated a diesel running on pea nut (at the request of the French government) but for the French otto company at the world fair in Paris, France in 1990. (12). Biodiesel has been known to breakdown deposits of residue in the fuel lines where Petro-diesel has been used. As a result, fuel filters may become clogged with particulates of a quick transition to pure biodiesel is made. Therefore, it is recommended to change the fuel filters on engine and heaters shortly after switching to a biodiesel blend. Biodiesel is light to dark yellow liquid immiscible with water, with high boiling point and low vapor pressure. It has been used as a substitute for diesel fuel in the automobile industry and referred to as a diesel equivalent processed fuel derived from vegetable oils (13). Several research have been performed on the production of biodiesel and some basic feedstock for the fuel includes animal fats,

vegetable oils, soy, rap-seed, jatropha, mahua, mustard, flax, sunflower, palm oil, hemp, field pennycress, pongamiapinnata and algae. Pure biodiesel is the lowest emission diesel fuel. Although liquefied petroleum gas and hydrogen have cleaner combustion, they are used to fuel much less efficient petrol engines and are not as widely available. Biodiesel is an oxygenated fuel, meaning that it contains a reduced amount of carbon and higher hydrogen and oxygen content than fossil diesel. This improves combustion and reduces the particulate emission from un-burnt carbon. Biodiesel is also safe to handle and transport because it is as biodegradable as sugar, ten times less toxic than table salt, has a high flash point of about 300°F (148°C) compared to petroleum diesel fuel, which has a flash point of 125°F (52°C). Current commercial production of biodiesel (FAME) is via homogeneous trans-esterification but this process has a lot of limitations, thus, making the cost of biodiesel not economical as compared to petroleum-derived diesel. One of the most significant limitations using this process is the formations of soap in the product mixture leading to additional cost required for the separation of soap from the biodiesel. Also, the formation of soap has also led to the loss of triglycerides molecules that can be used to form biodiesel. However, since the catalyst and the reactants/products are in the same phase, the separation of products (biodiesel) from the catalyst becomes complex. On the other hand, heterogeneous trans-esterification can overcome all these limitations in which solid based catalyst is used in place of homogeneous catalyst, making it a more efficient process for biodiesel production with lower cost and reduced environmental impact. Xie et al. studied the trans-esterification of soybean oil to methyl ester using potassium-loaded alumina catalyst (14). Also, Suppes et al. studied the trans-esterification reaction of soybean oil with zeolite and metal catalysts to produce biodiesel, while Jitputti et al. studied the trans-esterification of crude palm kernel oil and crude coconut oil using several acidic and basic solids (15). All these studies indicated that different oils would require different catalysts for optimum conversion to biodiesel. International Conference on Environment 2008 (16). Therefore, Rudolf Diesel designed a prototype of the engine. The engine was shown in the Paris World Expo in 1889. The engine was planned to use vegetable oil. The first test was done with peanuts oil. In 1908, Henry Ford made the first design of his automobile model T. This automobile used ethanol as fuel. From 1920 to 1924, the standard oil company sold gasoline with a 25% ethanol, in the Baltimore region. The project was then abandoned because of the high price of the corn (source of the ethanol) and the problems with storage and transport; (17). In the late twenties and during the thirties, Henry Ford and other experts joined their efforts trying to promote the use of ethanol. They built a fermentation plant in Atchinson (Kansas) to produce ethanol fuel. This plant produced 38000 litres ethanol per day for use as fuel (18).



Figure 3 Typical example of biodiesel engine car.

During the 1930s, more than 2000 fuel stations, in the USA Mid- west, sold this ethanol made from corn. This was called gasohol. Gasohol could not compete with the gasoline and the plant in Atchinson was closed in the 1940s, (19). In 1973, there was a sharp oil crisis associated to the second arab-israeli war. During this period, the fuel price doubled in just three months. The scarcity of this non-renewable resource jeopardized the supply. This fact: encourage the search a substitute for the oil, (20). In Brazil, the Proalcool project began in 1975. The objective of proalcool project was to encourage use of ethanol as transport fuel and for industrial uses, (21). The fast depletion of fossil fuels and the greenhouse gas emissions from fossil fuels are the main reason for efforts to develop biofuels. In 2003, the EU; promote the use of biofuels for transport. The target was that quantity of biofuels to be placed on the market should be 2% in 2005 and 5.75% in 2010 in relation to the fossil fuel. In 2007, the EU proposed with the objective to reduce the increase in global average temperature that 20% of the energy will come from renewable sources.

2.2. Advantages and disadvantages in the use of biodiesel

The use of biodiesel has energetic, environmental and economic advantages. Today’s diesel engines require a clean fuel to be burned, as well as it remains stable under the different conditions. Biodiesel can be used directly in any diesel engine without any necessary modifications in the engine. Their properties are like petroleum diesel fuel (equivalent density, viscosity only slightly higher). It can be mixed with fossil diesel in any proportion, without any problem (22). In comparison to fossil diesel, biodiesel has a lower calorific value (around 10%) and a worse performance at low temperatures with a tendency to solidify in extreme cold conditions, which requires the use of specific additives. Additional advantages include a high cetane number (23).

A summary of these characteristics is shown in Table below.

Table 2 Characteristics of the biodiesel and fossil diesel

Characteristics	Fossil Diesel	Sunflower oil	Sunflower Biodiesel	Rapeseed oil	Rapeseed Biodiesel
Specific density(kg/dm ³)	0.835	0.924	0.88	0.0916	0.88
Viscosity (cSt) at:	---	---	---	---	---
20 °C	5.1	65.8	---	77.8	7.5
50 °C	2.6	34.9	4.22	25.7	3.8
HHV (kcal/l)	9 216	8 760	8 472	8 928	---
LHV(kcal/l)	8 496	8 194	7 930	8 232	7 944
Cetane number	>45	33	45-51	44-51	52-56
Residue (%)	0.15	0.42	0.05	0.25	0.02
Sulphur (%)	0.005	0.01	0.001	0.002	0.001

Table 3 The advantages and disadvantages of the use of biodiesel.

Advantages	Disadvantages
Biodiesel is a renewable resource, biodegradable and nontoxic.	Increased emissions of NOx and aldehydes.
Lower emissions of carbon monoxide, unburnt hydrocarbons and carbon particles, contributing to the reduction of green-house gases.	Because it is a good solvent, it can dissolve sediments in the engine fuel system and cause filter plugging during its first use in engines usually working with fossil diesel. So, it is recommended to clean the fuel system when switching from diesel to biodiesel.
It can be used directly in direct injection engines without special adaptations.	Below 0 ° C, the biodiesel tends to freeze causing engine deposits.
The engine performance improves when using biodiesel instead of fossil diesel, due to its high lubricity.	Biodiesel has about 8% less energy per litre than diesel. The power and fuel consumption of the engine is decreased.
It is safer, because it has a high flash point.	The feedstocks for biodiesel require vast areas for cultivation and could affect the food prices.
The gases from combustion of biodiesel do not contain sulphur dioxide, main cause of acid rain.	Biodiesel tends to oxidize more rapidly than diesel.

Table 4 The global production of biodiesel has increased exponentially

Region	Million litres	Feed-stocks
EU	9 906	Rapeseed (50%), Soy (40%), Palm (5%), Tallow (5%)
USA	1 682	Soy (40%), Tallow (20%), Canola (20%), Palm (20%)
Brazil	1 386	Soy (80%), Tallow (10%), Other vegetable oils (10%)
Argentina	1 250	Soy
Thailand	614	Palm
Malaysia	284	Palm
Colombia	205	Palm
China	182	Waste vegetable oils
South Korea	----	Palm (33%), Soy (33%), Waste vegetable oils (33%)
Indonesia	170	Palm
Singapore	124	Palm
Philippines	108	Coconut
Canada	102	Tallow
Other South America	63	Palm
Australia	57	Tallow
Taiwan	43	Palm (33%), Soy (33%), Waste vegetable oils (33%)
Central America	38	Palm
India	23	Waste vegetable oils
Other, Oceania	6	Waste vegetable oils
Other, Asia	5	Waste vegetable oils
TOTAL WORLD	16 436	

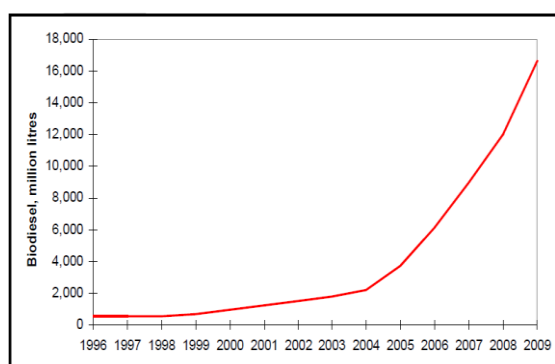


Figure 4 World production of biodiesel

Source: Lamers (2010)

2.3. Trans-esterification

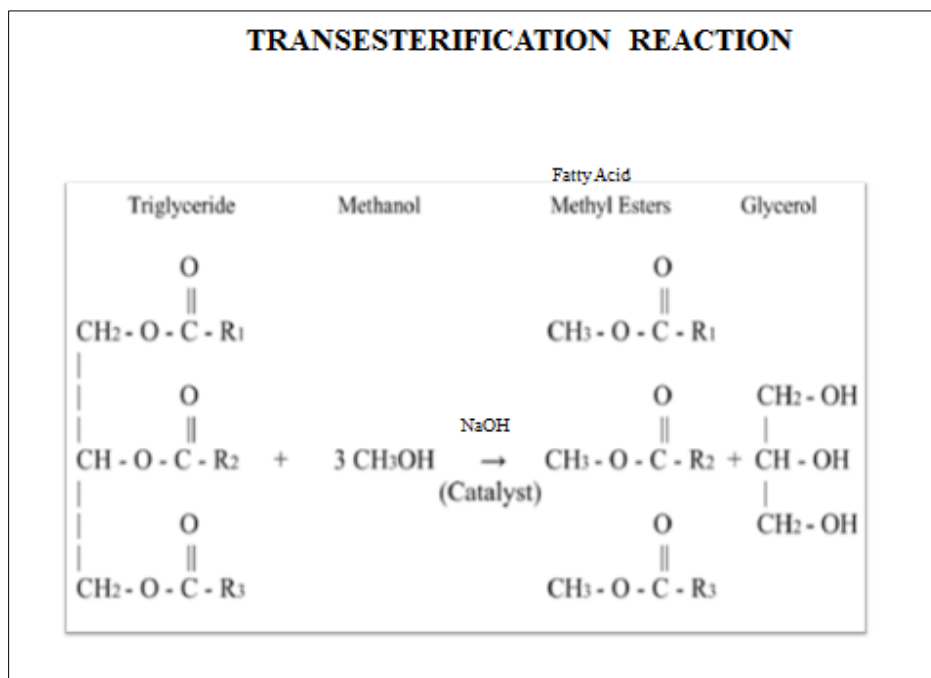


Figure 5 Stage in the trans-esterification reaction



Figure 6 Batch trans-esterification reaction set-ups

Biodiesel is usually obtained by trans-esterification of oils or fats by reacting, a short-chain alcohol, like methanol, in the presence of a homogeneous base-catalyst (typically NaOH or KOH). The most common raw materials for production of biodiesel are vegetable oils from sunflower, soybean, palm kernel oil, oil palm and other (12). The trans-esterification reaction mainly depends on the nature of the feedstock, catalyst concentration, the molar ratio alcohol-oil, temperature, agitation rate, pressure and reaction time as well as moisture content and amount of free fatty acids (24,25,26,27). In the trans-esterification reaction, one mole of triglyceride is reacted with three moles of alcohol to form one mole of glycerol and three moles of the respective fatty acid alkyl ester in a sequence of three reversible reactions where the triglycerides are converted to di-glycerides and then to mono-glycerides. Glycerol is produced as a by-product and biodiesel is the main product. After the reaction the mixture forms two phases: the glycerin-rich-phase and ethyl esters-rich-phase. The two phases can be separated by decantation or centrifuging. There are several types of catalysts

for trans-esterification. The most used catalyst for production of biodiesel is the homogeneous catalysis. The homogeneous catalysis used for biodiesel production can be divided mainly into alkaline and acidic catalysts. Heterogeneous catalysts (solid phase) are also used. Another interesting alternative may be to use lipases as enzymatic catalysts (28).

2.4. Glycerol Separation

Separation of glycerol from biodiesel (desired product) is very important, being the first step in obtaining pure biodiesel and to avoid possible reversible process. Glycerol can cause clogging of injectors and carbon residues in the engine if not completely removed (29). The common laboratory practice of glycerol removal is decanting using a separating funnel. After about 24 hours of allowing trans-esterification products separate to a clear light (biodiesel) phase and a denser phase (glycerol) are obtained (30). There is often a quality control check, for if there is no distinct separation (but emulsion or soap formation), then problems may have occurred during reaction because of any (or combination) of the followings: insufficient/excess usage of methanol or/and catalyst, extreme high/low reaction temperature, presence of water. Glycerol removed has a wide range of applications; it can be used in chemical, pharmaceutical, food, paint and automobile industries (31).

2.5. Biodiesel Purification

To get pure biodiesel that meets the ASTM or EN standards, raw FAME obtained from the reaction must essentially be free of residual glycerol, methanol, un-reacted oil and traces of catalyst. Common raw FAME refining processes include water washing, ion exchange resins, membrane separation and use of adsorbents such as magnesium silicate (32).

The purpose of refining the biodiesel is to remove glycerol, methanol, free fatty acids (or soap) present and to neutralize any residual catalyst present. The best practice for reducing the amount of warm water required for biodiesel refining is to ensure proper trans-esterification reaction (33).

The adverse effects of impurities found in unrefined FAME are listed table below: Effects of Impurities in Biodiesel on Engines

Table 5 Shows the impurities and effects in biodiesel

Impurity	Effect
Free Fatty Acids (FFA)	Corrosion Low oxidation stability
Water	Hydrolysis (FFA formation) corrosion Bacteriological growth (filter blockage)
Methanol	Corrosion of Al and Zn engine components
Metals (soap, catalyst)	Deposits in the injectors (carbon residue) Filter blockage, Engine weakening.
Glycerol	Deposits in the injectors (carbon residue) Increase aldehydes emissions.

Source: Lamers (2010)

2.6. Biodiesel Washing Water

Water is both a polar and universal solvent, this makes water a good solvent for purification purposes. Through the application of water for washing, high quality FAME can be obtained from raw FAME which is insoluble in water (34). Water washing involves mixing distilled water with raw FAME for a given short period of time for impurities in biodiesel to dissolve in water. Different methods of introducing water are possible, simple settling and decanting allows for water to be removed. Water Washing is preferred to other purification technologies available not only because it is economical, but also it does produce high quality FAME (32).

Water acts as a good medium for the addition of acid for neutralization of catalyst and as a carrier of impurities (34). 0.2 % sulphuric acid solution is added to the distilled warm water, and the mixture is added to raw biodiesel. The content is agitated for a short period of time and allowed to settle into two clear layers (biodiesel on top and cloudy washing water as bottom layer). Methanol, glycerol and catalyst are all soluble in warm water and therefore taken out with

washing (bottom layer). It is important to note that agitation of the content is a must for the total dissolution of impurities in water. And biodiesel is less dense than water, these make the separation very easy to achieve (35).

2.7. Factors Influencing Biodiesel Yield and Properties

2.7.1. Effects of Free Fatty Acid (FFA) and Water Content

Presence of Free fatty acid (FFA) and water content in the raw materials used for biodiesel production will significantly affect both the quality and quantity biodiesel in alkali-catalyzed trans-esterification. It implies that all starting materials (lipid feedstock, alcohol, and catalyst) should be substantially anhydrous. Prolonged contact of alkali catalysts with atmospheric air will reduce catalyst efficacy through the catalyst's interaction with moisture and carbon dioxide in air. Also, it is critical that feedstock used during alkali-catalyzed trans-esterification should contain free fatty acid that is less than 1.0 wt.% (Rashid and Anwar, 2008). The higher the acidity of oil, the lower is the conversion and yield of biodiesel. FFA present in the feedstock oil is converted to soap and then removed, through the addition of calculated alkali catalyst to the oil.

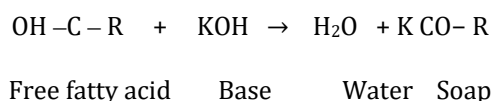


Figure 7 Saponification Reactions between Free Fatty Acid and Base

In addition, presence of water can promote hydrolysis of alkyl ester (biodiesel) to form FFA, which lowers ester yield (Figure 7). Soap formed during saponification causes increased viscosity or gel formation, which interferes with the trans-esterification reaction as well as

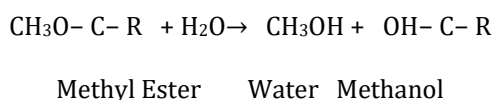


Figure 8 The reaction of Hydrolysis from Biodiesel

Fig.8: Formation of Free Fatty Acid from the Hydrolysis of Biodiesel Ma *et al.* (1999) investigated the effects of FFA and water on trans-esterification of beef tallow using sodium hydroxide as catalyst. It was discovered that when 0.6 % FFA was added, the yield of beef tallow methyl ester was minimal. Additional water present in the reaction mixture intensely diminished the ester yield. From their studies, they concluded that FFA and water content should be maintained below 0.5 and 0.06wt.% respectively. Pre-treatment of these oils to remove FFA and water is usually required. In this process, 12% aqueous potassium hydroxide solution is required to neutralize FFA. The treatment temperature and duration can be either 90°C for few seconds (short-mix process) or 40°C for 15 minutes (long-mix process). The oil-soap mixture is then centrifuged to separate the aqueous phase containing water, soap, and precipitated phosphatides. The treated oil usually has FFA reduced to < 0.05% and phosphorus to < 2 ppm (36,37). FFA can also be removed from vegetable oils through distillation (38). The distillation process should be performed under vacuum conditions to lower the operating temperature. If the operating temperature is too high, glycerides will degrade to generate more acids. The distillation temperature ranged from 100 – 180 °C. However, this approach is less preferred due to the additional cost incurred during the distillation process. Alternatively, a two-step acid-alkali esterification-trans-esterification process can be used (39). In the first step, FFA is esterified with a short-chain alcohol with acid catalyst to produce ester. Since FFA is converted into ester in the first step, an alkali catalyst can be used in trans-esterification in the second step.

2.7.2. Effects of Alcohol Concentration and Type

Stoichiometrically, three moles of alcohol react with one mole of triglyceride to produce fatty acid alkyl ester (biodiesel) and glycerol during trans-esterification process. To have high biodiesel yield (conversion) by shifting the reaction to the products side (being a reversible reaction), excess alcohol is usually utilized. Factors that help to establish an optimum alcohol to oil mole ratio in trans-esterification include level of alcohol purity, oil quality and type of vegetable oil used. Guo and Leung (2006) reported that 98% ester content can be obtained from trans-esterification of canola oil using 6:1 alcohol to oil ratio while trans-esterification of used cooking oil requires 7:1 alcohol to oil ratio to obtain 94% ester content (40). Trans-esterification of *Cynara cardunculus L.* oil requires 12:1 ethanol to oil ratio as an optimum ratio while an increase in ethanol to oil ratio to 15:1 decreases ester content (41). Rashid and Anwar (2008) also reported that a further increase in alcohol used in trans-esterification of rapeseed oil beyond its optimum ratio (6:1) would result in reduced ester yield (42). When too much alcohol is used in trans-esterification, the polarity of the reaction mixture is increased, thus increasing solubility of glycerol back into the ester phase and promoting the reverse reaction between glycerol and ester or glyceride, thereby, reducing ester yield. It is important to note that more molar ratio of alcohol to

oil would be required when waste cooking oil is used compared to using pure vegetable oil (40). Also, acid catalyzed reaction requires a higher alcohol to oil molar ratio (30:1), compared to alkali-catalyzed reactions (43). In some cases, the alcohol to oil ratio is increased to 245:1 to obtain 99% conversion (44). The type of alcohol used in trans-esterification can also affect reaction performance, methanol and ethanol are the two commonly used. In general, methanol is preferred to ethanol due to economic benefit, higher yield of biodiesel and shorter reaction time (45). Furthermore, methanol has a lower boiling point, thus excess methanol from the glycerol phase is easily recovered after phase separation. The lower reactivity experienced in ethanolysis is due to increased carbon chain length which leads to a decrease in nucleophilicity. It was found that when waste fryer grease is trans-esterified with a mixture of methanol and ethanol at equal molar ratio, the resulting biodiesel contains 50% more FAME than FAEE, illustrating the higher reactivity of methoxide as compared to ethoxide (40).

2.7.3. Homogeneous Base Catalysis

Homogeneous base catalysis is the most used in commercial biodiesel production processes, this is because the process offers high reaction yield (97 % or more) within a short time (10 minutes - 2 hours) with mild reaction temperatures (25 - 70 °C). According to Meher (2006), the reaction mechanism involves 3 steps as shown in Figure below: The first step is the attack of alkoxide ion (methoxide ion in the case of methanol as reacting alcohol) to carbonyl carbon of the TAG molecule to form a tetrahedral intermediate (46). In the second step, the tetrahedral intermediate reacts with alcohol to regenerate alkoxide ion. The last step involves the rearrangement of the tetrahedral intermediate to form alkyl ester and DAG. This mechanism can be extended to the reaction of DAG and MAG in the same manner. Homogeneous base catalysis in trans-esterification is much faster than homogeneous acid catalysis (47). However, the effectiveness of homogeneous base catalysis is evaluated by the quality of the feedstock used, that is, acid value of lipid must be lower than two (2.0) and all chemical reagents (feed) must be substantially anhydrous (46).

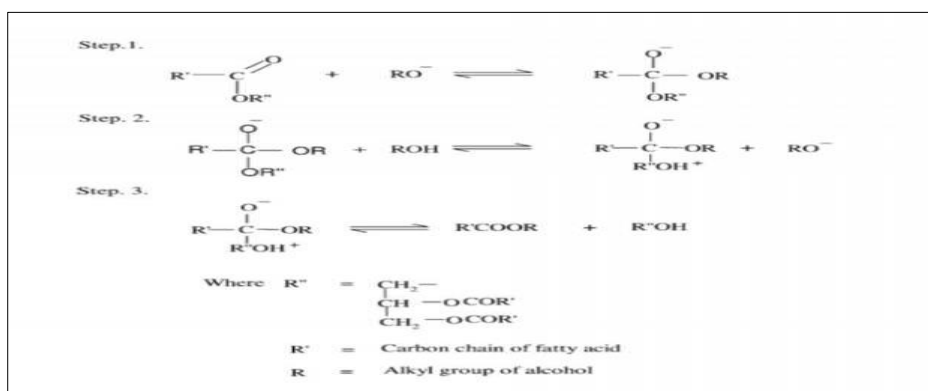


Figure 9 Mechanism of Homogenous Base Catalysis in Trans-esterification

Source: Meher, (2006)

The most common homogeneous catalysts are hydroxides and alkoxides of alkali metals such as NaOH, KOH, NaOCH₃, and KOCH₃. (27) Ma *et. al.*, 1999, found that hydroxide of alkali metal is more effective than alkoxide as NaOH and NaOCH₃ reach their maximum activities at 0.3 and 0.5wt.% respectively when subjected to the same condition using beef tallow feedstock. Mahajan *et. al.* (2007) showed that when NaOCH₃ was used, the acid value of the reaction product was significantly lower than when NaOH was used (48). However, alkali metal alkoxides are less popular than hydroxides in large-scale production due to their toxicity, higher price, and disposal problems. When alkaline metal alkoxides and hydroxides are used as catalysts in methanolysis, the active catalytic species are the same, (methoxide ion CH₃O⁻), concluding that these catalysts are equally effective (49). It was also reported that at 6:1 alcohol to oil molar ratio, the use of 0.5% NaOCH₃ is as effective as 1% NaOH (47). The reaction yield can also be increased by using two-step process by separating and removing glycerol at the end of the first step (50). The increase in reaction yield, compared to the one-step process, stems from a shift in reaction equilibrium to the product side due to the removal of glycerol during the production process.

2.8. Homogeneous Acid Catalysis

In biodiesel production from feedstock containing high FFA and water content, acid catalysis is preferred to base catalysis. This approach is employed to avoid saponification so that FFA can be converted directly to ester through esterification while glycerides are converted into ester through trans-esterification. Therefore, acid catalysts can be

used to catalyze both esterification and trans-esterification while base catalysts only catalyze trans-esterification but not esterification (51).

The disadvantages of homogeneous acid catalysis are that it requires a high reaction temperature, higher concentration of catalyst, and a longer reaction time due to slower reaction rate. In addition, it is possible to have residual acid catalysts corroding the metal reactor and metal parts of the reactor (52). The reaction mechanism is shown in Figure: 10.

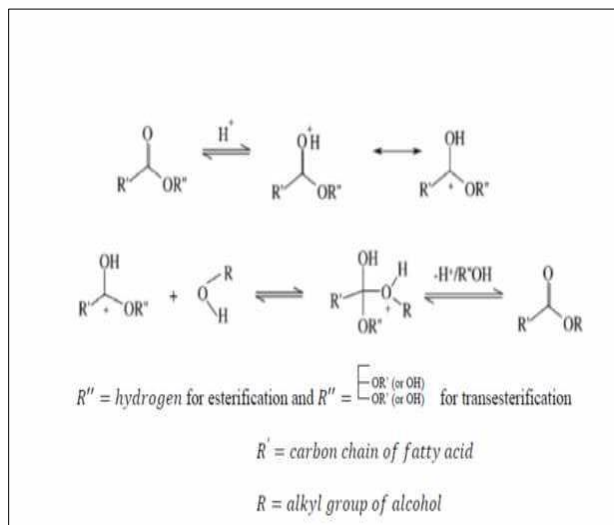


Figure 10 Mechanism of Homogenous Acid Catalysis in Esterification and Trans-esterification.

The first step is protonation of the carbonyl group in the glyceride molecule, which leads to carbocation. The attack of alcohol then produces a tetrahedral intermediate and the elimination of glycerol backbone from this intermediate leads to the formation of ester. Although saponification can be avoided, water is still being generated during esterification of FFA. Water can then undergo hydrolysis, which is the reverse of esterification, but, unlike esterification, it can occur in the presence of either base or acid. The resulting carboxylate anion from hydrolysis shows little tendency to react with alcohol to form ester but reacts readily with K^+ or Na^+ in the presence of base to form a stable salt. Therefore, it is essential to perform acid-catalyzed esterification and base-catalyzed trans-esterification separately (52).

Examples of homogeneous acid catalysts are H_2SO_4 , H_3PO_4 , HCl , BF_3 and CF_3CO_2H . Among these catalysts, H_2SO_4 is the most used catalyst due to its good catalytic activity and simplicity in $H_2SO_4/MeOH$ preparation as concentrated liquid H_2SO_4 can be added directly to Methanol (36). $HCl/MeOH$ was introduced for esterification about half century ago but is not a very popular choice due to complexity in preparation of the solution involving bubbling hydrogen chloride gas into methanol or adding acetyl chloride slowly to methanol (51), using a common concentration of 5%. BF_3 /methanol is prepared by bubbling BF_3 gas into cooled methanol. BF_3 has an empty orbital that can accept a pair of electrons making it a Lewis acid. It has been reported that FAME can be obtained from fatty acids within a very short time (10 minutes) using 6-14% catalyst loading (52). Due to its superior activity and short reaction time, the American Oil Chemists' Society (AOCS) has adopted BF_3 in the official method for preparing methyl ester from fatty acids (53). However, BF_3 is not used widely in literature as H_2SO_4 because it is expensive, toxic, and has a limited shelf life (51). Diazomethane (CH_2N_2) is not classified as an acid catalyst, but rather as a strong methylation reagent. Despite its inability to catalyze trans-esterification, diazomethane in ether esterifies free fatty acid at a much faster rate when compared to acid catalysts. However, its shortcomings such as high toxicity, short shelf life, and potentially explosive have prevented it from being used widely like other catalysts (52).

3. Methodology

3.1. Material and methods

3.1.1. The sample collection and treatment

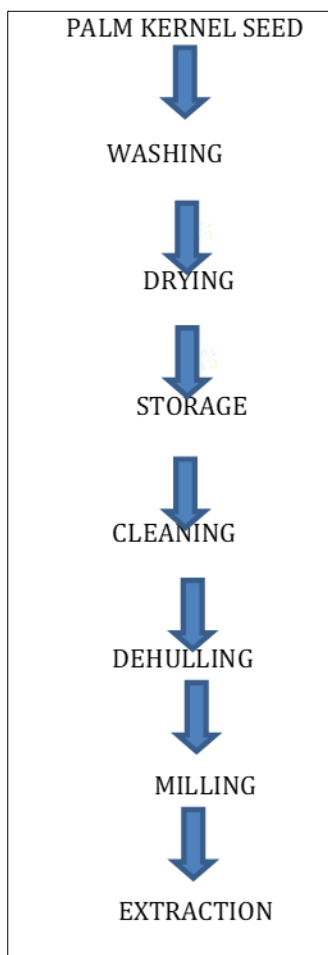


Figure 11 Extraction flow chart of the palm kernel nut oil from the seed

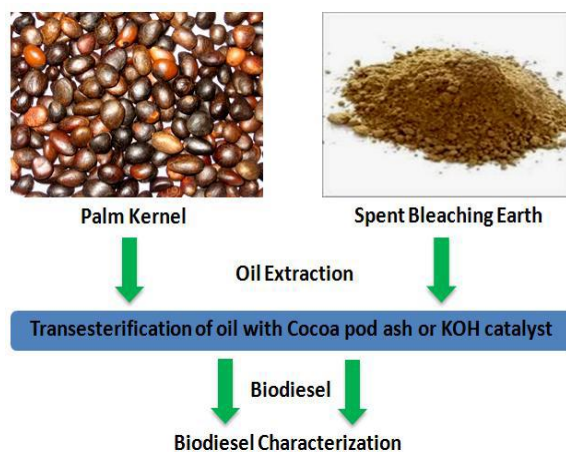


Figure 12 Palm kernel seeds

The palm kernel seeds (*Elaeis guineensis*) used for the project were picked from Futa farm (oil based- production), Federal University of Technology, Akure, Ondo State, Nigeria in 2018. The seeds were washed with water and slightly sun dried together with the hard seed coat and the husk is manually removed to obtain the palm kernel seed nut. The palm kernel nuts were pounded with pestle and mortar followed by grinded with blending machine and kept inside

air-tight container before the extraction process. The sequence of operations involved in the processing of the seed before extraction is as outlined below in fig.11

3.2. Methods

3.2.1. Chemical and Solvents

Petrol ether, ethanol, phenolphthalein, potassium hydroxide, hydrochloric acid, alcoholic KOH, Hanus iodine metal, glacial acetic acid (ethanoic acid), chloroform, distilled water, potassium iodide, starch indicator, sodium thiosulphate. All these chemicals and solvents are of good grade and required for the project.

3.2.2. Equipment

Analytical balance, hot plate, magnetic stirrer, magnetic stirrer bar, Soxhlet apparatus, stopwatch, thermometer, viscometer, water bath.

3.2.3. Sample Preparation.

The palm kernel seeds were washed, and sun dried for some days. The nuts of the dried seeds were removed and exposed to the sun. The seeds were dried and grinded into fine particles with the help of a pestle and mortar then followed by blending machine.

3.2.4. Soxhlet Extraction of Oil

Working principle of the apparatus

About 300ml of n-hexane was poured into the round bottom flask of the extractor. Portions of the milled sample of 200g were wrapped tightly in a white cotton fabric and were inserted batch wise in the Centre of the extractor in batches. The Soxhlet, equipped with a reflux condenser and was placed into a flask containing the n-hexane. The Soxhlet was incorporated in a round heating mantle and heated with temperature of 45-60°C. When the solvent was boiling, the solvent vapor travels up through a distillation arm and floods into the chamber housing the tumble of solid. The condenser ensures that the solvent vapors cool and drips back down into the chamber housing the solid material. The extract seeps through the pores of the thimble and fills the siphon tube, where it flows back down into the round bottom flask. This was allowed to continue for hours. It was then removed from the tube and dried in the oven, cooled in the desiccator.



Figure 13 Extraction of fat from the seed using the Soxhlet apparatus

3.3. Physicochemical properties of the extracted oil

The physicochemical analysis of the oil involves the determination of free fatty acid (FFA), acid value, saponification value and un-saponification matter, pH value, smoke point, flash point, fire point, refractive index and specific gravity. The procedures for determination of all these parameters are given below:

3.3.1. Preparation of neutral solvent

25ml of diethyl ether was measured into a conical flask. 25ml of methanol/ethanol was added to the premeasured diethyl ether in the conical flask, 1ml of phenolphthalein indicator was added and the resulting solution was neutralized with 0.1M KOH until a pink end was observed and color disappeared after 15 minutes.

3.3.2. Purpose of neutral solvent

The purpose of neutral solvent is to dissolve the oil. Ethanol/methanol allows the fat molecules to solubilize out so that the KOH will have enough surface area to react with the oil matter. The ethanol divides the oil into fine globules.

3.3.3. Acid Value Determination

The acid value was determined by directly titrating the oil in an alcoholic medium with aqueous KOH solution. Free fatty acid was calculated as oleic acid.

- **Reagents:** Ethyl-alcohol (95%) by volume and neutral solvent. Phenolphthalein indicator, 100ml of di-ethyl ether, 100ml methanol, standard aqueous 0.1M KOH solution.
- **Procedure:** About 1g of sample oil was weighed in a conical flask. 25ml of ethyl alcohol and 25ml of di-ethyl ether, the mixture was warmed for 5 minutes before 1ml of phenolphthalein was added. The titration was carried out as possible with 0.1M KOH (54).

Calculations

$$\text{Acid Value} = \frac{\text{Titre value} \times \text{Molarity of KOH} \times 56.1}{\text{Weight of the sample}}$$

3.3.4. Determination Of Free Fatty Acid (FFA)

The acid value was determined by directly titrating the oil in an alcoholic medium with aqueous KOH solution. Free fatty acid was calculated as oleic acid.

Reagents

About 1g of sample oil was weighed in a conical flask. 25ml of ethyl alcohol and 25ml of di-ethyl ether, the mixture was warmed for 5 minutes before 1ml of phenolphthalein was added. The titration was carried out as possible with 0.1M KOH (54).

Calculations:

$$\text{Acid Value} = \frac{\text{Titre Value} \times \text{Molarity of KOH} \times 56.1}{\text{Weight of the sample}}$$

$$\text{Free Fatty Acid} = \frac{\text{Acid acid}}{2}$$

3.3.5. Determination of Saponification Value

The oil was saponified by refluxing with a known excess of alcoholic KOH solution. The alkali consumed for saponification was determined by titrating the excess alkali with standard HCl.

Apparatus: 250ml conical flask, 1m long air condenser or reflux condenser, measuring cylinder, water bath

Reagents: Alcoholic potassium hydroxide solution – Dissolve 40g of potassium hydroxide in this 1 litre alcohol keeping temperature below 15° c while dissolving alkali. Allow to stand overnight, decant the clear liquid and keep in a bottle closed tightly with or rubber stopper, phenolphthalein indicator, 0.5M HCl standard solution.

Procedure: 2g of oil sample was weighed in a conical flask. 25ml of alcoholic KOH was added to it. It was refluxed for one hour and boiled gently until the sample was completely saponified. The flask and condenser were cooled then washed with about 10ml of hot neutral ethyl alcohol. 1ml of phenolphthalein indicator was added and titrated with standard

HCl solution. Blank was prepared by titrating a 25ml aliquot of standardized alcoholic potassium hydroxide with standard HCl (54).

Calculation:

$$\text{Saponification Value} = \frac{(B-A) \times \times \times 56.11}{\text{Weight (g) of sample used}}$$

Where B=volume of HCl used for blank,

A=titre value

3.3.6. Determination Of Moisture Content

The moisture content of the oil was determined by oven-drying method, because it is more accurate and precise, allowing fast removal of residual water without changing the organic matter.

Procedure:

Clean well labeled and dried dishes that had been oven dried at 105°C drying temperatures were weighed (W_1). 1g of the oil sample was put into respective dishes, spread as much as possible and weighed (W_2). They were transferred into desiccators immediately after each weighing, until all the weighing was completed to prevent absorption of moisture from the atmosphere. The dishes containing the sample were transferred into the oven maintained at 105°C and dried for 4 hours after which they are put in desiccators, to cool and weighed. The process of heating, cooling and weighing was continued at 30 minutes interval until a constant weight was obtained (W_3).

Calculation:

$$\% \text{ Moisture content} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \quad (54)$$

Where W_1 = weight of empty crucible (g)

W_2 = weight of empty crucible + sample before drying (g)

W_3 = weight of empty crucible + sample after drying (g)

3.3.7. Determination of Iodine Value of Oil

Iodine value is a measure of the degree of unsaturation in oil. It is constant for oil or fat. Iodine value is a useful parameter in studying oxidative rancidity of oil. The higher the unsaturation the greater the possibility of oils to go rancid. Oil contained both saturated and unsaturated fatty acids. Iodine gets incorporated into the fatty acid chain whenever double bonds exist. Hence, the measure of iodine absorbed by oil, gives the degree of unsaturation. Iodine value/number is defined as the 'g' iodine absorbed per 100g of the oil.

Reagents: Chloroform (CCl_4), Hanus iodine solution (Wij's), 0.1M sodium thiosulphate, distilled water, 1% starch indicator solution, potassium iodide.

Procedure: 1g of the oil sample into a 250ml conical flask, 10ml of chloroform solution, followed by 15ml of Wij's and it was shaking very well, then covered with foil moistened potassium iodide (10% KI solution) stand for 30 minutes in a darkroom. 10ml of KI (10% KI solution) was added followed by 100ml of distilled water and 2 drops of starch solution and was titrated against 0.1M sodium thiosulphate. Color was changed from black to pink then to colorless. Blank sample also was conducted.

Calculation:

$$\text{Iodine value} = \frac{(B-S) \times M \times 12.69}{\text{Weight of the sample (g)}}$$

Where B=blank titre, S=sample titre

M=molarity of $\text{Na}_2\text{S}_2\text{O}_3$

3.3.8. Determination of Peroxide Value of Oil

Rancidity is brought about by the action of air (oxidative) or microorganisms in oil. In oxidative rancidity oxygen is taken by the oil fat with the formation of peroxides. Peroxides value is a of the peroxides contained in the oil. The peroxides present are determined titration against thiosulphate in the present of potassium iodide (KI) using starch as indicator.

Reagents: Solvent mixture (mix two volumes of glacial ethanoic acid with one volume of chloroform, 5% KI solution, 1% starch solution, 0.002M Na₂S₂O₃).

Procedure: 1g of the oil sample was weighed into a conical and 1g of KI solution was added followed by 20ml solvent mixture (2 volume of acetic acid +1 volume of chloroform). It was boiled for one minute, then 20ml of 5% K.I, followed 25ml of distilled water and 2 drops of starch indicator was also added, it was then titrated against with 0.002M thiosulphate.

Calculation:

$$\text{Peroxide value} = \frac{T_s - T_b \times 0.002 \times 0.002 \times M \times 10000}{\text{Weight of oil sample}}$$

Where T_s = Titre value of sample

T_b = Titre value blank

3.3.9. Smoke Point, Flash Point and Fire Point

These parameters are used to test the volatility of oil and to compare them with other substances like kerosene to know the rate at which they burn. Seed oils tend to have higher values of smoke point, flash point, and fire point than paraffin oils.

3.3.10. Determination of Smoke Point

A petri dish was filled with 20ml of the sample oil, and this was heated continuously on a hot plate until the sample gave off a thin fume with continuous streams of bluish flame. A thermometer was clamped on the retort-stand, the sensitive part of thermometer was dipped into the petri dish to record the temperature at this point (54).

3.3.11. Determination Of Flash Point

The same oil sample was used and with the aid of a clamp holder, a thermometer was hung and dipped inside the oil, ensuring that the thermometer does not touch the bottom of the petri dish which is placed on a hot plate. The sample was heated until a sufficient vapor is produced when flame was applied, it causes burning for more than one minute. The temperature is then recorded. (54)

3.4. Determination Of Fire Point

The sample that was used for the flash point was used with the heating continued until sufficient vapor was produced and the flame was applied, it caused burning for a period of more than one minute. The temperature was then recorded (54).

3.4.1. Determination Of pH Value

The pH of the oil sample say 40ml can be determined using pH meter Jen way 3015 model and at a temperature of 25°C. The electrode calibrated firstly with buffer solution of pH 9.0, followed by buffer solution of pH 4.0 and then wiped with tissue paper, rinsed with distilled water and then insert into the oil sample. The pH of the oil is displayed on the screen of the pH meter and the reading was recorded.

3.4.2. Determination of Refractive Index

The refractive index was determined with a refractometer. The prism of the refractometer was wiping with tissue paper moistened with acetone to remove dirt, oil or grease. A drop of the oil sample was placed on the surface and clamped. The lens was viewed, and the control knob adjusted until a faint blue line was seen inform of a cross across the meter. The reading was then taken and recorded (54).



Figure 14 Abbe refractometer

3.4.3. Determination of Specific Gravity

This is the ratio of the mass (g) of oil to that of an equal volume of water. The density bottle was cleaned, weighed and filled with distilled water, then immersed in a water bath at 20°C until the water content reaches 20°C. The outside of the bottle was wiped and weighed. The bottle was emptied, dried and filled with the oil sample at 20°C. It was then kept in a water bath, wiped and weighed again (54).

$$\text{Specific gravity} = \frac{\text{Weight of oil}}{\text{Weight of equal volume water}}$$

3.4.4. Determination Of Viscosity

A cleaned dried viscometer with a flow time above 200seconds for the oil sample was selected. The viscometer was charged with the sample by inverting the tube's thinner arm into the liquid sample and suction force was drawn up to the time mark of the viscometer, after which the instrument was turned to its normal vertical position. The viscometer was placed into holder and inserted to a constant temperature water bath set at 25°C. The suction force was then applied to the thinner arm to draw the sample slightly above the upper timing mark. The efflux time was recorded by timing the flow of the sample as flows freely from the upper timing mark to the timing mark to the lower timing mark.



Figure 15 Falling-ball viscometer

$$\text{Viscosity (cp)} = \frac{\text{Flow time} \times \text{specific gravity} \times 1.002}{\text{Flow time of water}}$$

The viscosity can be determined by equation:

$$(\text{ball medium}) \eta = k * t * \rho - \rho \quad (2)$$

Where, η is the dynamic viscosity [g/cm, s], k is the geometrical constant of the ball

[m²], t is the fall time through the tube [s], ρ is the density of the ball [g/cm³] and

ρ is the density of the medium [g/cm³].

The kinetic viscosity:

$$v = \eta / \rho$$

There, v is the kinematic viscosity [g/cm, s]

3.4.5. Pretreatment of the Oil Sample







The palm seed oil has a high FFA content of 5%, a value which makes it unable to undergo direct trans-esterification. The oil was reformed to reduce the FFA value.

Reagents: Oil sample, catalyst (KOH), methanol, conical flask, water bath, aluminum foil, weighing balance, measuring cylinder.

Procedure: Weighed 50g of the oil sample into conical flask, 0.875g of KOH as a catalyst was added followed by 120ml of methanol. The content was covered by aluminum foil, and it was transferred to water bath for 15 minutes. The contents were later poured into separating funnel for an hour, later it was washed with warmed water three times then oven dried for an hour. Therefore, titration was conducted to check back the free fatty acid.

3.4.6. Homogeneous Trans-esterification Of the Pretreated Oil

The FFA value of the oil was reduced below 1%, the homogenous base-catalyzed trans-esterification of the pretreated oil was carried out using methanol with potassium hydroxide (KOH) as catalyst to obtained monoesters of fatty acids. A three round neck bottom flask incorporated with thermometer was clamped and refluxed was used as laboratory scale reactor vessel, magnetic- stirrer bar, magnetic-stirrer hot plate.

	
Equipment for production of biodiesel	An electronic scale
	
Magnet and a digital magnetic stirrer	
	
Biodiesel and glycerol	Biodiesel washed with water
Figure 16 Various equipment used for Biodiesel processes	

The controlling parameters for the alkaline trans-esterification were oil to methanol ratio (5:1), catalyst concentration (1%wt/wt. Oil), reaction temperature of (65-70°C), and rate of agitation at 450rpm. The mixture was agitated continuously, once the thermometer reach the reaction temperature, timing was started for 2 hours, after it was transferred to separating funnel for overnight. The mixture would separate into two layered, at the top light biodiesel

while bellow heavy glycerol. The biodiesel was decanted and washed with warmed water three times; oven dried for an hour to get pure biodiesel.

4. Result

4.1. Oil yield of palm kernel

The extraction of the palm kernel seed flour using Soxhlet extractor apparatus, the percentage yield of oil was calculated and physicochemical properties of extracted oil from the seed of palm kernel were determined and recorded. Calculation for The Percentage Oil Yield Form Extraction The extracted oil from the palm kernel seed flour using Soxhlet extractor apparatus, the percentage yield of the oil was 37.6%. Table 6 below shows the percentage oil yield from the sample.

Table 6 Percentage yield oil of Palm seed

Weight (g) of sample Before extraction (ml)	Weight (g) of sample after extraction oil	Quantity of extracted	Percentage oil (%)
1200	748.32	75	37.6

Table 7 Analysis of physicochemical properties of the Palm kernel oil

Parameters	Value
Colour	Yellow
Acid value (mg/KOH/g)	4.488
Free fatty acid (mg/KOH/g)	2.244
Peroxides value (meq/kg)	3.12
Refractive index	1.455
Moisture content (%)	0.46
Viscosity at 40°C (mm ² /C)	29
Saponification	115.00
Specific gravity	0.899

4.1.1. Fatty Acid Profile and Biodiesel

The fatty acid profile of the biodiesel prepared from PKO was determined by GC-MS analysis. The individual peaks of the gas chromatogram were analyzed, and the fatty acid components identified using MS database. This is an indication that the PKO-biodiesel is composed mainly of saturated fatty acids. This finding is to determine the saturated fatty acids which were found to be the major composition of palm kernel oil fatty acids. The GC-MS scan also indicated that the concentration of fatty acid ethyl ester in the PKO biodiesel was attached at back of this project hard copy.

Table 8 ASTM standards and the result gotten from PKO-biodiesel.

Parameters	ASTM method	PKO-biodiesel result	ASTM standard limit
Specific gravity @ 15°C	ASTM D 5002	0.899	0.865-0.885
Basic sediment and water, vol. %	ASTM D 1796	-	0.05max

Water content (Distillation), vol. %	ASTM D 95	–	< 0.01
Flash point (close cup), °C	ASTM D 93	90	130 min.
Kinematic viscosity @ 40°C, mm ² /s	ASTM D445	–	1.9-6.0
Total sulphur, wt%	ASTM D 4294	–	0.05
Pour point, °C	ASTM D97	–	Nil
Cloud point, °C	ASTM D2500	–	Nil
Basic sediment and water, vol. %	ASTM D 1796	–	0.05max
Cetane index	ASTM D 976	–	Min 47
Conrad's son carbon residue (CCR), wt. %	ASTM D 189	–	0.05max
Ash content, wt. %	ASTM D 482	–	0.02
Acid number, mg KOH/g	ASTM D664	0.8	0.8

4.2. Definition of Terms

Fractional volume = volume of biodiesel of/volume of oil used

Mass yield = fractional volume/density

Mole yield = mass yield/molecular mass of the biodiesel

Concentration yield = mole yield/volume of biodiesel.

$$M_{w\ TRI} = 3M_{w\ FFA} + M_{w\ GLY} - 3M_{w\ H_2O}$$

$$M_{w\ TRI} = (3 \times 268.93213) + (92.09382) - (3 \times 18)$$

$$M_{w\ TRI} = 806.79639 + 92.09382 - 54 = 844.89021$$

5. Discussion of the Result

5.1. Effects of Reaction Temperature on the Percentage Yield of Biodiesel

Considering the table below drawn, it can be inferred that there was a steady increase in yield of the biodiesel and there was a maximum at 50°C of temperature, hence; the subsequent activities on the biodiesel production were carried out at this temperature.

5.2. Effects of Reaction Time on the Yield of Biodiesel

Table 4.1.0 below shows the effect of temperature on the yield of biodiesel by alkaline trans-esterification, under optimal condition of 0.875g of KOH as catalyst, 5:1 oil/methanol molar ratio at constant speed and time.

Table 9 Effects of Reaction Temperature on The Percentage Yield of Biodiesel.

Reaction Temperature(°C)	Catalyst conc.(g)	Yield of Biodiesel(g)	% yield of Biodiesel
30	0.0875	37.64	34.50
40	0.0875	38.45	33.80
50	0.0875	39.31	34.07
60	0.0875	40.14	32.39
70	0.0875	41.00	31.78

5.2.1. The Effect of the Reaction on Temperature

The effect of the reaction temperature on the yield of biodiesel produced. The compared experiment using 1.5 g KOH were carried out with a ratio methanol to oil: 4.5- and 2-hours reaction time. The experiments with 0.9g NaOH were conducted for 1 hour with the same ratio methanol to oil (4.5). The highest yield was obtained at 60°C with KOH. Using NaOH the highest obtained yield (90%) was at 55°C but already at 40°C a good yield was obtained (89%). A further increase in temperature is not recommended. High temperature also can lead to loss alcohol as vapour.

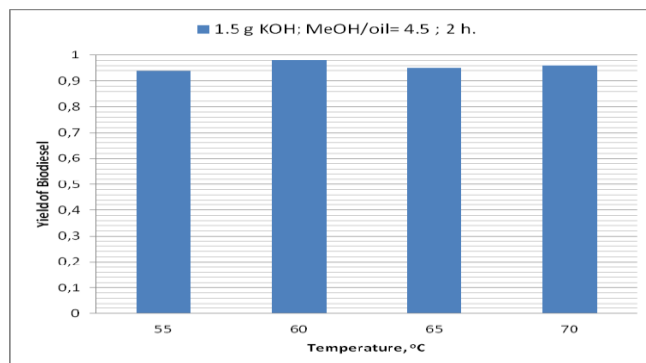


Figure 17 Influence of temperature. Methanol. KOH. 2 h.

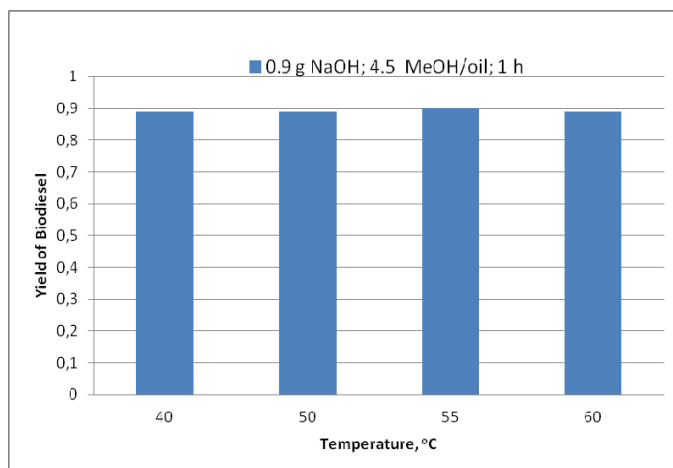


Figure 18 Influence of temperature Methanol. NaOH. 1h.

5.3. Effect of Rate of Mixing

The effect of rate of mixing was studied varying the rate of mixing between 500 and 1500 rpm. 0.9 g NaOH catalyst was used, and the reaction time was 1 hour. The yield of produced biodiesel increased from 90% to 94% when the rate of mixing was increased from 500 to 1500 rpm.

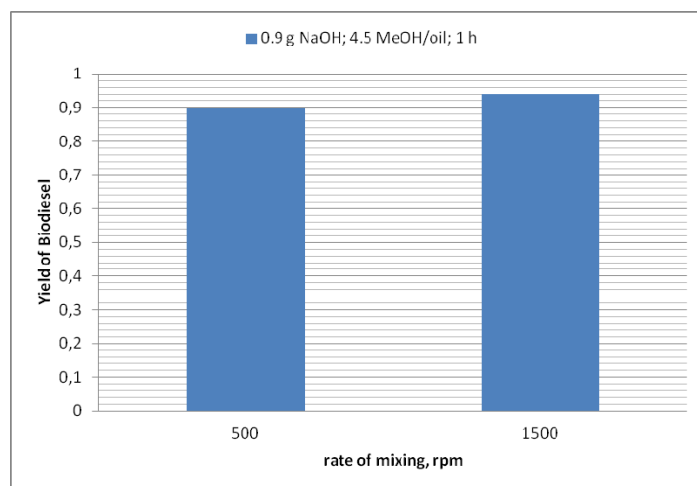


Figure 19 Influence of rate of mixing. Methanol. NaOH

5.4. Effect of Reaction Time.

The influence of the reaction time on the yield of produced biodiesel is studied using both KOH (1.5 g.) and NaOH (0.9 g.) as catalyst and a ratio

Methanol: oil= 4.5. The yield of biodiesel increases when the reaction time is increased from 1 to 2 hours.

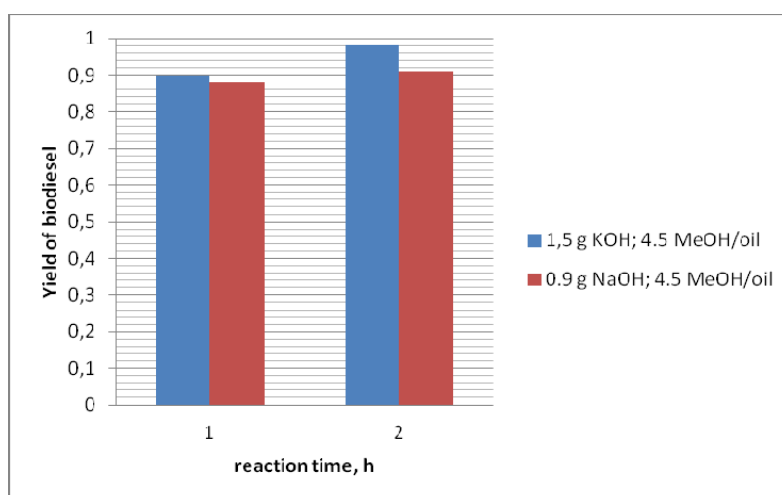


Figure 20 Influence of reaction time. Methanol/oil ratio: 4.5

6. Conclusion

From the study so far, it can be concluded that palm oil is viable for biodiesel production as an alternative to petroleum diesel. The fuel properties of palm oil biodiesel for KOH catalyst were found to be comparable to the ASTM standards. It could be inferred from the study also that the biodiesel produced from palm seed fat is an alternative to fossil fuel and it can replace the need for sulphur in petroleum. Using biodiesel can reduce the number of green gases emitted. They are a much cleaner source of energy than conventional sources. However, biodiesel can be used in any diesel vehicle made for this purpose and it reduces the amount of vibration, smoke and noise produced.

Finally, biodiesel has a high flash point, and other properties that make it safer and less likely to burn after an accident.

Recommendation

The study gave me good insight of generating diesel from biomass in addition to the previous petrol diesel therefore, I recommended that palm tree plant should be grown commercially and be guarded from destroyer, since the biofuel produced from palm oil seed is of high quality and has a clean burning alternative fuel, it is of environmentally friendly produced from domestic renewable resources. Therefore, biodiesel for use should be blended with petrol diesel to

minimize the potentiality of carbon deposition combustion engine chamber and to reduce the high viscosity encountered in vegetable oil. Lipase-catalyzed method can be employed in place of based-catalyzed method to achieve a very good yield of biodiesel. The use of lipase method makes the reaction less sensitive to high free fatty acid (FFA) content which is responsible for a problem with standard biodiesel process (Wikipedia).

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

References

- [1] Killmann W. Historical development and current status of the palm oil industry.: Palm Oil Research.; 2001.
- [2] USDA. Global production and trade of palm oil... USDA Agricultural Report.; 2009.
- [3] FEDEPALMA. Palm oil production statistics in Colombia. Federation of Oil Palm Growers Report. ; 2009.
- [4] Murillo J. Oil yields from palm trees. Journal of Oilseed Crops. 2003.
- [5] Rich P. Classification of the Areaceae family.: Palm Biology; 2008.
- [6] Rica A. Varieties of oil palm fruit.: Palm Oil Research.; 2008.
- [7] CORPODIB. Morphology and agronomic requirements of the oil palm. Palm Biology Journal. 2005.
- [8] Castro L. Climate and environmental requirements of oil palm. Agricultural Journal. 2007.
- [9] Gibon V. Composition and nutritional value of palm oil. Journal of Food Science. 2007.
- [10] IndexMundi. Palm oil prices and market data: Index Mundi Commodity Prices.; 2009.
- [11] William J. Alternative energy sources: The future of fuel... Energy Journal. 2006.
- [12] Knothe G. Historical perspectives on vegetable oil-based diesel fuels: Inform; 2001.
- [13] Biodiesel. Biodiesel properties and benefits. Biodiesel Magazine. 2007.
- [14] Xie W, PH, &CL. Transesterification of soybean oil to biodiesel using potassium-loaded alumina as a solid-base catalyst: Energy & Fuels.; 2006.
- [15] Jitputti J, KB, RP, BK, AL, &JP. Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. Chemical Engineering Journal. 2006.
- [16] ICENV. International Conference on the Environment. In; 2008.
- [17] Wik RM. Henry Ford and grass-roots America.: University of Michigan Press.; 1963.
- [18] Eckeland O. History of biofuels development.: Renewable Energy Review.; 2006.
- [19] Manchester J. he history of ethanol fuel in the United States. T. Energy Policy Journal. 1978.
- [20] Wright JC. The oil crisis of the 1970s: A history... Oil & Gas Journal. 2010.
- [21] Soccol CR. Proalcool project and ethanol fuel development in Brazil. Journal of Industrial Microbiology & Biotechnology. 2005.
- [22] Hilbert JA. Properties of biodiesel and their influence on performance in diesel engines. Renewable Energy Journal. 2007.
- [23] Sebastian H. Cetane number and its importance in diesel fuel quality. Journal of Fuel Technology. 2006.
- [24] Mittelbach M, &RC. Biodiesel: the comprehensive handbook: Boersedruck Ges.m.b.H.; 2004.
- [25] Canakci M, &VGJ. Biodiesel production from oils and fats with high free fatty acids. Transactions of the ASAE. 2001: 44(6), 1429.
- [26] Dorado MP, BE, AJA, SC, LHP, &KR. An alkali-catalyzed transesterification process for high free fatty acid waste oils.: Transactions of the ASAE, 2002.
- [27] Ma F, &HMA. Biodiesel production: a review.: Bioresource Technology; 1999.

- [28] Haas MJ, MPJ, RS, NA, &SKM. Production of FAME from acid oil, a by-product of vegetable oil refining. *Journal of the American Oil Chemists' Society*. 2003: 80(1), 97-102.
- [29] Lamers P, HC, JM, &FA. International bioenergy trade—A review of past developments in the liquid biofuel market... *Renewable and Sustainable Energy Reviews*. 2011: 15(6), 2655-2676.
- [30] Erickson D. *Biodiesel basics and beyond: A comprehensive guide to production and use for the home and farm.*: Aztext Press.; 2002.
- [31] Feto I. Utilization of glycerol from biodiesel production... *Journal of the Brazilian Chemical Society*. 2011): 22(4), 637-642.
- [32] Atadashi IM, AMK, AAAR, &SNMN. The effects of water on biodiesel production and refining technologies: A review.: *Renewable and Sustainable Energy Reviews*; 2010.
- [33] Berrios M, &SRL. Comparison of purification methods for biodiesel. *Chemical Engineering Journal*. 2008: 144(3), 459-465.
- [34] Gonzalo MEA. Water washing biodiesel purification.: *Renewable Energy Journal*, 2010.
- [35] Evangelos C. Biodiesel purification processes. : *Fuel Processing Technology*; 2013.
- [36] Issariyakul T, &DAK. Biodiesel from vegetable oils.: *Renewable Energy*; 2011.
- [37] Chen L, WX, &WD. Research on the purification of biodiesel from waste cooking oil by a combination of centrifugation and vacuum distillation. *Journal of Chemical Technology & Biotechnology*. 2009: 84(12), 1853-1858.
- [38] Martins S, NC, CJE, &GJ. Continuous esterification of free fatty acids from soybean oil using amberlyst 15.: *Fuel Processing Technology*; 2006.
- [39] Kaewta K, &KY. Biodiesel production from palm oil with used frying oil as co-solvent.: *Bioresource Technology*; 2008.
- [40] Guo Y, &LDY. Transesterification of neat and used frying oil: Optimization for biodiesel production.: *Fuel Processing Technology*; 2006.
- [41] Encinar JM, GJF, &RRA. Ethyl esters from used frying oil: Biodiesel preparation and characterization. : *Energy & Fuels*;; 2002.
- [42] Rashid U, &AF. Fuel, Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil.; 2008.
- [43] Bhatti S, OMR, &AN. Transesterification of palm oil to biodiesel using homogeneous catalysts.: *American Journal of Applied Sciences*; 2008.
- [44] Zheng S, KM, &DMA. Kinetics and equilibrium of methanolysis of soybean oil. *Journal of the American Oil Chemists' Society*. 2006: 83(5), 427-432.
- [45] Ayoola AA, AOS, &OMA. Kinetics and optimization studies of biodiesel production from the seed oil of *Telfairia occidentalis*.: *Journal of Taibah University for Science*; 2012.
- [46] Meher LC, DVSS, &NSN. Optimization of alkali-catalyzed transesterification of *Pongamia pinnata* oil for production of biodiesel.: *Bioresource Technology*; 2006.
- [47] Freedman B, BRO, &PEH. Transesterification kinetics of soybean oil.: *Journal of the American Oil Chemists' Society*; 1984.
- [48] Mahajan A, TYP, &LM. Transesterification of Beef Tallow for Biodiesel Production Using NaOCH₃ as Catalyst. : *Journal of the American Oil Chemists' Society*;; 2007.
- [49] Lang X, DAK, BNN, &RMJT. Synthesis and characterization of solid acid catalysts for biodiesel production: *Catalysis Today*; 2001.
- [50] Cayli G, &KSH. Optimization of two-step biodiesel production from sunflower oil.: *Bioresource Technology*; 2008.
- [51] Liu X, HH, &WY. Biodiesel production using acid catalysts: *China Oils and Fats*; 1994.
- [52] Morgenstern AJ, JDA, &AJA. Investigation of residual acid catalysts in biodiesel production.: *Industrial & Engineering Chemistry Research*; 2006.
- [53] AOCS. Official Method: BF3-Methanol Method for the Preparation of Methyl Esters. Edition. 5, editor.: *American Oil Chemists' Society, Official Methods and Recommended Practices of the AOCS*; 2006.

[54] AOAC. Official Methods of Analysis of AOAC International. 15th ed.; 1990.

Appendix**Acid value**

$$\text{Acid value} = \frac{\text{Titre value} \times 56.1 \times 0.1}{\text{Weight of the oil sample}}$$

Burette Reading(cm ³)	1 st Titration	2 nd Titration
Titre value	3.4	4.2

$$\text{Titre value} = 0.8$$

$$\text{Acid value} = \frac{\text{Titre value} \times 56.1 \times 0.1}{\text{Weight of the oil sample}}$$

$$\text{Acid value} = \frac{0.8 \times 56.1 \times 0.1}{1} = 4.48$$

$$\text{FFA} = \frac{\text{Acid value}}{2}$$

$$= \frac{4.48}{2} = 2.24$$

Peroxide value

$$\text{Peroxide value} = \frac{(\text{Sample-Blank}) \times 0.002M \times 1000}{\text{Weight of the oil sample}}$$

Burette Readings (cm ³)	Sample	Blank
Final Reading (cm ³)	1.00	10.80
Initial Reading (cm ³)	0.00	10.60
Titre value	1.00	0.20

$$\text{Peroxide value} = \frac{(\text{Sample-Blank}) \times 0.002M \times 1000}{\text{Weight of the oil sample}}$$

$$= \frac{(1.00-0.20) \times 0.002 \times 1000}{1}$$

$$= 1.6 \text{ meqkg}^{-1} \times 2$$

$$\text{Peroxide value} = 3.2 \text{ meqkg}^{-1}$$

$$\text{Iodine value} = \frac{(B-S) \times 0.1M \times 12.69}{\text{Weight of the sample (g)}}$$

Where B=blank titre

S=sample titre

M=molarity of Na₂S₂O₃

Burette Readings (cm ³)	Blank Titration	Sample Titration
Final Reading (cm ³)	18.90	17.50
Initial Reading (cm ³)	0.00	0.00
Titre value	18.90	17.50

$$\text{Iodine value} = \frac{(18.90 - 17.50) \times 0.1 \times 12.69}{1}$$

$$\text{Iodine value} = \frac{1.4 \times 0.1 \times 12.69}{1}$$

$$\text{Iodine value} = 1.7766 \text{mg/KOH/g}$$

$$\text{Moisture content} = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

Where W_1 = weight of empty crucible (g)

W_2 = weight of empty crucible + sample before drying (g)

W_3 = weight of empty crucible + sample after drying (g)

$$W_1 = 68.77 \text{g}$$

$$W_2 = 70.63 \text{g}$$

$$W_3 = 69.77 \text{g}$$

$$\begin{aligned} \text{Moisture content} &= \frac{W_2 - W_3}{W_2 - W_1} \times 100 \\ &= \frac{70.63 \text{g} - 69.77 \text{g}}{70.63 \text{g} - 68.77 \text{g}} \times 100 \\ &= \frac{0.86}{1.86} \times 100 \\ &= 0.423655914 \text{g} \% \end{aligned}$$

Saponification Value

$$\text{Saponification value} = \frac{(B - A) \times \dots \times 56.11}{\text{Weight (g) of the oil sample}}$$

Where B = volume of HCl used for blank,

A = titre value

Burette Readings (cm ³)	Blank Titration	Sample Titration
Final Reading (cm ³)	4.30	8.20
Initial Reading (cm ³)	0.00	0.00
Titre value	4.30	8.20

$$\begin{aligned} \text{Saponification value} &= \frac{(B - A) \times \dots \times 56.11}{\text{Weight (g) of the oil sample}} \\ &= \frac{8.20 - 4.30 \times 0.5 \times 56.11}{1} \\ &= 109.395 \text{mg/KOH/g} \end{aligned}$$