

The history of biodiesel biology essay

[Science](#), [Biology](#)



Introduction

Biodiesel, an alternative diesel fuel, is derived from renewable biological resources such as vegetable oils and animal fats. With the impending depletion of fossil fuel and limited oil reserves coupled with the high clamour by environmentalist for a clean and safe environment, biodiesel is increasingly becoming an important alternative fuel. It is biodegradable, non-toxic and has low emission profiles making it as such environmentally beneficial (Ayhan, 2009, Fangrui et al, 1998, Lene et al, 2008, Mata et al, 2010, Didem et al, 2011, Vivian et al, 2012). The research on biodiesel production has increased significantly in recent years owing to increasing energy demand. About hundred years ago, research had been conducted to derive alternate fuel using vegetable oils. However, the advent of cheap rapid evolvment of petroleum and crude oil fractions to serve as fuel hinders the research progression. With recent increment in crude oil prices, environmental concern and the ever increasing energy demand there has been a renewed focus on vegetable oils and animal fats to make biodiesel as an alternative fuel. With increasing air pollution challenges pose by continuous and increase use of fossil fuel, the use of biodiesel as an alternate fuel has a targeted potential of reducing the level of air pollutants and the level of probable carcinogens (Ayhan, 2009, Fangrui et al, 1998, Mark et al, 2003). With diesel consumption over the world at an approximate 934 million tonnes, the need for alternate fuel to tackle this demand became eminent. Given it renewable and potentially unlimited profile, biodiesel has recently been identified as the superlative alternative fuel and can be used in compression ignition engines with minor or no modification of engine

required. One major problem associated with the direct use biodiesel feedstock such as vegetable oils as fuels for diesel engines is the high-fuel viscosity of these oils in compression ignition engines. The introduction of biodiesel as an alternative to conventional fossil based diesel eases dependency on foreign energy supply from declining fossil fuel resources, aside that, the use of biodiesel in place of conventional fuels would slow the progression of global warming by reducing sulphur and carbon oxides and hydrocarbon emissions (Ghaly et al, 2010, Romano et al 2011). However, as a targeted fuel for future prospective, biodiesel will have to compete with petroleum diesel fuels economically. One proposed way of reducing biodiesel production costs is the use of less expensive feedstock such as inedible oils, animal fats, waste food oil and by-products of the refining vegetables oils. A crucial determinant in the supply of biodiesel on commercial level is the availability and sustainability of less expensive feedstock. Animal fats and inedible vegetable oils can serve as this alternative feedstock, with no competing food uses, this characteristics turn attention to beef tallow which is the feedstock employed in this research study (Johanes et al, 2007, Vivian et al, 2012).

1. 2 Aim and Objectives

The project is aim at producing biodiesel from beef tallow; a feedstock of high free fatty acid (FFA) via a two-step acid-base catalysed transesterification reaction process. This aim is targeted to be achieved through the realization of the following objectives

Characterisation of the animal tallow

Optimization of base catalysed transesterification by studying

the effect of temperature, catalyst concentration, mole ratio and time.

Characterization of the biodiesel product.

1. 3 Scope of Work

The scope of this work is limited to the production of biodiesel from beef tallow (after removal of impurities and rendering) via a two-step acid-base catalysed transesterification; first by acid-catalysed transesterification followed by base-catalysed transesterification.

1. 4 Justification of Work

One of the most significant demands in the world today is stable energy supply, and fossil fuels have mostly been employed to meet this demanding challenge. However, recent significant problems associated with fossil fuels such as short supply, drastic increase in price, non-renewability, pollution of the environment, and adverse effect on biological environment compels researcher to search for an alternative fuel, which promises a harmonious correlation with sustainable development, energy conservation, management efficiency, and environmental friendly. Hence, tallow has been proposed as a suitable feedstock for production of biodiesel as this alternate fuel.

Chapter two

Literature Review

2. 1 History of Biodiesel

In one sense, all fuel is biofuel; however, the term " biofuel" generally designate material that was recently living – to distinguish it from fossil fuel.

Biodiesel however refer to all biofuel produce by action of alcohols on

<https://assignbuster.com/the-history-of-biodiesel-biology-essay/>

triglycerides commonly tagged as transesterification process. In more general terms, biodiesel are domestic renewable fuel for diesel engines derived from natural oils like soybean oil that meets the set specifications. Petroleum and diesel come in the category of non-renewable fuel and will last for a finite period of time. Also, these non-renewable fuels emit pollutants in the form of oxides of nitrogen, sulphur, lead and carbon (Ayhan, 2009, Ghaly et al, 2010). The French government and Dr. Rudolph Diesel were first to carry out experiments on vegetable oil fuels, Dr. Rudolph, who had previously proposed the use of pure vegetable oils to power early diesel engines for agriculture in area where petroleum was not available at that time. At the World Fair in Paris in 1900, Rudolf Diesel won the Highest Prize for his diesel engine running on peanut oil – a biofuel, not biodiesel because it was not transesterified. Also, the first public demonstration of vegetable oil based diesel fuel was showcased at this Fair, leading to the French government commissioning of the Otto Company to build a diesel engine that would run on peanut oil. The interest of the French government was in the use of vegetable oils as a domestic fuel for their African colonies. Extensive work later carried out on vegetable oil fuels by Rudolph Diesel made him a leading proponent of such a concept, believing that farmers could benefit from providing their own fuel. However, it was not until almost a century before the reality of such an idea became a widespread. With the death Dr. Rudolph's in 1913 and followed closely by the boom of petroleum era and availability in a variety of forms, including the class of fuel we know today as diesel fuel, Dr Rudolph idea was somehow cast aside (Pacific oil, 2013, Ghaly et al, 2010, Mata et al, 2010). Modern

biodiesel fuel, derived by converting vegetable oils into compounds called fatty acid methyl esters, has its roots in research conducted in the 1930s in Belgium, but today's biodiesel industry was not established in Europe until the late 1980s. Despite of the widespread use of petro-diesel in the 1920s and 1930s, growing interest in several countries to use vegetable oils as fuels in engines was observed. Due to this widespread availability and low cost of petroleum diesel fuel, vegetable oil-based fuels gained little attention, except in times of high oil prices and shortages. The World War II coupled with the oil crises of the 1970s saw brief interest in using vegetable oils to fuel diesel engines. Unfortunately, the newer diesel engine designs could not run on traditional vegetable oils, due to the much higher viscosity of vegetable oil compared to petroleum diesel fuel. Hence, the challenge of lowering the viscosity of vegetable oils to a point where they could be burned properly in the diesel engine emanated. Varieties of methods such pyrolysis, blending with solvents, and even emulsifying the fuel with water or alcohols have been proposed to perform this task, none of which have provided a suitable solution. A Belgian inventor G. Chavanne in 1937 was the to first propose the use of transesterification in converting vegetable oils to fatty acid alkyl esters and use them as a diesel fuel replacement. This process of transesterification converts vegetable oil into three smaller molecules which are much less viscous and easy to burn in a diesel engine. The transesterification reaction hence became the basis for the production of modern biodiesel, which is the trade name for fatty acid methyl esters. By 1937, G. Chavanne of the University of Brussels " Procedure for the transformation of vegetable oils for their uses as fuels" was patented to him.

The patent describes the process of alcoholysis (also called transesterification) of vegetable oils using ethanol in order to separate the fatty acids from the glycerol by replacing the glycerol with short linear alcohols. In 1977, Expedito Parente, a Brazilian scientist produced biodiesel using transesterification with ethanol and filed a patent for the process. This process set the identity and quality of biodiesel as classified by international norms and standard (Energy revolution, 2012). Between 1979 and 1983, research into the use of transesterified sunflower oil and refining it to diesel fuel standards were conducted by South African Agricultural Engineers and by 1983, the process for producing fuel quality, engine-tested biodiesel was completed and published internationally. An Austrian company, Gaskoks, from 1987 and 1989 obtained the technology from the South African Agricultural Engineers and set up the first biodiesel pilot plant in November 1987 and in 1989 the first Industrial scale biodiesel plant with a production capacity of 30, 000 tons per year from rapeseed was opened (Energy revolution, 2012). Development of the biodiesel fuel industry in the early 1990s were advanced by work by pioneering researchers in Europe and South Africa such as Martin Mittelbach, and with the gradual growth of U. S. industry, due to lower prices for petroleum diesel. In 1996, Pacific Biodiesel became one of the first biodiesel plants in the United States, establishing a biodiesel production operation to recycle used cooking oil into biodiesel on the island Maui in Hawaii. The September 2011 attack in the U. S marked a historically high oil prices and an increased awareness on energy security and as a result the biodiesel industry became a household name. By 2005, worldwide biodiesel production had reached 1. 1 billion gallons, with most of

this fuel being produced in the European Union, although biodiesel projects worldwide have been on the rise due to rising crude oil prices and concerns over global warming (Pacific oil, 2013). Given its clean emissions profile, ease of use, and many other benefits, biodiesel is quickly becoming one of the fastest growing alternative fuels in the world, with a cost competition against petroleum diesel favoured by minimal subsidy on biodiesel, and millions of users have found and enjoyed the benefits of this fuel. The future of biodiesel lies in the world's ability to produce from renewable feedstocks such as vegetable oils and fats to keep the cost of biodiesel competitive with petroleum, without supplanting land necessary for food production, or destroying natural ecosystems in the process. Creating biodiesel in a sustainable manner will allow this clean, renewable, and cost effective fuel to help ease the world through increasing shortages of petroleum, while providing economic and environmental benefits well into the 21st century (Pacific biodiesel, 2013, Romano et al, 2011). Nigeria stands out as one of the leading countries in oil production but still faces challenges of energy crises like shortage of petroleum products and ever increasing price of product. These challenges coupled with the predicted shortage of fossil fuel, hence made it essential to search for alternative source of energy for Nigeria as a country. Until recently, research effort in Nigeria in this regard has been limited. However, Investigated reports such as that by Alamu et al on biodiesel production from Nigerian palm kernel oil, and the comparison of physico-chemical property of biodiesel by Belewu et al from Nigerian and Indian *Jatropha curcas* oil and recent study by Aransiola et al on the production of biodiesel from soybean oil are available in open literature and

predict positive prospect for the Nigeria in these regard. With Nigeria yearly biodiesel production placed at zero between the year 2005 and 2009 when compared with production from other countries. In view of the aforementioned statement, it is therefore become imperative to begin research on production of biodiesel in Nigeria from available and economically feasible feedstock. A good example of such is oil from *Jatropha curcas* and most recent study by Arinsiola et al focuses on the production of biodiesel from Nigerian *Jatropha curcas* oil (Aransiola et al, 2012).

Biodiesel Feedstock

Biodiesel production process involves mainly the combination of the following feedstocks; Vegetable oils or fats Alcohol Catalyst (Ayhan, 2009, Dominik et al, 2008, Romano et al, 2011)

2. 2. 1 Vegetable oils and Fats

This is the primary feedstock for biodiesel production and is usually from renewable resources that can either be in a solid state (fats) or a liquid state (oils). This feedstock could be crude, refined or waste such as frying oils/fats and are basically classified into; Plant derived oil, Animal derived oil, Microbial oil or Waste oil (Ayhan, 2009, Dominik et al, 2008, Romano et al, 2011). Research publications by Subramanian et al in 2005 identified more than 300 oil-bearing plants that can be utilized for biodiesel production. These plants derived oil are further classed into edible and non-edible oil. Most popular non-edible oil feedstock includes; *Jatropha*: *Jajoba* *Tung* *Castor* *Seed* Included in the edible oil categories are: *avocado* *canola*, *coconut*, *cottonseed*, *groundnut*, *karanj*, *olive*, *oil palm*, *peanut*, *rapeseed*, *safflower*,

soybean and sunflower oils (Ayhan, 2009, Dominik et al, 2008, Romano et al, 2011). There is however concern over the use of plant derived oils (especially, edible oil), since the crops used for biodiesel production are also needed for food, feed and oleo-chemical industries. As such biodiesel factories must compete with food, cosmetic, chemical and livestock factories for feed demand. The environmental impact posed by an increased demand for plant derived oils with regard to increase in fertilizers usage is a major concern as it contribute to greenhouse gas emissions. As a statement of fact, biodiesel production from heavy fertilized crops could result in a 70% increase (from current value) in greenhouse gas emission (Dominik et al, 2008, Ghaly et al, 2010). Animal derived oil is feedstock obtained mainly from animal tissue. Tallow, lard and chicken fats are the major feedstocks derived from animal that serves as primary feedstock in biodiesel production. Tallow is obtained by a process of known as rendering; which is converting animal tissue containing fat to oil whereas lard refer to fat rendered from fresh, clean, sound tissues of pigs in good health at the time of slaughter and chicken fat extracted from broiler slaughter residues (Dominik et al, 2008, Feddern et al, 2012, Ghazazi et al, 2012, Mata et al, 2010). Microbial oil derived from microalgae is another feedstock which has a great potential for biodiesel production, the oil yield from microalgae (usually in litres per hectare) could be one to two orders of magnitude higher than that of other raw materials. The oil content is usually from 20 to 50%, though, some species can have higher than 70% oil content. It is however, important to note that not all microalgae derived oil is adequate for biodiesel production. High levels of CO₂, water, light, nutrients and mineral salts are

necessary for the growth of microalgae. Production processes take place in raceway ponds and photo biological reactors (Dominik et al, 2008, Ghaly et al, 2010, Romano et al, 2011). Waste oils and fats such as waste cooking oil, the greasy by-product from omega-3 fatty acids production from fish are also alternative feedstocks for biodiesel production. Usually, for oil derived from waste, a pre-treatment is required as purification stage before feedstock is applied for biodiesel production (Dominik et al, 2008, Fjerbaek et al, 2008, Ghaly et al, 2010). The saturation level of the oil or fat is another important factor in biodiesel feedstock selection. Oils with higher levels of saturated fatty acids than unsaturated fatty acids (have one or more double bonds) may solidify and clog the fuel lines during the winter condition. Biodiesel derived from feedstock with high levels of unsaturated fatty acids are less viscous and show higher pour and cloud points properties which make the biodiesel suitable for warm and cold weather conditions. However, the use of these oils lower the cetane index and combustion temperature which reduce the quality of biodiesel. Biodiesel produced from Oils with large chain fatty acids (greater than 18 carbons) have a high cetane index and combustion temperature but have low cloud and pour points and greater viscosity. The choice of feedstock for optimum biodiesel production is a balance between the unsaturation and the length of fatty acid chains. It was reported that feedstocks with a high level of oleic acid (an unsaturated fatty acid that is 18 carbons long with a single double bond) are the best suited for biodiesel production. Biodiesel produced from feed stocks containing oleic acid has characteristics that are the most similar to conventional biodiesel (Ghaly et al, 2010, Romano et al, 2011). The choice of the primary feedstock in

biodiesel production also would depend on where the biodiesel is being produced and used as to meet norms of internationally accepted (ASTM) standards. Parameters such as saponification number, iodine value and cetane number of the oil, play an important role in selection of feedstock for biodiesel production. For instance, the United States largely uses soybean oil, Europe uses rapeseed and sunflower oils, southeast Asia uses palm oil and the Philippines uses coconut oil. Animal derived oil, microalgae oil and waste oil have been reportedly used across the world as biodiesel primary feedstock (Ghaly et al, 2010, Mata et al, 2010, Fjerbaek et al, 2008, Romano et al, 2011, Vivian et al, 2012). Table 2. 1 shows the fatty acid composition of vegetable oil and table 2. 2 shows oil composition of some biodiesel feedstock.

2. 2. 2Alcohol

Another important feedstock in the biodiesel production process is alcohol. Usually, Primary, secondary, straight chained and branched alcohols can all be employed in biodiesel production. Longer chain alcohols have also shown their effectiveness though lower yields of products were observed. In general, alcohols with short chains have been discovered to be the most effective in biodiesel production with regard to yield of product. Those with short chains usually employed include, methanol, ethanol, butanol, and amylic alcohol. Most widely used alcohols are methanol (CH₃OH) and ethanol (C₂H₅OH) owing to their low cost and properties. Methanol is often preferred to ethanol in spite of its high toxicity because its use in biodiesel production requires simpler technology; excess alcohol may be recovered at a low cost and higher reaction speeds are reached. The need for biodiesel as complete

renewable fuel would require a renewable primary feedstock obtained from plant or animal, together with an alcohol that is produced from biomass, such as bioethanol, instead of being a petrochemical product (Fjerbaek et al, 2008, Ghaly et al, 2010, Özçimen et al, 2011, Romano et al, 2011).

2. 2. 2. 1 Selection of Alcohol

There are ranges of compounds that have been deemed acceptable acyl acceptors for transesterification reaction. Methyl acetate and ethyl acetate have both been seen as appropriate acyl acceptors but are much more expensive than the more commonly used alcohols. The use of these two acyl acceptors however resulted in the production of a by-product other than glycerol. Primary, secondary, straight and branched chained alcohols can all be employed in the transesterification reaction. Longer chain alcohols have also shown their effectiveness; however they give lower yields than methanol. Commonly used alcohols are; methanol, ethanol, propanol, iso-propanol, 2-propanol, n-butanol and isobutanol. Owing to their low cost and desirable properties methanol (CH₃OH) and ethanol (C₂H₅OH) are the most widely used alcohol for transesterification reaction. Methanol is however often preferred to ethanol in spite of its high toxicity because its use in biodiesel production requires a much simpler technology; excess alcohol may be recovered at a low cost and higher reaction speeds are reached. For a completely renewable fuel would require the use alcohol derived from renewable feedstock. Ethanol (C₂H₅OH) can be used in place of methanol as the alcohol feedstock but its expensive nature limits its use commercially. However, Ethyl esters rather than methyl esters will be produced using ethanol and both will have somewhat different physical properties as the

molecular weights are about 5% higher, for example viscosities are about 7% higher than their methyl analogues. Generally, the differences between processing with methanol and ethanol are relatively minor, the major difference being in the alcohol recovery step where ethanol will form an azeotrope with free water. Overall the quality of ethyl esters will be lower than methyl esters as the reaction rate is slower with ethanol resulting in a somewhat lower level of conversion and higher levels of by-products; mono and di-glycerides and also glycerol in the final product (Dominik et al, 2008, Fjerbaek et al, 2008, Fangrui et al, 2008, Ghaly, 2010, Özçimen et al, 2011, Romano et al, 2011).

2. 2. 3Catalyst

The catalytic transesterification method of biodiesel production requires the use of catalyst, the catalysts used could be basic, acidic or enzymatic. Most of these catalysts are homogenous in nature. Potassium hydroxide (KOH), sodium hydroxide (NaOH), carbonates and their corresponding alkoxide (for instance, sodium methoxide or ethoxide) are common basic catalyst used. Acid catalysts commonly used include sulphuric acid, sulfonic acids and hydrochloric acid; though their uses have been less studied. Heterogeneous catalysts have however been considered in biodiesel production and included in these categories of catalyst are enzymes, titanium silicates, and compounds from alkaline earth metals, anion exchange resins and guanidine in organic polymers. The most frequently used enzymatic catalysts for biodiesel production are Lipases (Fangrui et al, 1998, Ghaly et al, 2010, Özçimen et al, 2011, Romano et al, 2011, Vivian et al, 2012,).

2. 2. 3. 1Catalyst Selection

A major criterion to consider in catalyst selection is the quality of raw material, the alcohol type, catalysts cost and technological route to be employed in production process are other important factors to consider when choosing a catalyst (Roseli et al, 2011). The acid catalysts are often employed in transesterification process, the most commonly used are; H_2SO_3 , HCl and H_2PO_3 . Despite the high yield and absence of soap formations, the corrosive nature of acid catalyst, very slow reaction rate and higher temperature conditions are the factors limiting the use of the process for transesterification reactions (Ghaly et al, 2010). The commonly used industrially are the base (alkaline) catalyst. The most used in these categories are sodium hydroxide (NaOH) and potassium hydroxide (KOH). Other alkaline catalysts include carbonates, methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Owing to the obtainable higher conversion rate of esters using alkaline catalyst under a low temperature and pressure environment with a short reaction time, the alkaline catalyst has proved to be the most economical. However, the catalyst sensitivity to feedstock purity is a drawback of the technology and presence of free fatty acids as well water in the feedstock has a significant impact on the transesterification reaction involving basic catalyst owing to catalyst consumption during soap formation (Ghaly et al, 2010). The acid and base catalysed transesterification reaction processes are energy demanding and usually require extensive downstream processing. A post treatments step normally accompany the transesterification reaction as the end products are a mixture of esters, catalyst, glycerol, mono-and diacylglycerols, pigments,

unreacted alcohol, and tri, di and mono-glycerides. The post treatment step is mostly a multi-step purification of end products which include: separation of glycerol by gravitational settling or centrifugation, neutralization of the catalyst, deodorization and removal of pigments (Ghaly et al, 2010). With varieties of feedstock application, downstream processing and low environmental impact, enzymatic transesterification stands out as an attractive method for biodiesel production over the acid and base transesterification process. The use of enzymatic catalysts eliminates problems associated with acid and alkali catalysts as well as presents other production benefits. Unlike the chemical catalyst, enzymes are non-corrosive, no soap formation and as such so no restriction on free fatty acid content feedstock as well absence of concerns with regards water formation during reaction. Immobilized enzymes are most often used, this make for simple separation of products, producing a high quality glycerol and reuse of the catalyst. Longer reaction time and higher catalyst concentration requirement for complete reaction coupled with high cost of producing enzymes and reduction in enzymes activity with time are drawbacks in enzymatic transesterification (Ghaly et al, 2010).

2. 3 Characteristics of Biodiesel Feedstock

2. 3. 1 Viscosity

The atomisation of the oil being injected into the combustion chamber of engine is affected by viscosity. A small oil drop is desired for complete combustion of oil, and as such, high viscosity oil like raw vegetable oil, will produce a larger drop of fuel in the combustion chamber of engines that may not burn as clean as a fuel that produces a smaller drop. This incomplete

combustion leads to unburned oxidised fuel build up around engine valves, injector tips and on piston sidewalls and rings. Biodiesel produce from various derived oil has a viscosity much closer to diesel fuel than the oil itself and as such producing a much smaller drop, which burns cleaner (Ayhan, 2009, Roseli et al, 2011).

2. 3. 2Cloud point

The cloud point of oils is the temperature at which the clear fatty acid becomes hazy (or cloudy), due to the crystallisation of higher melting components, when the oil is cooled under specified conditions. The cloud point is a critical factor in analysis of oil performance in cold weather. Some biodiesel feedstocks gives cloud point far above the desired cloud point owing to varying chemical composition. The cloud point is another oil parameter that can be correctly predicted with knowledge of the esters composition; however it is advisable to perform this test (Ayhan, 2009, Gerpen et al, 2004).

2. 3. 3Pour Point

Most oil of animal or plant origin at certain temperature (usually low temperature) form wax and ceases to flow. The pour point described the lowest temperature at oils can be handled without excessive wax crystals formation and cease of flow. A low pour point oil forms wax easily at low temperature and separate out in engine blocking the filters as well as building up on tank bottoms and on heating coils (Ayhan, 2009, Gerpen et al, 2004).

2. 3. 4Cetane Number

With regard to the primary feedstock employed in biodiesel production, cetane number rates the ignition properties of oil derived from this feedstock. A measure of the ignition performance of the biodiesel feedstock is obtained by comparing it to reference fuels in a standardized engine test. This is analogous to the octane rating in a spark ignition engine. The higher the cetane number of the oils or fat, the more efficient the biodiesel derived from it. This ignition quality affects engine performance, engine combustion, cold starting and warm up. A high cetane number could also in incomplete combustion and emission of smoke if ignition occurs too soon by not allowing enough mixing time with air for complete combustion (Ayhan, 2009, Gerpen et al, 2004, Roseli et al, 2011).

2. 3. 5Iodine Value

Is a measure of the unsaturation level of fats and oils and is expressed in terms of the number of centigrams (cg) of iodine absorbed per gram of sample (% iodine absorbed). Oils or fats having a low iodine value could be suitable for direct use as fuel without any further processing other than extraction and filtering, but vast majority of vegetable and animal oils have an iodine value that poses problems if directly used as fuel. Generally, an iodine value less than 25 is required for direct use of oil as fuel for long term applications in unmodified diesel engines. With iodine values between 25-50, engine life would be generally unaffected by this effect if a slightly more active maintenance schedule is maintained such as more frequent change of lubricating oil and decoking of exhaust system (Ayhan, 2009, Gerpen et al, 2004, Roseli et al, 2011).

2. 3. 6 Acid Number

Most oils or fat employ in biodiesel production contain fatty acids of various proportion. A measure of this acid content usually termed acid value and defined with reference to the number of milligrams of alkali (usually potassium hydroxide) required to neutralize the fatty acids present in one gram of oils or fat. Generally, it is a measure of the free fatty acid groups present in the primary feedstock. A simple titration of feedstock with alkali to a phenolphthalein end point is used for most fatty or rosin acid contained feed. And, as defined in the American Oil Chemists' Society standards the neutral equivalent of the acid may be determined simply by a different type of calculation from titre result. The neutral equivalent is described as the molecular weight of the acid if it is free from non-acid impurities (Gerpen et al, 2004, Roseli et al, 2011).

2. 3. 7 Saponification Value (SV)

The saponification value is an estimate of the mean molecular weight of the constituent fatty acids in oil or fat sample and is defined as the number of milligrams of potassium hydroxide required to saponify one gram of the oil or fat. It is a measure of the free fatty acid plus any material which will be saponified or form soap under the conditions of the analysis. A higher saponification value indicates a lower mean chain length of the triglycerides. For feedstocks containing fatty acid free of esters, the acid number and the saponification number will be the same. However, presence of esters indicate a higher saponification number than the acid number. In feedstock containing glyceride, the difference between acid number and saponification number gives rough estimates of the glycerol present (Gerpen et al, 2004).

2. 3. 8Unsaponifiable Content

Unsaponifiables or unsaps, refers to any material in the oils or fat that will not saponify (convert into soap) when mixed with an alkali. This basically covers all components in the feedstock that are not triglycerides. The determination of unsaponifiable content is based upon saponification (saponification value) followed by extraction with solvents and washing. A large saponification value indicates low unsaponifiable content (Gerpen et al, 2004).

2. 3. 9Specific Gravity

The specific gravity is a measure of the relative density of a substance. It is defined as the ratio of the density of the substance, ρ , to a reference density, ρ_{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 1kg/m³. In place of density, the weight of the substances could be used (Gerpen et al, 2004). Table 2. 3 shows the fatty acid profile of beef tallow feedstock, table 2. 4 shows the fuel-related properties and Iodine values of various feedstocks and table 2. 5 displays the biodiesel quality versus feedstock properties. Table 2. 3: Fatty acid profile of beef tallow (Miller kien) C14 2-6% C16 24-37% C16: 1 2-4% C18 14-29% C18: 1 26-50% C18: 2 1-5% C18: 3 0-2% C20 C20: 1 C22 C22: 1 Table 2. 4: Fuel-related properties and Iodine values of various feedstocks (Journey to Forever Organisation) Fuel specific properties Canola Tallow Palm Cotton seed Viscosity mm²/s at 40 °C 37. 60 51. 15 32. 4 33. 50 Cloud point °C -3. 9 - 28 1. 7 Pour point °C 31. 7 - 22 15. 0 Cetane number 37. 6 - 42 41. 8 Iodine number (cg/g) 94-120 35-48 35-61 90-110 Heating value (MJ/kg) 39. 70 40.

00 39. 46 Table 2. 5: Biodiesel (Methyl ester) Quality versus Feedstock (mg engineering Lurgi Life Science and Murdoch University). Fuel specific properties Canola Tallow Palm Viscosity mm²/s @ 40 °C 5. 6 4. 8 5. 7 Cloud point °C 0 16 13 Pour point °C -15 16 8 Cetane number 62 73 62 Iodine number 110 50 37 Heating value MJ/kg 40. 5 39. 9 37. 8

2. 4 Biodiesel Production Process

Biodiesel is an alternative fuel for diesel engines that can be made from straight vegetable oil, animal fat such as tallow (a by-product of the meat processing industry) and waste oils. The basic routes to biodiesel production from oils and fats are: Transesterification: which is further classed into; Base catalysed transesterification of the oil. Direct acid catalysed transesterification of the oil. Enzymatic transesterification. Ultrasound assisted process Microwave assisted process and Non- catalytic transesterification: which is also divided into; Co-solvent method Supercritical method. Owing to the high viscosity and low volatility of most primary feedstock, the direct use of this feedstock in diesel engines can cause problems including: high carbon deposits, scuffing of engine liner, injection nozzle failure, gum formation, lubricating oil thickening and high cloud and pour points. In order to avoid these problems, the feedstocks need to be chemically modified to its derivatives which have properties more similar to conventional diesel (Ayhan, 2009, Fangrui et al, 1998, Özçimen et al, 2011, Kok et al, 2008).

2. 4. 1 Transesterification process

The use of transesterification process dated back to as early as 1846 when Rochieder described glycerol preparation from castor oil through ethanolysis. Ever since then, alcoholysis has been studied in many parts of the world. Work by other researchers have also included investigation of the important reaction conditions and parameters in the alcoholysis of triglycerides such as safflower, peanut, fish oils, tallow, cottonseed, sunflower, soybean, rapeseed, and linseed oils. Transesterification is a process which reduces free fatty acids and triglycerides contained in the oil to Fatty Acid Alkyl Esters (FAAEs) is employed for this modification. This chemical reaction converts an ester (vegetable oil or animal fat) into a mixture of esters of the fatty acids that makes up the oil (or fat) by reaction of the oil or fat with an alcohol in presence of a catalyst. Biodiesel is obtained from the purification of the mixture of fatty acid methyl esters (FAME) (Dinesh et al, 2013, Dominik et al, 2008, Fangrui et al, 1998, Özçimen et al, 2011). The transesterification catalyst is used to ease the reaction rate and yield of product, according to the catalyst used, transesterification can be termed base catalysed, acid catalysed or enzymatic transesterification. The base catalysed transesterification most frequently used and catalyst commonly employed include NaOH, KOH, and NaMeO. For the acid transesterification process, H₂SO₄, H₃PO₄, and CaCO₃ are mostly used why lipase enzymes are used for the enzymatic transesterification process (Gerpen et al, 2004,).

2. 4. 1. 1 Factors affecting the transesterification process

The most important variables that influence the transesterification reaction and conversion efficiency are; temperature, catalyst type and its concentration, alcohol to oil ratio, reaction time and stirring rate.

2. 4. 1. 1. 1 Effect of temperature

Transesterification reaction can occur at varying temperatures, depending on the feedstock (oil) employed; however care should be taken as not to exceed the boiling temperature of the alcohol employed. Smith in 1949 reported that the methanolysis reaction of castor oil to methyl ricinoleate preceded most satisfactorily at $20 \pm 35^\circ\text{C}$ with a molar ratio of 6: 1 \pm 12: 1 and NaOH catalyst weight per cent by oil of $0.005 \pm 0.35\%$. In 1984, Freedman et al also reported the transesterification reaction of soybean oil with methanol with a molar ratio of 6: 1 using 1% NaOH catalyst at three different temperatures. As reported, after 0.1 hour, ester yields of 94, 87 and 64% were obtained for a temperature of 60, 45 and 32°C respectively. After 1 hour, ester formation was identical for the 60 and 45°C runs and only slightly lower for the 32°C run. From the above reports, temperature clearly influenced the reaction rate and yield of esters, at start of reaction a higher temperature signifies a higher yield but as time increases the reaction yield is slightly or not affected by temperature (Ayhan, 2009, Fangrui et al, 1998, Roseli et al, 2011, Kok et al, 2008).

2. 4. 1. 1. 2 Effect of Catalyst

The catalysts for biodiesel production are classed as homogeneous or heterogeneous. The homogeneous catalysts form a single phase mixture

when added to alcohol and oil and are divided into acid and base catalyst while the heterogeneous catalysts do not mix in the reaction medium and are divided into metal oxides, metal complexes, zeolite, resins, membranes, and lipases. However, the acidic, basic and enzymatic catalysts are the most employed catalyst categories (Ayhan, 2009, Roseli et al, 2011). The base-catalysed transesterification is much faster than acid-catalysed. However for feedstock of higher free fatty acid and water content acid-catalysed transesterification is suitable. The acid catalysts include H_2SO_4 , H_2PO_3 , HCl or organic sulfonic acid. Base catalyst includes $NaOH$, $NaOCH_3$, KOH , $KOCH_3$, $NaNH_2$ and so on. Sodium methoxide was thought to be more effective than sodium hydroxide owing to the assumption of small water formation upon mixing $NaOH$ and $MeOH$, However, results observed by Ma et al in 1998 show otherwise. $NaOH$ and $NaOCH_3$ reached their maximum activities at 0.3 and 0.5% w/w of beef tallow, respectively. Freedman et al also reported that conversions at the 6:1 ratio for 1% $NaOH$ and 0.5% $NaOCH_3$ were almost the same after 1 hour. Report by Freedman et al on the transesterification of soybean oil with methanol, ethanol and butanol, using 1% concentrated sulphuric acid, shows its yield was unsatisfactory when the molar ratios were 6:1 and 20:1. However a 30:1 ratio resulted in a high conversion to methyl ester. More recently, an immobilized lipase was employed in the catalytic methanolysis of corn oil in flowing supercritical carbon dioxide with an ester conversion of greater than 98% (Fangru et al, 1998, Roseli et al, 2011).

2.4.1.1.3 Effect of mole ratio

Molar ratio of alcohol to triglyceride is one of the most important variables affecting the yield of ester. From stoichiometry, three moles of alcohol

requires one mole of glyceride to yield three moles of fatty acid ester and one mole of glycerol. The molar ratio is depends on catalyst type. Freedman et al reported that acid catalysed transesterification reaction of butanol and soybean oil required am mole ratio of 30: 1 while the base-catalysed reaction required only a 6: 1 ratio for same ester yield at given reaction time. In 1944, Bradshaw and Meuly stated that the practical range of molar ratio for transesterification of vegetable oil was from 3. 3 to 5. 25: 1 methanol to vegetable oil. However, a ratio of 4. 8: 1 has been used in some instances, with a yield of $97\pm 98\%$, depending upon the quality of the oils. Higher molar ratios resulted in greater yield of ester with in a shorter time. In the ethanolsis of peanut oil as reported by Feuge and Grose, a 6: 1 molar ratio liberate significantly large amount of glycerine than did a 3: 1 molar ratio. Investigation on the methanolysis of rapeseed oil by Nye and Southwell in 1983 using 1% NaOH shows that the molar ratio of 6: 1 of methanol to oil gave the best conversion. However, for oil with high free fatty acids, a molar ratio as high as 15: 1 was required under acid catalysed transesterification. Freedman et al studied the effect of molar ratio from 1: 1 to 6: 1 on ester conversion with vegetable oils. At a molar ratio of 6: 1, soybean, sunflower, peanut and cotton seed oils behaved similarly and achieved highest conversion range between 93 ± 98 per cent. In 1981, Tanaka et al using novel's method two-step transesterification of oils and fats such as tallow, coconut oil and palm oil, using molar ratios of 6: 1±30: 1 with base catalyst achieved a 99. 5 % conversion. Zhang in 1994 reported 80 % conversion of esters in the laboratory using a molar ratio of 6: 1 for beef tallow transesterification with methanol (Fangrui et al, 1998, Roseli et al, 2011).

2. 4. 1. 1. 4 Effect of time

The conversion rate increases with reaction time, freedman et al in 1984 reported a yield of 80% after 1 minute for transesterification of cottonseed, soybean oils, peanut and sunflower at 60 oC, with 0. 5% sodium methoxide catalyst and methanol to oil ratio of 6: 1. After 60 minutes he reported an almost equal conversion for all four oil. The reaction rate was very slow during the first minute for the transesterification of beef tallow feedstock as reported by Ma et al in 1998 due to the mixing and dispersion of methanol into beef tallow. However, the reaction was reported to have proceeded very fast from one to five minutes with apparent yield of beef tallow methyl esters surging from 1 to 38 per cent. The reaction was reported to then slow down and reached the maximum value at about 15 minutes (Ayhan, 2009, Fangrui et al, 1998, Roseli et al, 2011).

2. 4. 1. 1. 5 Effect of Stirring rate

The stirring rates also affect the transesterification process, higher stirring rates would signify a higher a shorter time and improved yield of esters. Purity of reactants, for example, presence of water, free fatty acids, and other contaminants found in unrefined oils (or other feedstocks) is also very important factor affecting the transesterification process (Fangrui et al, 1998, Roseli et al, 2011).

2. 4. 2Ultrasound assisted process

The ultrasound assisted process involves the use of ultrasonic waves to enhance the transesterification reaction as against normal conventional method employed. Ultrasonic waves are energy application of sound waves

which is vibrated more than 20, 000 per second. In another words, it can be defined as the sound waves beyond human hearing limit, its application was first into medical research and detectors in the 1930s and 1940s. Industrially since the 1980s, idea on the use of ultrasound began to develop rapidly, and today a wide range of applications using ultrasonic waves are well noted.

The investigated effect of ultrasonic irradiation such as the rapid movement of fluids caused by a variation of sonic pressure causes solvent compression and rarefaction cycles, also effect like cavitation which is the most important is observed. When a large negative pressure gradient is applied to the liquid, the liquid will break down and cavities (cavitation bubbles) will be created.

Small cavity may grow rapidly through inertial effects at high ultrasonic intensities. So, bubbles grow and collapse violently, this formation and collapse of micro bubbles are responsible for most of the significant chemical effects. A major factor which influences on reaction speed is cavitation. By disrupting the interfacial boundary layers known as the liquid jet effect, cavity collapse increases mass transfer. Another effect of ultrasound is acoustic stream mixing. This effect has been used to accelerate the rates of numerous chemical reactions, as well as increased catalytic surface areas and improve mass transfer. Low frequency ultrasonic irradiation has been widely used for biodiesel production in recent years. Mixing is important factor for increasing biodiesel yield in transesterification reaction. Oil and methanol are not completely miscible in biodiesel processing; hence, ultrasonic mixing is an effective mixing method to achieve a better mixing and enhancing liquid-liquid mass transfer. Vigorous mixing increases the contact area between oil and alcohol phases while producing smaller

droplets than conventional stirring. Ultrasonic cavitation also provides the necessary activation energy for initiating transesterification reaction. Chemical reactions and processes that employ the use of ultrasound waves are referred to as sonochemistry. Industrial sonochemical reactors were designed more than 40 years ago by Sarocco and Arzono and they show effect of reactor geometry on reaction kinetics. Reactors were later developed by researchers for different chemical reactions. For conventional biodiesel production, batch and continuous reactors have been developed in industry. Catalyst type, alcohol type, ultrasonic power and frequency are factors that affect the ultrasonic assisted biodiesel production process (Özçimen et al, 2011).

4. 4. 3 Microwave assisted process

In biodiesel production process, heating coils are employed to heat the raw material. Using microwave assisted method, this treatment can be carried out. The " microwave irradiation" has been used in transesterification reactions as an alternative heating system in recent years. Microwaves are electromagnetic radiations which represent a nonionizing radiation that influences molecular motions such as ion migration or dipole rotations, but not altering the molecular structure. The microwave irradiation activates the smallest degree of variance of polar molecules and ions with the continuously changing magnetic field. The changing electrical field, which interacts with the molecular dipoles and charged ion, causes these molecules or ions to have a rapid rotation and heat, is generated due to molecular friction. The absorption of microwaves causes a very rapid increase of the temperature of reagents, solvents and products. The

microwave assisted process is employed in the transesterification reaction for biodiesel production. The oil, methanol, and base catalyst contain both polar and ionic components. These polar molecules and ions are activated by microwaves, leading to molecular friction, and hence the initiation of chemical reactions. Owing to the energy interaction between the samples on a molecular level, very efficient and rapid heating is obtained by microwave heating. This energy interacts with the molecules at a very fast rate, the molecules do not have time to relax and the heat generated can be for short times and much greater than the overall recorded temperature of the bulk reaction mixture. Under the assisted microwaves process, transesterification is efficiently accelerated in a short reaction time, yielding a drastic reduction in the quantity of by-products and a short separation time with high yield of pure products within such a short time. This production process is cost effective and minimal by-products are produced. In comparison to conventional methods of biodiesel production, where heating is relatively slow and inefficient owing to dependence of energy transfer into a sample on convection currents and the thermal conductivity of the reaction mixture, the microwave heating is favourable (Özçimen et al, 2011).

2. 4. 4 Non-catalytic transesterification

Another method of biodiesel production is the non-catalytic transesterification. The non-catalytic options have the advantages of overcoming the reaction initiation lag time caused by the extremely low solubility of the alcohol in the triglycerides phase. One method that is nearing commercialization is the use of a co-solvent; the supercritical

method is another non-catalytic transesterification method that has been widely employed in biodiesel production (Ayhan, 2009, Gerpen et al, 2004).

2. 4. 4. 1Co-solvent method

The co-solvent process (also known as BIOX) was originally developed by a Canadian Professor David Boocock of the University of Toronto and since then has attracted considerable attention. Through the selection of inert co-solvents that generate an oil-rich one-phase system, Professor Boocock has been able to transform this production process. With reaction going into 99% completion in matter of seconds at ambient temperatures, compared to previous processes that required several hours. BIOX is a technology development company that is a joint venture of the University of Toronto Innovations Foundation and Madison Ventures Ltd. The co-solvent production process first converts the free fatty acids (by way of acid esterification) and then the triglycerides (by way of transesterification), by the addition of a co-solvent, through a two-step, single phase continuous process at atmospheric pressures and near-ambient temperatures. The co-solvent is then recycled and reused continuously in the process. The co-solvent process is applicable to wide range of feedstocks including waste cooking greases and animal fats. Tetrahydrofuran and heptane are common co-solvent use to solubilize the alcohol in the co-solvent method (Ayhan, 2009, Kok et al, 2008).

2. 4. 4. 2Supercritical method

The presence of free fatty acids and water in biodiesel feedstock (animal fats and vegetable oils) employed in the conventional transesterification method produce negative effects. The free fatty acids and water present causes soap

formation, consuming the catalyst, and reducing the catalyst efficiency, all of which led to low conversion. The conventional transesterification method using either base or acid catalysts is time-consuming and poses difficulty in separation of the catalyst from product couple with the energy consumption demand and high production cost are some of the drawbacks of this process. To overcome these drawbacks, the supercritical non-catalytic transesterification method has proposed and demonstrated in Japan for biodiesel production. By supercritical, it means any substance at a temperature and pressure above its critical point. At this condition, there are a number of unusual properties exhibited by the substance and there no longer exist a distinct liquid and vapour phase, but only a single fluid phase is present. As a result, solvents containing hydroxyl (OH) group, such as water or primary alcohols, take on the properties of super acids which resulted in a very high reaction completed within a very short time. In addition, the supercritical method requires a much simpler purification of products and is more environmentally friendly requiring a lower energy usage. However, the reaction must be quenched very rapidly as to avoid the decomposition of the products (Ayhan, 2009, Gerpen et al, 2004).

Biodiesel Production From Tallow

All described production methodology for biodiesel production process can be applied with tallow feedstock. However, within the scope of this research only the transesterification method has being considered.

2. 5. 1 Tallow Feedstock

Like most common feedstock derived from plant or animal origin, tallow consist of esters of saturated and unsaturated monocarboxylic acids with the tri-hydric alcohol glyceride. Such esters are termed triglycerides and have the following general chemical formula: Triglyceride Fatty (Monocarboxylic) Acids $\text{CH}_2\text{-O-CO-R H-O-CO-RCH- O-CO-R' H-O-CO-R'CH}_2\text{-O-CO-R'' H-O-CO-R''}$ The hydrocarbon groups from the monocarboxylic acids (commonly referred to as long chain fatty acids) are represented by R, R' and R'' and are of the form $\text{CH}_3\text{-(CH}_2\text{)}_n$ for the saturated groups (those without double bonds). Majority of the fatty acids in the glycerides consist of unbranched chain and with even number of carbon atoms though small amount of branched chain acids are present. Fats and oils have been found to contain saturated acids with 4 to 26 carbon atoms but those occurring in greatest quantity are lauric acid (12 carbon atoms), myristic acid (14 carbon atoms), palmitic (16 carbon atoms) and stearic acid (18 carbon atoms). The unsaturated acids range from 10 to 24 carbon atoms with the most important being oleic acid with one double bond, linoleic acid with two double bond and linolenic acid with three double bond, all with 18 carbon atoms in the hydrocarbon chains (Duncan, 2005). The main constituent of tallow are triglycerides containing fatty acids with 16 or 18 carbon atoms, and dominant components being approximately: oleic (40%), stearic (26%), palmitic (22 %), myristic (3%), linoleic (1%) and linolenic (1%) acids, with the remainder being made up of a complex range of isomers (Duncan, 2005). As a statement of fact, triglycerides with more saturated acid components have a higher melting point than those of similar chain lengths and more

unsaturated components. Thus, tallow has higher melting point (45 to 55°C) is than most plant derived (seed) oils. The viscosity and melting point of tallow is also much higher than diesel fuel (with cloud point below 0°C) and with a molecular weight about 890 much greater than that of diesel (about 270) (Duncan, 2005). With triglycerides making up 95 % of raw tallow and the remainder predominantly made up of free fatty acids, lesser amounts of water, unsaponifiable and insoluble components. However, most of the free fatty acids are removed prior to the processing of tallow to biodiesel (Duncan, 2005).

2. 5. 2 Rendering of tallow

To convert animal tissue containing fat to tallow a process known as rendering is employed. The rendering process basically is the separation of lipid material from meat tissue and water using heat and pressure. Thus so far, two principal rendering methods are most common: wet rendering and dry rendering (NRA, 2008).

2. 5. 2. 1 Wet Rendering Process

The wet rendering process is the oldest rendering method and is fast becoming less common, it involves superheating of the animal tissue with steam in an enclosed pressure vessel (cooker). The superheated steam injected provides both heat and agitation. At the end of the cooking period, the mixture having being cooked at 110-120°C for three to six hour settles into three phases: a top fat layer which is drawn off; with an intermediate water layer and a bottom layer primarily made up of proteinaceous material.

Protein and fat quality are more easily affected during prolonged cooking time and high temperature (NRA, 2008).

2. 5. 2. 2 Dry Rendering Process

In the dry rendering process, the fat tissue is heated in a jacketed container, mechanical agitation is provided, and the water is evaporated either at atmospheric or at increased pressure. This is a modern rendering process, continuous rendering process with automated operation are used in most modern rendering plants having highly sophisticated air and water pollution prevention equipment (NRA, 2008).

2. 5. 3Pre-treatment of tallow

The amount of free fatty acids, water and non-saponifiable material presence in the feedstock (animal or plant derived oil) are important parameters that affect the conversion efficiency in the transesterification reaction for biodiesel production. Aside low humidity and acid content, another desired properties of raw material for biodiesel production is low level of non-saponifiable substances. Presence of this in significant amounts becomes soluble in biodiesel and reduces the level of esters in the product. It is not advisable to use of basic catalysts in feedstocks with high free fatty acids content, as part of this free fatty acid react with the catalyst to form soaps. As a result, part of the catalyst is spent, and it is no longer available for transesterification. However, basic transesterification is viable if the content of free fatty acids content is less than 2%. Generally, transesterification reaction efficiency diminishes with increasing acidity of the primary feedstock employed. For highly acidic raw materials however,

such as most animal fats and vegetable oils from cotton, coconut and all used oils, an acid transesterification step becomes necessary as a preliminary stage, to reduce the level of free fatty acids (FFAs) to below 2 % (Hanny et al, 2007, Romano et al, 2011). For tallow, a feedstock with a high FFAs water content, pre-treatment with an acidic catalyst is needed to esterify the FFAs before basic transesterification of the fat. The FFAs are converted into methyl esters bypassing the acid containing oils or fats through a packed column of a special catalyst resin. Pre-treatment is necessary to reduce soap formation during the transesterification reaction and ease the extensive handling for separation of biodiesel and glycerol as well as removal of catalyst and alkaline wastewater (Romano et al, 2011).

2. 5. 4Alcohol – Catalyst Mixing

Prior to introducing the primary feedstock into the reaction mixture, the alcohol employed for biodiesel production is first mixed with the catalyst. The alcohol-catalyst mixture is stirred until the catalyst is completely dissolved in the alcohol. Alcohol used is to be water free (anhydrous) so as to prevent hydration of product and catalyst consumption. The widely used catalysts are sodium and potassium hydroxides but for industrial scale production, sodium or potassium methoxides or methylates are commercially available. Due caution must however be exercised, side by side with the application of all safety regulations when working with these corrosive and irritating chemicals, independent of the production scale. The alcohol-to-oil volume ratio is a key variable of the transesterification process. The stoichiometric ratio requires of oil to react with of alcohol, to obtain biodiesel and glycerine should be determine. Owing to the reversible nature

of the reaction, excess alcohol as a reactant will shift the equilibrium to the right side of the equation, increasing the amount of products in accordance to Le Chatelier's principle. Though a high alcohol-to-oil ratio does not affect the properties of biodiesel, it will however make for difficult separation of biodiesel from glycerine, since it will increase the solubility of the former in the latter. In practice, a 100 % excess alcohol is used. Finally, it must be noted that acidity of the oil feedstock determined by titration decides the necessary amount of catalyst that would be used (Romano et al, 2011).

2. 5. 5 Transesterification process

The transesterification process earlier discussed is to be employed in the biodiesel production process. This process basically involves reacting triglyceride (fat/oil) with an alcohol, usually methanol, to form esters and glycerol. It is one of the commonest methods of biodiesel production, with tallow feedstock; it is carried out by the reacting the tallow with methanol in the presence of sodium hydroxide (NaOH) catalyst. This reaction involving a base catalyst is commonly termed base-catalysed transesterification and produces methyl esters and glycerine. If ethanol is used in place of methanol as the preferred alcohol, ethyl esters and glycerine are produced. Vast majority of biodiesel is produced using base catalysed transesterification as it is the most economical process yielding a product of 98 % conversion and requiring only low temperatures and pressures (Duncan, 2005, Dinesh et al, 2013, Dominik et al, 2008, Roseli et al, 2011).

Chemistry of Reaction

Biodiesel is the methyl esters of the fatty acids contained in the triglycerides of plant or animal derived oil. Biodiesel has a high cetane number, good lubricity properties, and energy content comparable to conventional mineral diesel fuels and can be easily blended with its conventional counterpart.

Biodiesel has molecular weights similar to that of conventional diesel fuels, with their transport properties and melting points superior to the fats and oils from which they were derived. Technically, biodiesel are considered a good quality component for mixing into diesel fuel, usually at concentrations of up to 20%, provided it is produced in line with the quality specifications.

The most common means of biodiesel production is the transesterification process whereby the tallow or vegetable oil triglyceride is reacted with methanol in the presence of a catalyst to form the fatty acid methyl esters according to the reaction below (Romano et al, 2011):

$$\begin{array}{l} \text{CH}_2\text{-O-CO-R} \\ \text{CH}_2\text{-OH} \\ \text{CH}_3\text{-O-CO-R} \\ \text{CH-O-CO-R}' + 3\text{CH}_3\text{-OH} = \text{CH-OH} + \text{CH}_3\text{-O-CO-R}' \\ \text{CH}_2\text{-O-CO-R}'' \end{array}$$

Triglyceride Methanol Glycerol Biodiesel

As described in the previous paragraph, the chemical reaction takes place upon mixing the oil with the alkoxide (alcohol-catalyst mix). However, the optimum yield of product requires certain conditions of time, temperature and stirring rate. As alcohols and oils do not mix at room temperature, the chemical reaction is usually carried out at a higher temperature and with continuous stirring to increase the mass transfer between the phases. However, there is the formation of emulsions during the course of this reaction which are much easier destabilised quicker with methanol as alcohol, in comparison to ethanol. Prolong stability of emulsions formed when using ethanol in the

reaction makes it difficult for phase separation and purification of biodiesel. The transesterification process may be carried out at different temperatures; however, for the same reaction time conversion is greater at higher temperatures. As boiling point of methanol is approximately 68°C (341 K), under atmospheric pressure the ideal temperature for transesterification is usually in the range between 50°C and 60°C. A knowledge of the chemical composition of the mixture during the reaction coupled with understanding of the reaction mechanism and kinetics of the process can be used to optimize the process. Determination of the mixture composition is however not easy, as more than a hundred substances are reported present (Ayhan, 2009, Ghaly, 2010, Romano et al, 2011). However, previous reports have shown the reaction is an equilibrium reaction, in that it will not proceed to completion, with traces of the feed triglyceride and methanol still present in the product. Conversion of triglycerides to methyl esters can however be increased by increasing the concentration of methanol and decreasing that of glycerol in the reaction mix. The partial reaction of the triglycerides and methanol can also lead to production of mono- and di- glycerides of the form below. These factors significantly affect the production process design, quality of product and necessary purification of the final products (Ghaly, 2010, Romano et al, 2011).

$$\begin{array}{l} \text{CH}_2\text{-OH} \quad \text{CH}_2\text{-OH} \quad \text{CH-OH} \quad \text{CH-O-CO-R}' \quad \text{CH}_2\text{-O-CO-R}'' \\ \text{CH}_2\text{-O-CO-R}'' \end{array}$$

Monoglyceride Diglyceride

2. 7 Separation of the Reaction Products

Separation of reaction products are usually by decantation; the product mixture containing majorly the fatty acids methyl esters (biodiesel) separates from glycerine forming two phases and since these two main

product have different densities; immediately upon stoppage of stirring two phases begin to form in the mixture. Owing to the different in chemical affinities, most of the catalyst and excess alcohol will concentrate in the lower phase (glycerine), while most of the mono-, di-, and triglycerides will concentrate in the upper phase (biodiesel). Upon clearly and completely defined interphase observance, separation of the two phases may be done physically. Decantation under gravity alone takes several hours to complete and as such constitutes delay in the production process. A faster separation method is centrifugation, though a more expensive alternative. After the separation of glycerine, the biodiesel mixture contains impurities such as catalyst, unused alcohol, as well as the mono-, di-, and triglycerides are collected. The characteristics of biodiesel are affected by presence of these impurities, characteristics such as increased cloud point and pour point, lower flash point etc. and as such purification of final product to comply with standards becomes necessary (Ayhan, 2009, Ghaly, 2010, Romano et al, 2011).

Purification of the Reaction Products

Biodiesel produce by the transesterification reaction usually requires a purification stage so as to meet with established quality standards for biodiesel. Hence, biodiesel need to be washed, neutralized and dried.

Washing with water at successive steps remove the remains of methanol, catalyst and glycerine, since every of these contaminants are water-soluble. However, formation of emulsions must be avoided during the washing steps, as it reduces the efficiency of the process. Acidified water is used in the first washing step, to neutralize the mixture of esters. Two further washing steps

using water only were carried out. Drying of the product (biodiesel) is finally carried out to remove any traces of water in the product. After drying, the purified product is ready for characterization as biodiesel according to international standards. The purification process described above can also be alternatively carried using ion exchange resins or silicates (Ayhan, 2010, Romano et al, 2011). Likewise, glycerine obtained directly from the biodiesel production process is not of high quality and has no commercial value. Therefore, after the phase separation, a purification step is also necessary. This is however of no economically viability in small scale production of biodiesel, due to small yield of glycerine. This is however an interesting purification alternative for large-scale production plants, since, in addition to deriving high quality glycerine, part of the methanol is recovered for reutilization in the transesterification reaction (from both biodiesel and glycerine), and thus lowering biodiesel production costs. Recent trend in increase biodiesel production is encouraging research for novel uses of glycerine in the production of high-value-added products. The stages required of the biodiesel production process would be noticeable the same for all the production scales (laboratory, pilot plant, small, medium, and large-scale industrial); however, the necessary equipment will be significantly different (Ayhan, 2009, Ghaly, 2010, Romano et al, 2011).

2. 9 By Product

The transesterification reaction between triglycerides in oil of plant or animal origin and alcohol in the presence of a catalyst yield mainly fatty acid methyl ester (commonly refer to as biodiesel) and glycerine. The products usually contain unreacted feedstock and alcohols as impurities with mono and di-

glyceride also present owing to partial reaction of feedstock and alcohol (Duncan, 2005). The compound 1, 2, 3-propanetriol usually known as glycerine. It is also referred to as glycerol or glycol alcohol and is an important by-product of biodiesel production process. Though chemically an alcohol, glycerine is a liquid of high viscosity at room temperature, colourless, odourless, transparent, and of sweet taste with low toxicity. Glycerine has boiling point of 290°C, and observed viscosity increment noticeably at low temperature, down to its freezing point of 18 °C. It is a hygroscopic polar substance and a good solvent as such can be mixed with water and alcohols, and has humectant (retains or preserve moisture) properties (Romano et al, 2011). Up until the late nineteenth century, glycerine was a product of candle manufacturing and was mainly deployed in the production of nitro-glycerine for explosives. With advent of separation processes from soap, glycerine became obtainable from soap industry as a sub-product. Since the mid twentieth century however, synthetic glycerine were obtained using raw materials from the petrochemical industry. At present, glycerine is obtained as a sub-product of soap or biodiesel production, and it is normally purified before use to eliminate the contaminants (mainly partially dissolved soap or salt for the sub-product of soap production or catalyst and methanol from biodiesel production) (Romano et al, 2011).