EVALUATION OF SMALL-SCALE BATCH BIODIESEL PRODUCTION OPTIONS FOR DEVELOPING ECONOMIES

SUBMITTED IN FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF TECHNOLOGY: CHEMICAL ENGINEERING

IN THE FACULTY OF ENGINEERING AND THE BUILT ENVIRONMENT AT DURBAN UNIVERSITY OF TECHNOLOGY

GABRIEL CHUKWUKA

PROMOTERS:

S.RATHILAL

S.RAMSUROOP

VL. PILLAY

FEBRUARY 2014

Declaration

I, the undersigned, solemnly declare that this project has been completed entirely by me and this project work has not submitted in whole or in part for a degree at another University

_____   _____   _____

GA Chukwuka   Place   Date

Approval by Supervisor

NAME: **Dr. Sudesh Rathilal**
                        _____

SIGNATURE:
                        _____

CONTACT: **(031) 373 2498**
                        _____

QUALIFICATION: **Ph.D. (Engineering) UKZN**
                        _____

DATE:
                        _____

Abstract

Biodiesel is a renewable fuel that can be produced from animal fats, vegetable oils or recycled used cooking oil. From the 1970's, biodiesel received increased focus as an alternative to crude oil and its component products. Among various processes used for biodiesel production, transesterification of glyceride and alcohol in the presence of a catalyst to produce ester (biodiesel) and glycerin remains the most common. In Africa, biodiesel is currently produced industrially in a number of ways via different methods. In South Africa, there are a number of biodiesel production plants that are continuous processes with feed samples from different sources. Reviewing the batch systems for developing economies, various observations were made. Some produced biodiesel using batch systems at room or day temperatures, another used different temperatures, some also used flat based buckets for their mixing and so on. This becomes difficult for local producers who desired to produce biodiesel on a very small scale for their farms or business. Hence, the study was aimed at evaluation batch biodiesel systems and to come up with a simplified approach for a producer in a developing economy or a local user.

The objectives of this study were as follows;

- To evaluate biodiesel production options, and hence develop a simplified process that can be used to produce biodiesel in developing economies. The criteria for evaluation will include: ease of operation, non-specialist equipment, range of feedstock, product quality and product yield.
- To evaluate various factors that affect these criteria and make recommendations that will enable a local producer to remain within an optimum range
- Compare the produced biodiesel properties against general biodiesel and petroleum diesel ASTM standard range
- Recommend simplified equipment design for a local producer

- Perform economic evaluation to establish cost required both for equipment and raw materials for a local producer.

After literature review on the existing processes, base catalyzed transesterification was selected. This is because of the simplicity as well as ease of operation.

Experimental trials commenced using feeds from pure vegetable oil (PVO) and waste vegetable oil (WVO) to familiarize biodiesel production, as well as study the behavior of each having the research criteria in focus. Various variables that affect ease of operation, product quality, and yield were also investigated. These include temperature, type of catalyst (KOH or NaOH), type of alcohol (Methanol or Ethanol), concentration of catalyst, and purity of alcohol, and nature of feed (PVO or WVO). The effect of temperature was compared against product quality, yield, and ease of operation. Other variables were also compared against the same criteria. Treatment of WVO because of impurity and moisture contamination associated with such samples was also studied. The product was then tested using some ASTM procedures to compare biodiesel quality to acceptable standards.

Efficient reaction time is paramount for a quality biodiesel. It was observed that biodiesel required between 25 and 30 minutes for a complete reaction. Lower temperatures clearly affected the quality of biodiesel produced. Best operating range was found to be between 55 ^{o}C – 75 ^{o}C. 65 ^{o}C is usually recommended for a transesterification reaction to obtain optimum yield and quality. The use of KOH compared to NaOH yields similar results even though NaOH is usually selected because of the reduced cost. The use of methanol compared to ethanol also yields similar results, even though methanol is usually preferred due to cost. Purity of available alcohol is vital as its reduction from 99.5 % to 75 % during experimental trials, yielded poor quality biodiesel. This is mainly due to moisture content that usually gives room for bacteria growth and corrosion of fuel lines in engines. As long as a titration test is carried out on the feed, the use of WVO is a good option. Varying catalyst concentrations from 0.5 % to 1.75 % were considered and the best regimes identified. This test will enable a producer from a growing economy to use

the appropriate reagent, which will ensure the transesterification reaction is complete.

After comparing appleseed and cone based design, the latter was selected as it will eliminate any difficulty that a local producer might encounter in making the biodiesel batch. In terms of costs, it was discovered that the major costs to a local producer will be the biodiesel mixer and fittings which will be fixed costs. Other variable costs are considered to be affordable, as the cost of waste vegetable oil is very low as well as other industrial reagent grade that will be required.

In summary, batch biodiesel production for a local user or developing economy is a very feasible exercise. One needs to ensure that the recommendations regarding pre-treatment of feed oil, basic reaction criteria and other generic parameters are considered during production.

Preface

The investigative and laboratory trials of this project were carried out at the Engen Refinery production laboratory. This involved using various feed stocks like pure oil samples, waste vegetable oil, and titration test to predict how to handle samples with water content. The yield from this stage was examined using various ASTM analyses to see their range of properties.

Mr. Suresh Ramsuroop and Professor VL Pillay both from Durban University of Technology supervised this project. This project was completed over a period of 36 months from February 2010 to February 2013.

Acknowledgments

Table of Contents

List of Figures

List of Tables

Index of Abbreviations

ASTM	American standard testing method
AN	Acid Number
COD	Chemical oxygen demand
CO_2	Carbon (IV) oxide
CP	Cloud point
CFPP	Cold filter plugging point
EU	European Union
EPA	Environmental protection Act
FAME	Fatty acid methyl ester (known as Biodiesel)
FP	Freezing point
H_2SO_4	Sulphuric Acid
HCl	Hydrochloric Acid
KOH	Potassium hydroxide (caustic potash)
MDPE	Medium density polyethylene
MP	Monopotassium phosphate
NaOH	Sodium hydroxide (lye)
PVO	Pure vegetable oil
PP	Pour point
ROI	Return on investment
SAGIS	South African Grain Information Service
SAPIA	South African Petroleum Industry Association
TN	Titration number
WVO	Waste vegetable oil
WVO 1	Used restaurant oil
WVO 2	Used canola oil

Chapter 1

Introduction

Simply defined, biodiesel is a renewable fuel that can be produced from animal fats, vegetable oils or used cooking oil. The report (SAPIA, 2006) suggests that the interest in renewable energy sources was motivated mostly by increasing oil costs, ecofriendly alarms and also as part of a wider energy expansion strategy. Besides other means by which biodiesel is produced, it is commonly produced from a chemical reaction between oil and alcohol in the presence of a catalyst with glycerine as by-product and biodiesel (methyl ester) as product. This reaction is usually known as transesterification.

The production of biodiesel remains a profitable area of renewable energy technology that has remained for over a century after Rudolf Diesel tested vegetable oil (usually known as straight vegetable oil – SVO) as fuel for his engine (Nitske and Wilson, 1965). Throughout the 1990s, plants were opened in many countries, which includes United States, Brazil, China, Canada, Germany and France just to mention but a few (Friedrich, 2003). In Europe, 100 % biodiesel is now available at a number of fuel service stations. Recently, because of increased crude oil prices, limited resources of fossil oil and environmental concerns, there has been a renewed focus on vegetable oils, animal fats, waste vegetable oils, etc. to make biodiesel fuels. As of late 2007, there were about 171 biodiesel production plants in the United States, yielding a total annual production of 10 billion liters. About 85% of these plants were on an industrial scale (defined as 7.5 million liters or more in annual capacity), while the rest were smaller facilities.

Currently in Africa and the Southern African region, some large scale skilled farmers are exploring and producing biodiesel for their own consumption. The procedures used are technically approved by and documented in simple formats. The equipment designs and set up comes from biodiesel equipment suppliers, which makes it easy for them to handle. For example, there are known suppliers based in the Gauteng

region that are reachable and well marketed through the internet. Most of these equipment are automated, thus it saved time but may have increased costs. It is necessary to note that affordability in relation to cost was a key motivation that will encourage a local producer to explore biodiesel production and benefits.

For small-scale farmers and developing economies that were unskilled, the concern of what is the best production process to use, types of equipment and best operating regime remained incompletely answered. There are various small-scale operations that are available. One producer uses a batch process with feedstock collected from various fast food outlets and restaurants using a base-catalyzed process at a temperature of 55 $^{\circ}$C and yield of 85%. Another producer uses low cost sunflower via base-catalyzed process with no heating involved which takes almost a day to complete. Yield is above 90% and the biodiesel is consumed in a private diesel vehicle. This signified that there is no well documented general process for biodiesel production in unskilled regions with recommended regime for optimum yield and quality.

Choice of equipment and feedstock is also a major challenge that small-scale farmers face. It was observed that equipment used varied from one producer to another. A producer uses a simple paint bucket of about 20 litres capacity; some use a mini cylindrical steel drum while others used transparent containers with a cone base of about 500 litres in capacity. It was then gathered, that even though production capacities may vary, there is also no acknowledged simple equipment design recommended for producers from developing economies. Again, feed stocks vary from one region to another. For instance, waste vegetable oil would differ from a supplier in Kwa-Zulu Natal to that in Gauteng due to different diets and composition of the feed depending on the sources. In summary, there are various recommended pre-test methods but no accepted approach for unskilled small-scale farmers as yet.

Hence, this study focuses on the evaluation of small-scale batch biodiesel systems for locally available PVO and WVO. Thus an acceptable production process may be

recommended for local farmers using the best operating regime and having additional economic benefits.

1.1 Project Objective

The objectives of this study include;

- To develop a simplified small-scale biodiesel production process that could be implemented in rural or semi-urban areas using locally available vegetable oil or waste vegetable oil.
- To evaluate the best operating regime for efficient biodiesel production for a local producer or small-scale farmers.
- To perform an economic evaluation to establish the cost involved from start to finish.

1.2 Approach

The approach of the study involved the following steps:

a) Survey of biodiesel production literature to identify most suitable biodiesel method for a developing producer, essential equipment and optimum operating conditions.

b) Survey of current small-scale operations locally that are used to identify advantages and disadvantages, in terms of production procedures, equipment and costs.

c) Experimental determination of effects of varying operating regimes and raw materials on biodiesel production using local vegetable oil (VO) and waste vegetable oil (WVO). From this, determine the most viable operating regimes

d) Propose the most suitable production process based on simple equipment, ease of operation and economic viability.

This research was based in Durban and experimental trials were performed at the fuel laboratory, Engen Refinery, Durban. Various surveys were also made in other recommended areas of Kwa-Zulu Natal. The laboratory was used because of the

available facilities that would enable us to verify quality according to ASTM standards.

1.3 Thesis Organization

Chapter 1: Introduction: This involved introduction of study, motivations for investigation, objectives, research methodology and thesis organization.

Chapter 2: Background information on biodiesel: This involved historical background, definition, chemistry, quality, properties, and safety.

Chapter 3: Determination of viable operating regime

Chapter 4: Equipment design

Chapter 5: Guidelines: Pretreatment, titration and washing of biodiesel

Chapter 6: Economic analysis

Chapter 7: Conclusions and Recommendations

Chapter 2

Background

2.1 Chemistry of Biodiesel

Biodiesel is a name given to fuel for diesel engines created by the chemical conversion of animal fats or vegetable oils. Biodiesel is defined as esters obtained through the transesterification of pure vegetable oil. Hence, they are produce obtained when vegetable oil or similar feedstock reacts with methanol in the presence of a catalyst. Alternative alcohol like ethanol and other waste oil can also be used for this process. Glycerol and ester are produced as end product (Friedrich, 2003).

$$_3H_5(RCOO)_3 \ + \ 3R'OH \ \xoverset{Catalyst}{\Longleftrightarrow} \ R'_3(RCOO)_3 \ + \ C_3H_5(OH)_3 \quad (1)$$

Triglyceride	**Alcohol**	**Methyl Ester**	**Glycerol**
1 mole	3 mole	3 mole	1 mole
		(Biodiesel)	
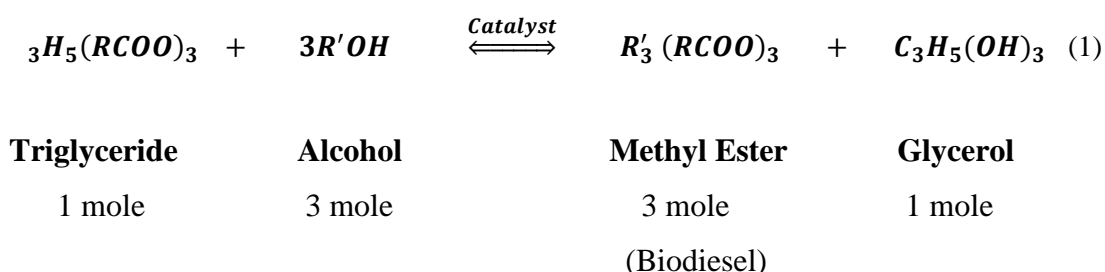
Equation 1: Reaction mechanism for transesterification of triglycerides with alcohol

Technically, biodiesel is defined as the mono-alkyl esters of fatty acids resulting from vegetable oils or animal fats. It is chemically known as a "methyl ester". In simpler terms, biodiesel is the end product of a vegetable oil or animal fat that has been chemically reacted with an alcohol and a catalyst to remove the glycerine. Transesterification is essentially the process of breaking down the oil molecule to replace a form of alcohol with another (e.g., methanol).

Transesterificationon is the general term used to describe an organic reaction, where an ester is transformed into another through interchange of the alkyl group. It is an equilibrium reaction, and the transformation occurs essentially by mixing the reactants. In the transerification of vegetable oils, triglyceride is reacted with

methanol (alcohol) using a strong acid or base as catalyst, producing a mixture of fatty acids alkyl esters and glycerol. The stoichiometric reaction requires 1 mole of a triglyceride and 3 moles of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow phase separation from the glycerol formed.

$$Fatty\ acid\ (R_1\ OOH) + Alcohol\ (ROH) \leftrightarrow Ester\ (R_1\ OOR)$$
$$+Water\ (H_2O) \tag{2}$$

$$Triglyceride + ROH \leftrightarrow Diglyceride + RCOOR_1 \tag{3}$$

$$Diglyceride + ROH \leftrightarrow Monoglyceride + RCOOR_1 \tag{4}$$

$$Monoglyceride + ROH \leftrightarrow Glycerol + RCOOR_3 \tag{5}$$

$$RCOOH \overset{H^-}{\leftrightarrow} RCOOH_2^+ \overset{R'OH}{\Longleftrightarrow} RCOOHR' \overset{-H^+}{\Longleftrightarrow} RCOOR' \tag{6}$$
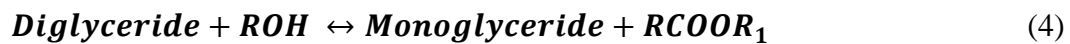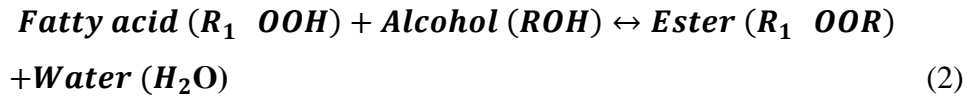
The equations above shows mechanism of acid catalyzed esterification of fatty acids (Fangrui and Milford, 1999). The initial step is the protonation of the acid to give an oxonium ion (1), which would undergo an exchange reaction with an alcohol to give the intermediate (2), and this becomes an ester (3). Each step in the process is reversible, but in the presence of a large excess of the alcohol, the equilibrium point of the reaction is displaced so that esterification proceeds almost to completion.

Transesterification consists of a number of consecutive reversible reactions. The triglyceride is converted stepwise to diglycerides, monoglycerides and finally glycerol. The formation of alkyl esters from monoglycerides is believed to be a step that determines the reaction rate, since monoglycerides are the most stable intermediate compound. In addition, breaking of monoglycerides and diglycerides are vital as they cannot be seen with the naked eye, but both can be harmful to the engine (Fangrui and Milford, 1999). The completion of the reaction is very critical to obtain a high quality ester.

2.2 Uses of Biodiesel

Biodiesel may be used in its direct form and is known as **absolute biodiesel or B100.** When used in this manner, it offers the maximum reduction with regards to exhaust particles, and also reduces carbon (II) oxide or unburned hydrocarbon. Using biodiesel in its pure form is also the most appropriate way to use it when parameters like decay rates and level of toxicity are highly very essential. Neat biodiesel do not result in problems while using it, but the property of solvent used may as it will cause deposits in the engine to be removed and so doing degrade or block fuel lines. Users of biodiesel have testified that such a challenge usually happen at the first couple of weeks of using biodiesel. Some materials are not well-suited with biodiesel (e.g. BUNA rubbers), and may remove paints the fill ports in a fuel tank (Biodiesel Education, 2004).

Blending biodiesel with another fuel is also another way of preventing the problems above. This blending is usually reported in percentages like B10 which implies that biodiesel content of the fuel mix is 10%. This can go from B20, B30, etc., depending on the desired blend. A positive side of blending is that the effect of cost is reduced while maintaining its emission reduction ability. According to Friedrich (2003), such reductions are proportional to the blending percentage of the biodiesel that is used. According to Energy Policy (2007), the most common blend is a mix of 20 % biodiesel with 80 % petroleum diesel, or B20 under recent scientific investigations. In Europe, the current regulation foresees a maximum of 5.75 % biodiesel in the blend.

Biodiesel are very good additives. This normally ranges from 1 to 2 % and is usually written as B01 or B02. Biodiesel is an efficient lubricity improver. When used as low as 0.35 %, it could yield a notable difference while using up to 1 % is adequate to turn a low lubricity product into a fuel that is well acceptable (Friedrich, 2003). According to Ma et al., (1999) and Knothe and Steidley (2005), biodiesel as a diesel fuel has liquid nature portability, ready availability, renewability, higher combustion efficiency, lower sulphur, and aromatic content. According to Mudge and Pereira

(1999), and Zhang et al (2003), biodiesel has high cetane number and higher biodegradability. According to Mittelbach and Remschmidt (2004), Knothe and Steidley (2005), main advantages of biodiesel given in the literature include domestic origin, reducing the dependency on imported petroleum, biodegradability, high flash point and inherent lubricity in the neat form.

2.3 Merits and Demerits of Biodiesel

2.3.1 Merits of Biodiesel

According to Journey to Forever (1999), biodiesel usage is necessary to an end user because of the following benefits:

- Modification of engine is not necessary: Majority of engines produced after 1995 can be operated with biodiesel mix or absolute biodiesel.
- It is good for the atmosphere from an environmental point of view. It burns better than oil diesel because it reduces to incombustible carbon (II) oxide in the atmosphere. It also removes sulphur (IV) oxide discharges in exhaust fumes.
- It is renewable in nature and so does not increase CO_2 into the environment.
- It is not toxic when compared to other hydrocarbon fuel sources. It also decays naturally.
- Biodiesel cetane ratings are high: This improves the performance of engines and prolongs the life span for automobile engine. It also lubricates better than petroleum diesel.

Other general advantages of biodiesel are as follows:

- To a certain degree, it reduces dependence on oil diesel and contributes to our own society as well as a small-scale producer who is interested in cutting cost.
- Biodiesel is plant-based and considered carbon neutral, as it adds almost no CO_2 to the environment.
- Biodiesel has a flash point that is double that of petroleum diesel. This makes it unlikely to ignite in a car wreck.

- It can minimize usual diesel engine "knocking" noise.

2.3.2 Demerits of Biodiesel

Even though the benefits present biodiesel as attractive, there are also some downsides to consider (Bee and Grant, year unknown):

- It generates fairly high NO_x levels during combustion as a result of high oxygen content.

- The conditions at which biodiesel is stored must be watched carefully as biodiesel has a low stability in terms of oxidation. Some of the oxidized particles can be harmful to automobile parts.

- The volumetric energy density is usually low. This implies that additional fuel might be required for transportation over the same distance covered.

- It has a higher cold filter plugging point (CFPP) temperature than petroleum diesel. This indicates that it will turn into a gel at low temperatures.

- It is a strong solvent and can remove varnishes or tars from petroleum in the fuel system. This may likely require the fuel filter to be replaced after initial stages of biodiesel use. This was confirmed by one of the domestic producer and using during a survey in the Durban area.

World Biodiesel Production

At present, biodiesel covers about 10% of the global generation of biofuel while ethanol retains the remaining coverage. World production has increase about four times in the last ten years particularly in 2000 and 2007. According to the World Watch Institute (2006), the largest producers are from countries like Italy, Germany, Brazil, USA and France. The graph below shows the present biodiesel world production.
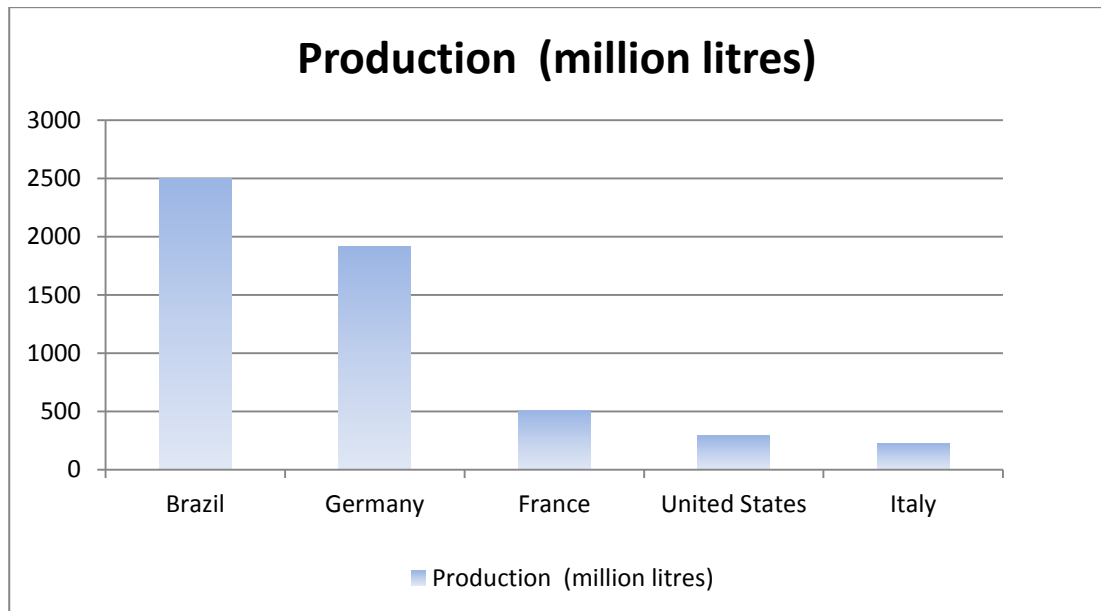
Figure 1: Global biodiesel production, 1991-2005 (World Watch Institute, 2006).

According to a recent statistical review of world energy by BP, world biofuels production grew by 0.7 % in 2011, the smallest increase since 2000. Based on this report, biodiesel accounts for about 27.5% of global biofuels output (BP Statistical Review, 2012).

2.4 Biodiesel Properties and Quality

2.4.1 Biodiesel Properties

There are some major differences between biodiesel and petroleum diesel with regards to chemical composition. This obviously gives biodiesel different behaviours. The nature of the feed used during biodiesel production affects the behaviour and properties of the diesel produced. The following fuel properties are considered:

- Cetane number
- Flash point
- Lubricity
- Sulphur content
- Cold filter plugging point
- Cloud point

- Pour point

The **Cetane Number (CN):** this is the propensity of any fuel to kindle after it has been fed into the engine component. According to current specification, it is required to maintain a CN of above 40 and most refiners make diesel with numbers ranging from 40 to 45. The CN for biodiesel falls within 46 to 60 but is influenced by the feedstock used (Biodiesel Education, 2004). This also reduces delay during ignition and makes the combustion ability of the engine better (Biodiesel Education, 2004). There are a few methods for measuring CN which are basically measurement of cetane index. Some use ASTM D4737, while some use ASTM D976. The first is calculated based on density and recovery temperatures of 10, 50 and 90 % while the latter only relates it to density and 50% recovery temperature.

Flash Point (FP): This can be defined as the lowest temperature after which the vapour over the fuel can ignite. Petroleum diesel is innately safe as they have a FP temperature ranging between of about 50 and 80 ^{o}C. The flash points for biodiesel are over 160 ^{o}C which reduces the fire hazard related to their transportation or storage. This makes them better than petroleum fuels in terms of ease of use, storage and transportation (Biodiesel Education, 2004). There are various methods for the determination of FP's of liquids available in many standards which include ASTM D93 and IP34.

Lubricity: This can be defined as the extent to which a lubricant can reduce friction. It has been said that it is difficult to measure material lubricity even though it can be obtained by a laboratory test. When the friction is low, it implies that the lubricity is high (Friedrich, 2003). It is also vital to note that reduction in fuel sulphur content according to recent regulations have decreased fuel lubricity. Biodiesel has good lubricity as quality blends of biodiesel have shown that the mixture improved greatly in relation to lubricity (Biodiesel Education, 2004). Lubricity for diesel can be measured by using ASTM D6078.

Sulphur: Based on the current global sulphur regulation, sulphur levels are required to be less than 50 ppm from the beginning of 2005 (SAPIA, 2006). South African refiners are currently aligning their operations to meet this regulation not later than 2016. Biodiesel is free of sulphur particularly when made from pure vegetable oil. Biodiesel generated from waste vegetable oil may have a low in sulphur content. This needs to be checked to ensure that the quality is acceptable (Mittelbach and Remschmidt, 2005). This can be measured using ASTM D5453.

Cold Flow Properties of diesel fuels: All diesel fuels are susceptible to start-up and performance problems when vehicles and fuel systems are subjected to cold temperatures. As ambient temperatures cool towards their saturation temperature, high-molecular-weight paraffins (C18 − C30 n-alkanes) present in petroleum diesel begins to nucleate and form wax crystals suspended in a liquid phase composed of shorter-chain n-alkanes and aromatics (C1–C5). If the fuel is left unattended in cold temperatures for a long period of time (e.g., overnight), the presence of solid wax crystals may cause start-up and performance problems the next morning. It is essential to know the cold temperature behavior of biodiesel, particularly in regions where temperatures are less than 5 $^{\circ}$C. **Cloud point (CP)** can be defined as the temperature when the first solids are formed.

Pour Point (PP): This can be defined as the lowest temperature which a fuel sample can be cooled to while still retaining its properties. In mid-1960s, attention focused on developing laboratory bench-scale tests independent of CP or PP to predict minimum operability temperatures for diesel fuels. In Western Europe, this work resulted in the development of the CFPP test method. This method (ASTM standard D6371) calls for cooling the oil sample at a specified rate and drawing it under vacuum through a wire mesh filter screen. CFPP is then defined as the lowest temperature at which 20 ml of oil safely passes through the filter within 60 s. Guy (2008) recommends to blend biodiesel with petroleum diesel and to also blend it with antigen additives.

Heating Value: This is sometimes called the **heat of combustion** represented by **HG**. This is also dependent on the nature of the feed stock. Comparing petroleum diesel to biodiesel, petroleum diesel contains more HG than biodiesel even though it is less dense than biodiesel. According to Mittelbach and Remschmidt (2005), the **HG** of petroleum diesel is 13% more than that of biodiesel. For an equal injection volume, automobiles using biodiesel have less power and force. Multi-fuel automobile utilizes motors that can detect the nature of fuel and spontaneously switch the injection parameter (Mittelbach and Remschmidt, 2005). If biodiesel is used, consumption is high as there is an increase in injection capacity. The described behaviour of biodiesel is specific to pure biodiesel. When biodiesel is blended with petroleum diesel as B5 or B10, the behaviour of the petroleum diesel will not change.

Table 1 below shows the characteristics of petroleum diesel and biodiesel from different PVO sources (Mittelbach and Remschmidt, 2005)

Table 1: Properties of Petroleum Diesel and Biodiesel

		Fossil Diesel	Biodiesel from Palm oil	Biodiesel from Canola oil	Biodiesel from Soybean oil	Biodiesel from Sunflower oil
Density	Kg/m^3 (T in ^{o}C.)	835 (15)	867 (15)	888 (15)	884 (25)	880 (25)
Kinematic Viscosity	Mm^2/s (at 38°C)	2.7	4.3 – 6.3	3.50 – 5.00	3.05 – 4.08	4.20 – 4.40
Cloud Point	^{o}C	-15	13 to16	-3 to 1	-2 to 2	0 to 3
Pour Point	^{o}C	-33	-	-15 to –9	-3 to –1	-3
CFFP	^{o}C	-18	9 to 11	-19 to –8	-2	-3
Flash Point	^{o}C	50-80	155 – 174	153 – 179	141 – 171	164 – 183
Heating Value	MJ/kg	42.7	41.3	40.07	39.8	39.71
Cetane Number		47	52	56	50	53

2.5 Biodiesel Quality and Standards

In order to market biodiesel properly, it is required to meet certain specifications from a quality point of view. These standards then act as guidelines during biodiesel production to monitor quality. These standards also serve as warranty to customers that the products they buy are of high quality and that they are also protected against safety and other environmental regulations (Prankl, 2002).

Considering the variety of feedstock that can be used for biodiesel production and end product properties that can be obtained, it is very appropriate to pay close attention to these specifications. Many biodiesel guidelines are presently in place in some countries like the EN14214 applicable in EU. In the United States, there is ASTM D6751 that is also used (Mittelbach and Remschmidt, 2005). In South Africa, the standard known as SANS 1935 is used. This standard is a minor modification of EN14214. According to Manaka (2006), there are several weaknesses of SANS 1935 based on South African Bureau of Standards (Manaka, 2006). Such as;

- There is a constricted definition of biodiesel as esters obtained only via vegetable oil. It does not account for esters produced from other alcohols and feed oil sources.
- Some of the compulsory parameters that need to be tested make the overall testing very expensive. This is also because of the needed equipment.
- It covers the ideal characteristic or behaviour desired from pure biodiesel. It does not take into consideration the impact of blended products particularly when diluted.

Taking into consideration that such regulation and standards are active documents that are constantly reviewed, they will most likely be amended in the close future.

2.6 Production Process

Figure 2 is a simplified diagram of the start to finish procedure for the production of biodiesel. This is discussed in detail in the sections that follow. The feed used to

produce biodiesel is usually extracted from oil crop and are also treated (i.e. waste vegetable oil) prior to undergoing transesterification to generate biodiesel as end product and glycerol as by-products.
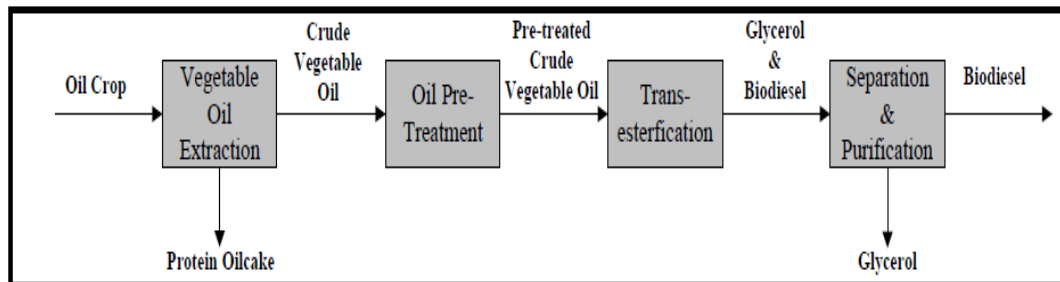
Figure 2: Simplified diagram of the start to finish biodiesel process.

2.6.1 Industrial Production

2.6.1.1 Pre-treatment of Feed Oil

Many raw feed oils with the exclusion of soybean and palm oil, are easily used for the biodiesel transesterification process without initial treatment of the feed. The likes of soybean and palm oil may require degumming before use because they contain high level of phosphatides (Mittelbach and Remschmidt, 2005). Phosphatides are in direct relationship to phosphorous content which usually deactivates the catalyst used in the exhaust (Tyson et al 2004). Some feed oil also need to be deacidified more especially when the fatty acid content is greater than 5% (Mittelbach and Remschmidt, 2005). Deacidification is basically the elimination of excessive free fatty acids (FFA) in the feed oil, a specification of < 1 mgKOH/g is normally used. FFAs are greatly undesired as they reduce the activity of the catalyst. They also inhibit the separation of biodiesel and glycerol. The process of degumming and deacidification can be conducted simultaneously by injecting a catalyst like KOH which will react with the free fatty acid to form soap. If hot water is present, swelling of the phosphatides will occur and both products can be obtained (Tyson et al., 2004). In a case where the total acid number of the feed oil appears high (e.g. waste vegetable oils), it is then recommended to use pre-esterification of

the FFA with alcohols like ethanol or methanol. This is also known as an acid catalyzed pre-esterification process (Mittelbach and Remschmidt, 2005).

The last phase on this treatment is to remove all water particles remaining via the use of a process known as dehydration. Water needs to be eliminated as it reduces the conversion of a base catalyzed transesterification. It also harms the acid based transesterification (Mittelbach and Remschmidt, 2005). In other to dehydrate, a distillation process may be used by applying low-pressure or it can be done by passing nitrogen via the treated oil (Mittelbach and Remschmidt, 2005). For a developing economy, the guidelines on Chapter 5 for pre-treatment may be used.

2.6.1.2 Separation and Purification

Separation of glycerol is the next stage after the transesterification reaction is complete. The layers of glycerol and methyl ester occur simultaneously because of methanol which is used for base-catalyzed transesterification. To make the separation faster, extraction is carried out by adding water and more glycerol while the centrifugation process is initiated. Each phase is then purified after separating the ester from the glycerol. Recovery of methanol is then carried out via vacuum distillation. Complete removal of glyceride or glycerol is done through water washing or acid washing. Mittelbach and Remschmidt (2005), does not approve this process as the ester is lost through hydrolysis.

FFA is also removed from the ester phase when required, by the process of distillation. This is possible as free fatty acids have higher boiling points than methyl ester. As the catalyst is soluble in a water phase, methyl ester is eliminated while washing with water. It was also noticed that some traces of catalyst may remain in the ester layer. It is recommended to eliminate the catalyst by passing the ester layer via resins in a moist state (Mittelbach and Remschmidt, 2005).

It is also necessary to purify the glycerol phase as they contain FFA and traces of free acid methyl ester (FAME). Initial stage is the decomposition of soap into free fatty acid by the addition of phosphoric acid. The FFA is not soluble in glycerol and

will create a different phase which is later separated (Mittelbach and Remschmidt, 2005). If the catalyst used is KOH, monopotassium phosphate (MP) will be generated which may be used as fertilizer (Mittelbach and Remschmidt, 2005). The remaining free fatty acid can be esterified with H_2SO_4 and ethanol. It can also be passed through free acid methyl ester with basic glycerol at about 170 ^{o}C to yield triglycerides. According to Mittelbach and Remschmidt (2005), these end products can be recycled into the feed to repeat the process of transesterification.

Various Methods of Transesterification

This section describes various methods of transesterification reaction with regards to the production of biodiesel. They include;

- Lipase catalysed transesterification
- Acid catalysed transesterification
- Base catalysed transesterification
- Non-catalytic superficial alcoholic transesterification

Lipase Catalyzed Transesterification

Due to their ready availability and the ease with which they could be handled, hydrolytic enzymes have been widely applied in organic synthesis. They do not require any co-enzymes, they are reasonably stable, and often tolerate organic solvents. Although the enzyme-catalyzed transesterification processes are not yet commercially developed, new results have been reported in recent articles (Demirbas , 2006). The common aspects of these studies consist of optimizing the reaction conditions (solvent, temperature, pH, type of micro-organism which generate the enzyme, etc.) in order to establish suitable characteristics for an industrial application. However, the reaction yield as well as the reaction time is still unfavorable compared to the base-catalyzed reaction system.

Acid Catalysed Transesterification

Acids like sulphuric acids catalyses the transesterification process. These catalysts give very high yields in alkyl esters, but the reaction is slow, requiring typically,

temperatures above 100 ^{o}C and more than 3 hours to complete conversion. Recent study by Freedman et al., (1984), shows that the methanolysis of soybean oil, in the presence of 1 mole percent of sulphuric acid with an alcohol/oil molar ratio of 30:1 at 65 ^{o}C, takes 50 hours to reach complete conversion of the vegetable oil (> 99 % yield). Demirbas (2006) also confirms that alcohol/vegetable oil molar ratio is one of the main factors that influence the transesterification. An excess of the alcohol favoured the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol / oil ratio have to be established empirically, considering each individual process (Demirbas, 2006)

Base Catalysed Transesterification

This process proceeds faster than the acid-catalyzed reaction. It is a unique process as the alkaline catalysts are less corrosive than acidic compounds, industrial process usually favours base catalysts, such as hydroxides as well as sodium or potassium carbonates. According to Demirbas (2006), the first step is the reaction of the base with the alcohol, producing an alkoxides and the protonated catalyst. The nucleophilic attack of the alkoxides at the carbonyl group of the triglyceride generates a tetrahedral intermediate from which the alkyl ester and the corresponding anion of the diglyceride is formed. The latter deprotonates the catalyst, thus regenerating the active species, which is now able to react with a second molecule of the alcohol. To start another catalytic diglycerides and monoglycerides, it is converted by the same mechanism to a mixture of alkyl esters and glycerol (Demirbas, 2006). Alkaline metal hydroxide was the most active catalyst, since it gives very high yields (> 98 % yield) in short reaction times. They are also unique as they are cheaper than metal alkoxides. They also do not require the presence of water.

Sodium Methoxide Catalyzed Esterification: This is an example of base catalyzed transesterification. A number of detailed recipes for sodium methoxide catalyzed transesterification is available. According to Demirbas (2006), the methodology can

be used on quite a large scale if needed. The reaction between sodium methoxide in methanol and a vegetable oil is very rapid. It has been shown that triglycerides could be completely transesterified in 5-10 minutess at 15 $^\circ$C above room temperature. The methoxide anions are prepared by dissolving the clean metals in anhydrous methanol. Sodium methoxide (0.5 – 2M) in methanol affects transeterification of triglycerides much more rapidly than other transesterification agents. At equivalent molar concentrations with the same triglyceride samples, potassium methoxide effects complete esterification more quickly than sodium methoxide does. Because of the dangers inherent in handling metallic potassium, which has a very high heat of reaction with methanol, it is preferred to use sodium methoxide in methanol and reaction are generally slower with alcohols of higher molecular weights (Demirbas 2006).

Non-catalytic Supercritical Alcohol Transesterification

A non-catalytic biodiesel production approach with supercritical methanol has been developed and this allows a simple process with a high yield, because of simultaneous transesterification of triglycerides and methyl esterification of fatty acid (Demirbas, 2006). The parameters affecting the methyl esters formation are reaction temperature, molar ratio, water content, and free fatty acid content (Demirbas, 2006).

Comparism Between Acid-catalyzed and Base-catalyzed Transesterification Process

Two best alcohols to be used for transesterification are methanol and ethanol. Other alcohols could be explored but this was not covered within the scope of this study. Notwithstanding the alcohol that is used, a catalyst must be introduced to enable high yields to be reached. The most used methods are acid and alkali catalyzed (base-catalyzed) transeterification reaction. Table 2 shows comparism between the two processes (Mittelbach and Remschmidt, 2005).

Table 2: Comparism between alkali and acid catalyzed transesterification

Catalysis	Alkali	Acid
Samples	• KOH and NaOH	• H_2SO_4
Merits	• The ratio of alcohol to oil is low – 1:4 • Lower reaction temperature and lower temperature for high yield • Faster reaction time. Most alkaline reaction occurs within 20 – 45 minutes • Less corrosive to equipment means lower capital cost as the choice of equipment with stronger metallurgy but expense is reduced. • Alkaline catalyst are relatively cheaper	• Not sensitive to free fatty acids in feedstock
Demerits	• The sensitivity to free fatty acids in the feed is high – waste oil needs to be pre-treated. • They require the absence of water, which makes them inappropriate for industrial process. Waste vegetable oil is usually treated to eliminate the presence of water	• Requires higher temperature, pressure and alcohol volume • The reaction time is slow • Materials are corrosive • Sensitivity to water in the feed is high

From the comparism above, base-catalyzed transesterification was selected because of its simplicity, cost consideration, and the suitability for developing economies. The investigation during this research was therefore narrowed down to a base-catalyzed transeterification process.

2.7 Small Scale Production (Local Survey) and Raw Materials for Biodiesel Production

2.7.1 Small Scale Production – Local Survey

Under small scale production of biodiesel, three production approaches from a South African context were studied. This was because the study centred on development of

small scale batch biodiesel systems for developing economies. In addition, there was no standardized approach used as different small users used what was convinient or what works for them.

2.7.1.1 Local Producer A

Introduction/Raw Materials:

This is a domestic producer in the Pinetown area of Kwazulu-Natal and consumes the product on a biodiesel powered vehicle. Producer has a chemical engineering background with over 30 years of industrial experience. Monthly consumption is averagely about 150 litres with feedstock ranging from used sunflower, palm oil or vegetable oil (often mixed with canola oil). Cost of the feed oil used ranges from R1.5 to R2.5 per litre. Quality of the feed oil used requires no pretreatment. Other reagents used are potassium hydroxide, methanol and hydrochloric acid.

Method/Washing:

A 20 litre graduated paint bucket is used in which the dissolved KOH, methanol and feed oil was poured and mixed using a small hand-held mixer (a manual wooden material could also be used). After about 1.5 hours, unwashed biodiesel which stays on top of the mixer bucket is poured off leaving the layer of glycerol behind. HCl of about 7-8 % strength is poured into the biodiesel batch for washing, stirred gently and biodiesel also poured off. This HCl is also used for other tests. After this, 1 litre of wash water is used to wash off the biodiesel batch for about 5 times until the effluent produced is clear. A small pump of about 3 Watts is also used to create bubble inside the biodiesel after which the sample is ready for use. The 27/3 method is used to test if transesterification is complete. Before testing, the biodiesel must also be at room temperature. In summary, 3 ml of biodiesel is collected, mixed with 27 ml of methanol in a sealed cylindrical glass. For a fully converted batch, no oil will settle out or one can also look out to ensure no yellow bubbles are formed in it.

Conclusion:

No heater is required for the whole exercise as producer A performs everything at ambient temperature. Economically, production is very feasible for the producer as

the cost price of finished biodiesel considering feedstock plus other raw materials used is about R4 per litre. This means that at a selling price of R9 per litre, his profit could be over 100%. The user runs his vehicle on B100 and there are no issue encountered in the engine except for early change of the filters. This is because biodiesel is a good system cleaner of impurities, which is stored up in the vehicle storage hands. The vehicle goes up to Gauteng Province once a month with no problems encountered.

2.7.1.2 Local Producer B

Introduction/Raw Materials:

This is a batch producer based in Pietermaritzburg. Efforts were made to visit the site, but the producer opted to respond to the survey by electronic communications which limited the amount of information received. Production capacity is about 1000 litre per day but depends on availability of used oil. The feedstock used was cooking oil (WVO) which is pre-treated before use. Cost of WVO was not supplied by the producer.

Methods/Washing:

WVO is pre-treated, heated up to 50 ^{o}C before pouring into the processor or mixer. Methoxide is generated in the catalyst mixing tank by adding NaOH and Methanol at the correct proportion. The methoxide mixture is routed into the processor where the heated WVO is mixed with methoxide at about 60 ^{o}C by the use of a propeller stirrer at about 500 rpm. The processor/mixer is conical based of about 1000 litres. After about 15 minutes, the mixer is stopped and allowed to settle. The glycerine is collected from the bottom while the biodiesel is routed into another tank for washing. Unlike most producers, producer B does not wash using water but by air drying and HCl. The 27/3 method is also used to check the quality of biodiesel produced.

Conclusion:

After checking the batch using the 27/3 testing method, the biodiesel is ready for use. The cost of production for the producer is about R5 per litre while product is

sold as B50 (50% biodiesel and 50% petroleum diesel) at about R10.90. The glycerine from this process is sold to the soap manufactures.

2.7.1.3 Local Producer C

Introduction/Raw Materials:

Producer C is based in Durban and uses the biodiesel produced for the running of private business owned small trucks and a personal vehicle which was still on bank repayment. Feedstocks used are purely WVO collected from fast foods and restaurant oil. These WVO are collected from as far as Newcastle and the Mpumalanga area. Batch approach was also used, even though the equipment is supplied from Gauteng Province with testing kits, processor and wash tanks.

Methods/Washing:

The WVO is fed into the mixer of 200 L in capacity. The methanol and sodium hydroxide which is mixed in a different drum on the set up, is also fed into the mixer. The mixer has a fixed stirrer fitted that is used to turn the mixture automatically, but at a lower rotating speed to avoid over agitating the mixture. The temperature of the mixer is operated by a heater which is set to keep the mixer temperature at about 60 $^{\circ}$C. The mixer is allowed to only run for about 10 minutes and switched off. The mixture is then allowed to stay for about 1 hour in the mixer before being separated. The producer indicated that they independently adopted the duration of 1 hour to ensure that separation is complete. The glycerol is first drained off into a small flow bin via the connected piping, after which methyl ester is then washed using a water pipe that is put into the mixer from the top. This washing is not sprayed but is just introduced to the top at a normal water tap pressure. After each washing, the sample is allowed to sit for 1 hour and then washed for about three times. This final methyl ester batch is then drained off into the 1000 litre flow bin.

Conclusion:

After checking the batch using the 27/3 testing method, the biodiesel is ready for use. The product cost considering all the expenses involved is about R6 according to

the producer. However, this biodiesel is not sold but used for the running of the company diesel powered vehicles.

2.7.2 Raw Materials for Biodiesel Production

2.7.2.1 Oil Crops and Vegetable Oil.

Biodiesel can be made from various types of oil seed like canola, sunflower, etc. The feedstock that is frequently used for local producers is waste vegetable oil. Because of the varying or free fatty acid content, they are usually blended with low FFA oil. They are also pretreated to establish the acid number before use.

Table 3 below summarizes the main crops South Africa produces based on a survey done in 2005/2006, the harvest obtained and the amount of oil they yield. According to SAGIS (2006), groundnuts had the maximum yield of oil but the annual production was low. Hence, groundnuts were not the perfect oil seed for large scale biodiesel production. The production of canola was less than groundnut but it is believed that if the price of canola is cheaper, it may improve the required feedstock volume for biodiesel production locally. The highest yield per hectare came from Sunflower. It is the leading oil seed which South Africa produces and contributes largely to the domestic oil used locally. Another crop with fewer yields was soybeans however with a higher production rate. According to Mittelbach and Remschmidt (2005), soybeans and rapeseed oil are the main oils used for biodiesel production globally.

Table 3: South Africa's major crops (Mittelbach and Remschmidt, 2005)

Crop	Oil Yield	Area Harvested	Production	Yield	Oil Yield
	kg/ton	Thousand Ha	Thousand Tons	Tons/ha	kg/ha
Maize	50	3,223	11,716	3.63	182
Wheat	-	805	1,905	2.37	-
Sunflower	380	460	620	1.35	513
Soy beans	180	150	272	1.82	328
Sorghum	-	260	86	3.01	-
Drybeans	-	48	72	1.5	-
Groundnuts	420	40	64	1.6	672
Canola	400	44	40	1.1	440
Cotton seed	130	23	32	1.36	177

2.7.2.2 Industrial Raw Materials – Oil Crops and Vegetable Oil

Industrially, various raw materials could be used for biodiesel production on a large scale. This also depends on the country and availability of such raw materials in the region. Some of the raw materials for industries include;

A. Palm Oil: In Nigeria like in most Sub-Saharan African countries, agriculture is a strong sector of the economy. It accounts for 15% of the nations GDP. A major product produced in Nigeria is palm oil. For biodiesel developing industries, palm oil is strongly considered as a feed stock for biodiesel production in West Africa.

B. Palm Kennel Oil: This is also another by product of palm oil extraction where the nut is mechanically crushed and pressed for oil production. This is also another biodiesel feedstock source (Alamu et al., 2007).

C. Rapeseed (Canola) Oil: In Europe and America, rapeseed oil is a major source of feedstock for biodiesel production (Bender, 1999).

D. Animal Fats: In United States, animal fat is one of the sources of biodiesel feedstock used on an industrial scale (Bender, 1999).

E. Soyabean oil: This is a major feed stock for biodiesel production in countries like United States and Canada. It is among the highest feed used for industrial production in developed nations. (Haas, 2005).

F. Jatropha Oil: Jatropha seed, from which the oil is produced, is another major feedstock. Estimates of Jatropha seed yield vary widely due to a lack of research data.

2.7.2.3 Small-Scale Feedstocks (Raw Materials) – Oil Crops and Vegetable Oil

An important consideration while using a small-scale raw material is to ensure that the contaminants are as low as possible. Obtaining this at a low cost is also important, as high feed stock cost might rule out the economic benefit of small-scale biodiesel production for a local producer. The use of pure vegetable oil (PVO) for biodiesel production has already been discussed and is considered to be not the best option for local biodiesel production. This is because the cost of PVO compared to the profit of the end product (biodiesel) does not have economic justification. Some of the alternative feedstock that can be used locally includes;

A. Domestic: Home waste vegetable oils

B. Waste vegetable oils: This range covers restaurants like KFC, Chicken Licken, Chip Shops, etc. These however must be pretreated before use

C. Industrial used canola oil

The scope of this study will however focus on using pure vegetable oil (PVO), domestic waste vegetable oil, restraunt waste vegetable oil (WVO).

2.7.2.4 Alcohol

According to Mittelbach and Remschmidt (2005), methanol is the most common alcohol used for transesterification because of the affordable price and high reactivity compared to other longer chain alcohols. Another advantage that methanol has over ethanol is that it could easily be obtained in the pure form. This is of great importance as even traces of water drastically affects reaction rate of the transesterification reaction.

The stoichiometry of the reaction requires 3 mole of alcohol per 1 mole triglyceride, but in order to shift the equilibrium of the reaction to the right hand side, an excess amount of alcohol is used. According to Mittelbach and Remschmidt (2005), the suggested molar ratio of 6:1 methanol to vegetable oil in alkali catalysis was not exceeded. Acid catalysis however, requires molar ratios of methanol to vegetable oil of up to 30:1. Although ethanolysis was considered more environmentally friendly; as ethanol could be produced by fermentation, and gives the biodiesel a higher cetane number, it was more energy consuming and creates problems for the product separation process. The scope of this work in this study was also limited to methanol and ethanol.

2.7.2.5 Catalyst

In general, there are three categories of catalysts used for biodiesel production: alkalis, acids, and enzymes (Canakci and Van Gerpen, 1999). Enzyme catalysts have become more attractive recently since it can avoid soap formation and the purification process was simple to accomplish. However, they are less often used commercially because of the longer reaction times and higher cost. In an attempt to

reduce costs, researchers developed new biocatalysts recently. An example was called **whole cell biocatalysts**, which was immobilized within biomass support particles. One advantage was that, no purification was required for using these biocatalysts. When compared with enzyme catalysts, the alkali and acid catalysts were more commonly used in biodiesel production (Ma and Hanna, 1999). The alkali and acid catalysts includes homogeneous and heterogeneous catalysts. Due to the low cost of raw materials, NaOH and KOH are usually used, as alkali homogeneous catalysts and alkali-catalyzed transesterification is the most commonly used method commercially. These materials (KOH and NaOH) are the most economical, because the alkali-catalyzed transesterification process is carried out under a low temperature and pressure environment, and the yield rate is high with no intermediate stages involved.

However, the alkali homogeneous catalysts are highly hydroscopic and absorb water from air during storage. They also form water when dissolved in the alcohol reactant and affects the yield (Leung and Guo, 2006). Therefore, they should be properly handled. On the other hand, some heterogeneous catalysts are solid and it could be rapidly separated from the product by filtration, which reduces the washing requirement. More so, solid heterogeneous catalysts could stimulatingly catalyze the transesterification and esterification reaction that could avoid the pre-esterification step, thus these catalysts are particularly useful for those feedstocks with high free fatty acid content (Kulkarni et al., 2006). However, using a solid catalyst, the reaction proceeds at a slower rate because the reaction mixture constitutes a three-phase system, which, due to diffusion reasons, inhibits the reaction.

2.7.2.6 Acid

Sulphuric acid and hydrochloric acid can be used in the production of biodiesel. The first is used for biodiesel production via acid transesterification while the latter is mainly used for testing of soap in biodiesel or washing of biodiesel after production using base catalyzed transesterification. Sulphuric acid can also be used for a two-stage biodiesel process where the feed has high FFA.

2.8 Summary of Important Considerations

There are few things that require attention in other to properly develop small-scale batch biodiesel systems for developing economies. This section will briefly summarize these vital areas.

2.8.1 Equipment

The choice of equipment used for biodiesel is vital to the success and simplicity of the biodiesel production. The following are used industrially;

- Continuous flow reactors
- Semi-continuous flow reactors
- Batch reactors

Continuous and semi-continuous reactors are typically used for industrial biodiesel production which limits our focus to batch reactors/mixers. A 200 litre chemical metallic drum could be used for biodiesel production but the limitation is that there will be no visibility of the separation from glycerol after reaction completion. For the study, a cone shaped design will be used and discussed in detail as it is easy to use. To also eliminate cost, a local producer will resort to using only one mixer which means that both reaction and washing will be done in the same cone shaped mixer.

2.8.2 Raw Materials

In other to remain within the scope of study, the following raw materials will be used.

- Alcohol (Methanol, Ethanol and Isopropyl alcohol)
- Catalyst (NaOH and KOH)
- Indicators (Turmeric indicator solution)

2.8.3 Reaction Variables

The following variables and factors below are essential for the conversion of biodiesel to petroleum diesel.

- Reaction temperature: Biodiesel production by the use of a base catalyzed process requires a certain temperature regime for complete reaction and

yield. According to Kumar (2011), the rate of reactions increased with temperature during a study to understand the relationship between temperature and reaction rate. Since this factor affects the reaction, it will be studied to establish how it will affect a local producer and recommendations will be made.

- Reaction time: Transesterification reaction is very dependent on time as reaction kinetics always varies with time.
- Catalyst concentration.
- Purity of alcohol.

2.9 Safety Practice and Washing of Biodiesel

Using the right safety approach, biodiesel can be made at home however, care is required as the chemicals required are very hazardous if used incorrectly (Guy, 2008). Chemicals with high concern are KOH, NaOH, and methanol as all could cause great harm.

According to Guy (2008), methanol's advantage over gasoline comes from several physical and chemical properties:

- It has lower volatility – Methanol does not produce vapour as compared to gasoline. At similar conditions gasoline will release two to three times' greater vapour than methanol.
- It is highly flammable.
- The vapour density is lower.
- Methanol has a lower heat release rate.

It is therefore essential to handle these chemicals using recommended safety materials.

2.9.1 Safety Practice for Biodiesel

2.9.1.1 Recommended safety materials

In other to be safe while using any of the required chemicals, the following items are advised to be worn at all times (Guy 2008).

- Gloves – Gloves that are chemically resistant are recommended and they should be tough against alcohols and caustics.

- Goggles or full face shield.

- Chemically resistant apron.

- Respirator – This will prevent inhalation of KOH, NaOH and methanol dust or fumes.

- Long-sleeved clothing is also recommended.

- Pants – Properly fitted full length pants are highly recommended.

2.9.1.2 Ventilation and Spontaneous Combustion

According to Guy (2008), it is essential to have appropriate ventilation while handling methanol, NaOH or KOH. It is also advised not to use methanol near ignition sources as this could spark or create fires. Hence, methanol should rather be kept outdoors or in a ventilated area even when mixing it with catalyst.

Biodiesel-soaked materials should be stored in a safety can or dried individually to avoid any chances of spontaneous combustion. Biodiesel is made from vegetable oils or animal fats that can oxidize and degrade over time. This oxidizing process can generate heat. In some situations, a pile of oil-soaked materials can develop enough heat to result in a spontaneous fire. This can also happen with rags soaked with any oil, and combustible liquid.

2.9.1.3 Other Important Safety Notes

According to Guy (2008), some other possibly dangerous situations can arise when making biodiesel locally or at home. By observing basic safety procedures, and following set procedures for biodiesel production, safety can be guaranteed (Guy 2008). Additional notes on safety are included below;

a. Ignition sources around the system must be avoided at all cost.

b. Hoses connected to the system must be checked from time to time to avoid leaks on the system.

c. Acceptable ventilation should be provided in case of a methanol spill.

d. It is encouraged to always observe the processor or mixer several minutes after the mixing process, to verify that everything is going well.

2.9.2 Washing a Biodiesel Batch

During biodiesel production, the pH usually ranges from 8 to 9. Washing of biodiesel removes remaining catalyst, alcohol and impurities which reduces the pH to about 6. It is generally recommended to wash biodiesel so as to remove impurities of any sort.

2.9.2.1 Reasons for Washing Biodiesel

Below are some of the reasons for washing biodiesel:

- Removal of unreacted reagents and any soap remains.
- Biodiesel is also washed to remove catalyst that may attach to engine components
- Biodiesel when unwashed is alkaline and could damage engine parts. Washing it reduces the pH to about 6.
- Washing biodiesel helps to remove soap particles that may have formed during the reaction.

2.9.2.2 Washing Techniques

Common techniques exist for washing of biodiesel. This ranges from bubble washing, mist or agitated washing. The process of washing biodiesel involves mixing it with water. Water is heavier than biodiesel and absorbs the excess alcohol, catalyst and soap suspended in the fuel. After washing and settling, the water and the impurities in the water can be drained from the bottom of the container. Several wash cycles are generally needed. The first water drained off is usually clear. Excess catalyst in the biodiesel will form soap when mixed with water, and it takes a while for the soap to settle out. Depending on the method used, it takes roughly the same volume of batch in water to wash off the biodiesel batch.

- Agitation Washing: This means stirring water into the biodiesel, letting it settle and draining it.

- Mist Washing: This is spraying a fine mist of water over the surface of the biodiesel. Tiny droplets of water falls through the biodiesel and picks up impurities on the way down.

- Bubble Washing: Bubble washing is done by putting a bubbler in a layer of water beneath the biodiesel. The rising bubbles are coated with water, which picks up impurities as the water travels up and then back down through the biodiesel.

2.9.2.3 Drying the Washed Biodiesel

After washing, it is advised to allow the biodiesel to be dried. This can be done by keeping the biodiesel uncovered in a sunny atmosphere for a few days which can be easily achieved by a local producer. Alternatively, it could be heated to 50 ^{o}C for few hours. For the purpose of this research work, a simple approach for the washing was used. The water was then drained off the biodiesel mixer after settling. This may not be the most ideal approach but would be sufficient for a local producer with little expertise and education.

Chapter 3

Determination of Viable Operating Regime

3.1 Chapter Overview

This Chapter covers the following:

- Experimental procedure and laboratory trials.

- Experimentally determined viable regime in terms of process conditions for optimum biodiesel production for the developing economy.

- Discussion of observed trends and recommendation in relation to the small-scale equipment to be discussed in the next Chapter.

3.2 Experimental Apparatus, Set up and Procedure

3.2.1 Apparatus:

The equipment and materials used were as follows:

1. Infra-red thermometer
2. 1.5 litre conical bottom glass processor/mixer
3. Retort stand for the conical bottom glass processor
4. Sodium hydroxide NaOH pellets (lye)
5. Potassium hydroxide KOH pellets
6. Titration kit (as described in Chapter 5)
7. A 1 litre empty bottle (as many required collection of different biodiesel batches)
8. 0.5 litre glass beaker (for collection of dirty water from the process)
9. 2 litre bottle for collection of glycerin
10. Weighing scale to measure KOH or NaOH, accurate to 0.1 g
11. 1 litre empty container for mixing of KOH/NaOH with methanol (must have a leak proof lid)
12. Alcohols include: Methanol, ethanol and propanol
13. Funnel
14. Hot plate

15. Spatula (for collecting NaOH/KOH)
16. Petri-dish for lye/KOH
17. 100 ml conical flask (for collecting methanol)

3.2.2 Set up of 1.5 litre conical bottom glass mixer

The trials for this research work were done in a laboratory using the simple set up shown on Figure 3 below:

Figure 3: Set up of laboratory bottom glass mixer.

3.2.3 Standard Procedure for Biodiesel Laboratory Production

The standard procedures for biodiesel production from a laboratory point of view are enumerated below:

1. Collection and preparation of feed to be used. This may be pure or used vegetable oil. Used oil was prepared by pre-treatment (Refer to Testing the

biodiesel). For all experimental trials, vegetable oil of 200 ml was used throughout the study (whether PVO or WVO).

2. Heating of the vegetable oil: The PVO was measured and heated to between 65 to 75 ^{o}C with a hot plate or stove.

3. Measurement of catalyst: The catalyst was measured based on the quantity of PVO to be used. This could be sodium hydroxide or potassium hydroxide.

4. Mixing of catalyst with ethanol/methanol: With the aid of a scale, 50 ml of methanol was measured and poured into a 1litre glass container and 2 gram of NaOH was carefully added to the container. The container was swirled around thoroughly for not less than 25 minutes (KOH dissolved faster), to enable the NaOH to dissolve in methanol to form sodium methoxide. This took some time depending on the catalyst used.

5. Transfer of catalyst and oil into mixer: Both prepared catalyst and PVO were then poured into a mixer for proper mixing. Infra-red thermometer was used to ensure the temperature of the mixture was up to theoretical specification.

6. The reactor/mixer was swirled manually to ensure proper mixing took place while opening the valve from the bottom intermittently to reduce the pressure in the mixer. This was done for about 10 minutes (mixing can be achieved with an automatic mixer for large sized reactor with a pressure relief system included)

7. Reaction time observation: Afterwards, the separation of the two layers of glycerine and biodiesel occurred. This was also allowed for up to a minimum of 30 minutes to ensure complete reaction.

8. Separation of glycerine and biodiesel: At the end of the reaction time, separation of glycerine from biodiesel was done.

9. Washing of biodiesel: Biodiesel was then washed to remove impurities and unreacted substances before the product was collected for ASTM test.

For all experimental trials,
- Pure vegetable oil (sunflower oil) was used
- Waste vegetable oil (Domestic and fast food sources were also used)
- Industrial ethanol and methanol of 99% purity was used

- Industrial sodium hydroxide and potassium hydroxide was also used.

3.3 Factors to be Investigated:

The factors below were investigated while following the above procedure, in other to determine how these factors will affect small-scale biodiesel systems for developing economies. They include:

- Time
- Temperature
- Catalyst
- Concentration of catalyst
- Purity of alcohol

3.3.1 Effect of Reaction Time

Reaction time always has great effect on the result of the reaction in terms of yield. This was considered as a key parameter, as incomplete reaction resulted in biodiesel yield with more contaminants, which will then reduce the yield after washing. A rule of thumb of allowing the reaction to stay for not less than 30 minutes was used as a basis, to ensure quality biodiesel for the entire trial. This effect was studied ranging from 5 to 30 minutes using the same standard procedure at constant 100 gram of PVO/WVO, 20 gram of methanol/ethanol, 65 ℃ and 30 minutes respectively.

3.3.2 Effect of Temperature

This was also another parameter that affects the production of biodiesel which an unskilled or local producer needed to aware of. Following the same standard procedure, the trial was done by varying temperatures while other factors remained constant. The temperature ranges were 25, 35, 45, 55, 65, and 75 ^{o}C. At room temperature of 25°C, there was no impact on the mixture. The temperature of 75 ^{o}C was not exceeded as further increase resulted in no further noticeable change on the result (details on the result section).

3.3.3 Choice of Catalyst

This investigation was restricted to KOH and NaOH which was as a result of the objective of the study. The trial was done using both catalysts. Impact of cost was also considered as these two were readily available with reasonable cost. The view of using either catalyst for the developing economy is also supported in the work of Guy (2008).

3.3.4 Effect of Catalyst Concentration

Varying catalyst concentrations ranging from 0.5 to 2 grams were used for the trial. As earlier stated, most researchers have used 0.1 to 1.2 % (in relation to oil mass) of catalyst for biodiesel production. To investigate the possible effect of catalyst concentration on yield of PVO and WVO biodiesel, different concentrations of KOH (0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0 % by mass of PVO/WVO) were used to produce biodiesel. The feed oil quantity, methanol/ethanol quantity, reaction temperature, and reaction time used with the different NaOH/KOH concentrations were held constant at 100 g of PVO/WVO, 20 gram of methanol/ethanol, 65º C, and 30 minutes respectively. The number of levels considered for the KOH concentration implies 7 batches of triplicated experimental runs.

3.3.5 Purity of Alcohol

The effect of alcohol (methanol/ethanol) purity was also investigated. This was done at constant 100 g of PVO/WVO, 20 gram of methanol/ethanol, 65 ºC and 30 minutes respectively. Since 99 % alcohol purity was used, the purity effect on the reaction was investigated by decreasing the effect of alcohol by adding distilled water to the alcohol.

3.4 Results and Discussion

In this section, the results and trends observed from the trials will be discussed; recommendation for implementing these factors in a small-scale biodiesel system will also be evaluated.

3.4.1 Repeatability and Validation

According to Friedrich (2003), potassium hydroxide and sodium hydroxide are the two catalysts mostly recommended for transeterification reaction. For a developing economy or local producer, it was the most suited option because of the availability and cost consideration. However, most farmers would go for NaOH as it is the cheapest of both. To validate this study, both catalysts were used in all trials to get a broader understanding of the behavior of each catalyst in regards to biodiesel yield and quality.

Pure vegetable oil and waste vegetable oil was used throughout this study. Pure vegetable oil was mainly sun flower oil while waste vegetable oil was collected from domestic homes and restaurants. PVO and WVO were used since the developing economies that were considered are always dependent on WVO. For the trials performed, both samples of feed were used as this most ideally depicts a pilot result. Yield was also defined as the percentage of the feed oil that was converted to biodiesel

Repeatability: The results obtained after many runs were similar, hence average values were used for NaOH and KOH. For example, the trends observed while comparing relationship of biodiesel yield against temperatures are shown below:
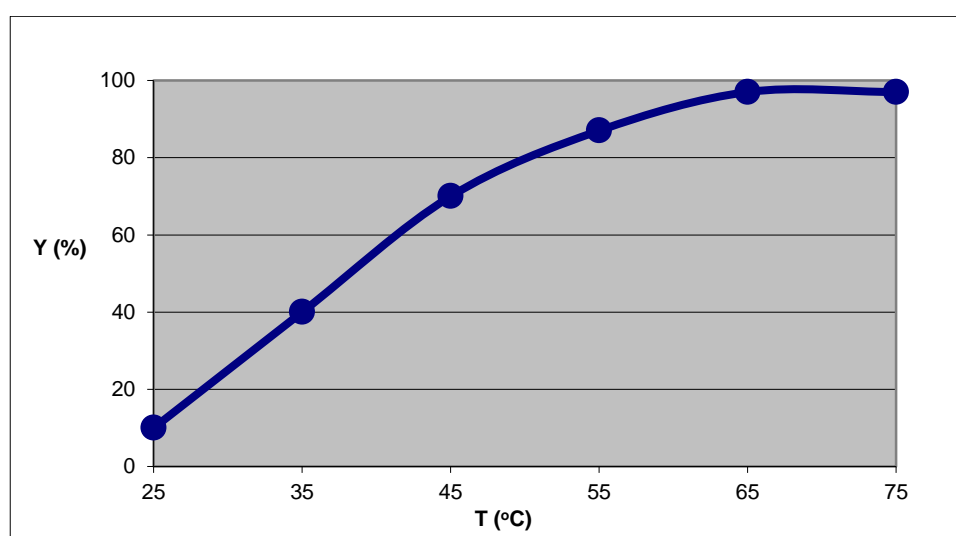
Figure 4: Yield versus temperature using NaOH (PVO).
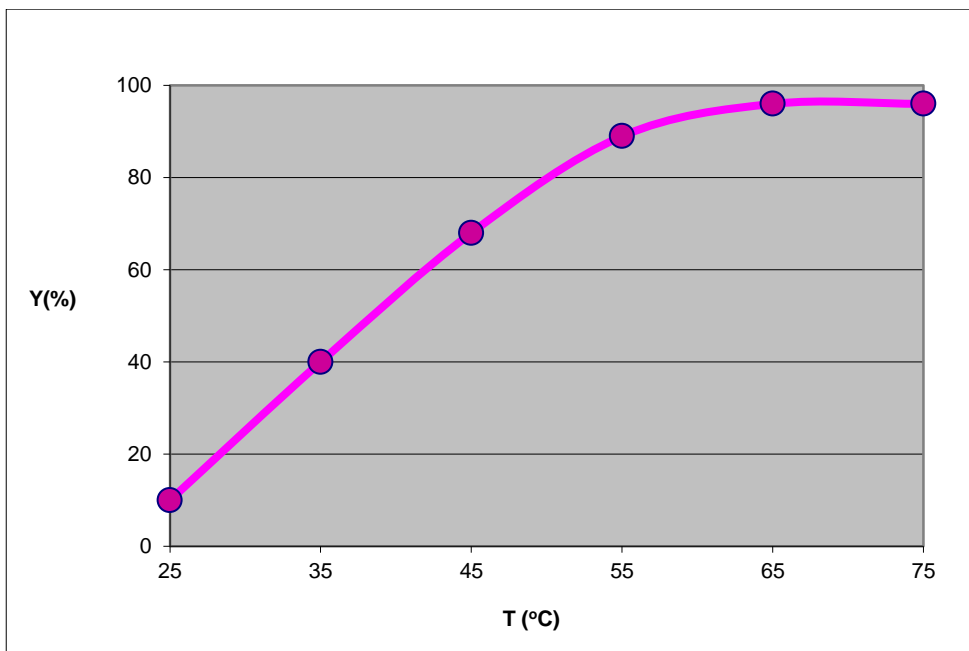
Figure 5: Yield versus temperature using KOH (PVO).
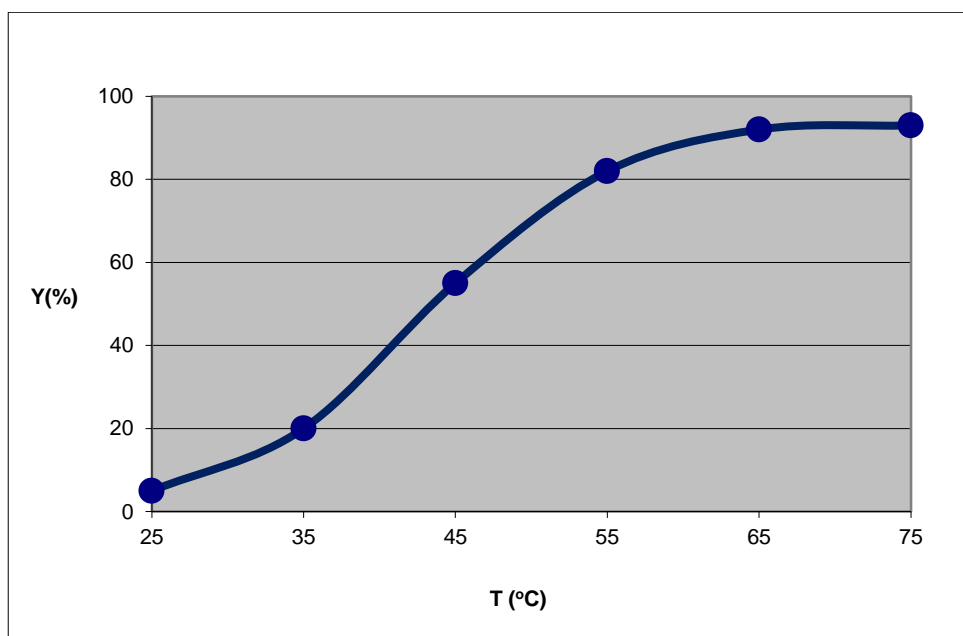
Figure 6: Yield versus temperature using NaOH (WVO).
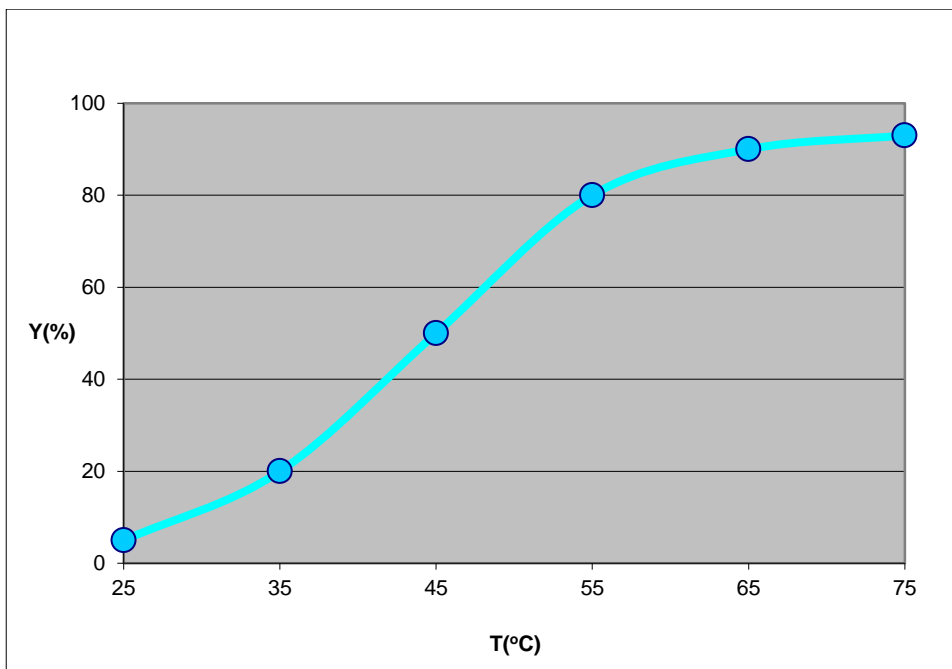
Figure 7: Yield versus temperature using KOH (WVO).

3.5 Investigation of Factors

3.5.1 Reaction Time

The effect of reaction time on yield for pure vegetable oil and waste vegetable oil using sodium hydroxide or potassium hydroxide is shown in Figure 8 below.
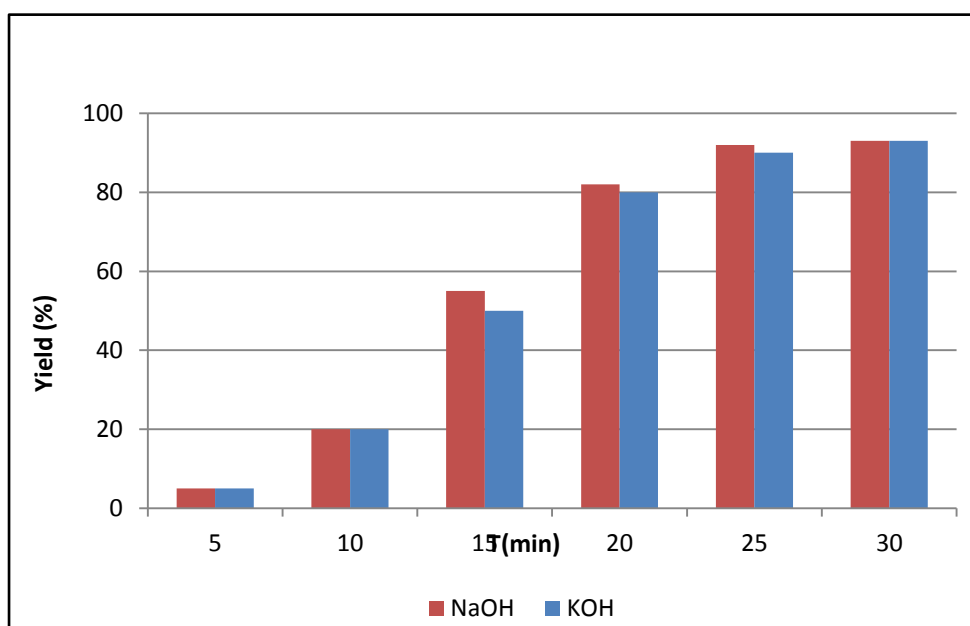
Figure 8: Effects of reaction time on yield.

The chart is a plot of biodiesel yield in percentage against time in minutes. This showed the effect of reaction time on yield as each batch reaction proceeded. The time on the horizontal axes was limited to 30 minutes as this was generally required for a complete reaction. From the chart, the biodiesel yield increased with time after the reactants were mixed. This continued to rise proportionally to the yield but appeared to stabilize at 25 minutes with little or no difference at 30 minutes.

Base-catalyzed transesterification reaction time is said to be proportional to yield (Colucci et al., 2005). During the trial, the reaction time was proportional to the methyl ester yield and constant when a particular time is reached. From the graph, it meant that after 20 minutes, 95-99 % conversion was reached which implied that the catalyst used had converted all the feed to biodiesel. The trend was the same regardless if using NaOH or KOH except for little variance on the yield as with other factors. Theoretically, a base catalyzed transesterification reaction was quick and was usually completed in a maximum time of 25 minutes, after all reactants were mixed.

In summary, it is strongly recommended that each batch be allowed to stay for more than 25 minutes after mixing to ensure that all the oil (PVO or WVO) is converted to biodiesel before the washing process. This will also help a local producer to maximize yield, drawing off glycerine and washing of the biodiesel batch. 30 minutes can then be used as a rule of thumb.

3.5.2 Reaction Temperature

The effect of temperature on yield for pure vegetable oil and waste vegetable oil using sodium hydroxide or potassium hydroxide is shown in figure 9 below.
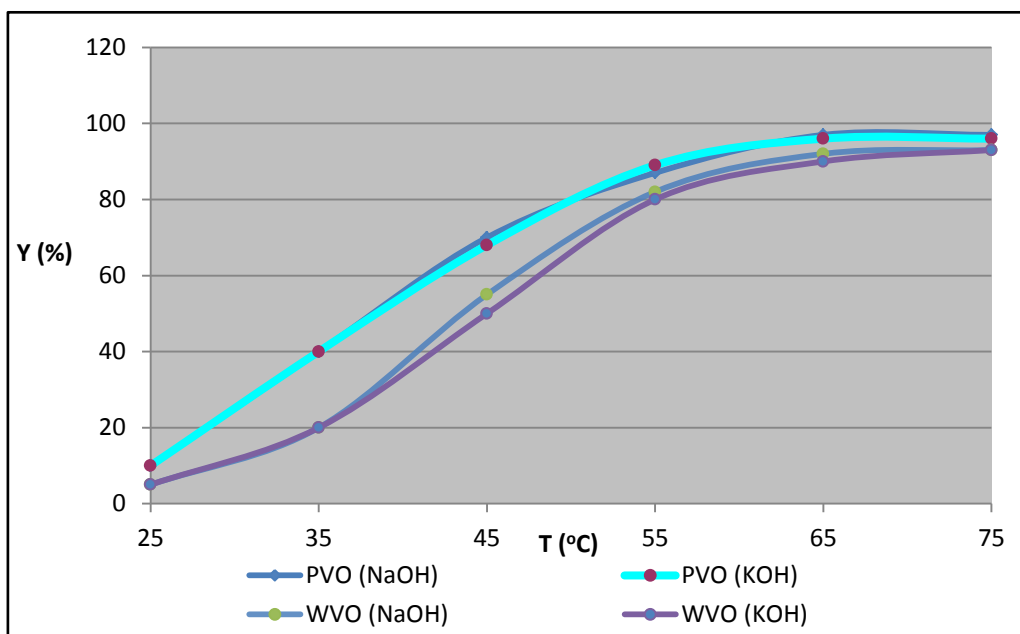
Figure 9: Effects of temperature on yield.

Temperature range of 25 °C to 75 °C was used for this trial. Also this was carried out using NaOH and KOH catalysts respectively. WVO and PVO were also used as feed for this trial. As the reaction started, the yield of biodiesel achieved for each catalyst and feed increased with temperature. Starting at a room temperature of about 25 °C, this was increased by 10 °C for each case until 75 °C. As the temperature increased, the yield remained fairly constant after 75 °C. The trial was stopped at this temperature, as further increase in temperature did not produce a significant rise in biodiesel yield. According to Canakci and Van Gerpen (1999), similar conclusions were reached, i.e. biodiesel via catalyzed reactions are usually best in the domain of 30 to 80 °C.

Equilibrium conversions increased substantially at about 10 °C rise in temperature during transesterification reaction, which also signified that the rate of reaction was strongly dependent on temperature. In summary, transesterification reaction is dependent on temperature increase (Alamu et al., 2007) and the trend shown on Figure 9, is in agreement with literature as well as fundamental theory.

In this case, two homogenous catalysts NaOH and KOH were used starting from room temperature up to 75 $^{\circ}$C. It was also important to note that PVO produced higher yield than WVO as shown in the trend. Further increase in temperature would generally increase energy consumption but would not produce significant increase in yield.

Therefore, lower temperatures below 55 $^{\circ}$C would greatly reduce the yield in each biodiesel batch. It was therefore encouraged to stay in the operating regime of 55 $^{\circ}$C - 65 $^{\circ}$C. For a local producer or developing economies, the temperature of the reactants in the mixer should be maintained within this regime using a simple thermometer. Maintaining this temperature range would result in an easy operation, which must be adhered to for good quality biodiesel. The graph also shows that increasing temperatures above this range will not necessarily increase the yield.

3.5.3 Effect of Catalyst Concentration

The effect of catalyst concentration on yield for pure vegetable oil and waste vegetable oil using sodium hydroxide or potassium hydroxide are described below in Tables 4 and 5

Table 4: Results for the seven batches of experiment with varying KOH concentration

Experimental Condition	Three Run Average Data for Seven Batches of Transesterification Experiements						
	Batch1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7
KOH Quantity (g)	0.5	0.75	1	1.25	1.5	1.75	1.75
Reaction Temperature ($^{\circ}$C)	65	65	65	65	65	65	65
Reaction Time (min)	30	30	30	30	30	30	30
PVO or WVO quantity (g)	100	100	100	100	100	100	100
Ethanol/Methanol Quantity	20	20	20	20	20	20	20
Biodiesel Obtained (g)	90.5	95	95.8	85.2	73.3	71.1	71.3
Glycerol obtained (g)	25.7	21.1	22.4	32.8	46.8	46.6	48.5
Losses (g)	4.3	4.4	2.8	3	1.4	3.8	1.7
Biodiesel Yield (%)	90.5	95	95.8	85.2	73.3	71.1	71.3

Table 5: Results for the seven batches of experiment with varying NaOH concentration

Experimental Condition	Three Run Average Data for Seven Batches of Transesterification Experiements						
	Batch1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7
NaOH Quantity (g)	0.5	0.75	1	1.25	1.5	1.75	1.75
Reaction Temperature (^{o}C)	65	65	65	65	65	65	65
Reaction Time (min)	30	30	30	30	30	30	30
PVO or WVO quantity (g)	100	100	100	100	100	100	100
Ethanol/Methanol Quantity	20	20	20	20	20	20	20
Biodiesel Obtained (g)	91.5	96.5	97.5	86	75.3	71.1	71.3
Glycerol obtained (g)	24.7	20.1	20	32	42.5	46.6	48.5
Losses (g)	4.3	3.9	3.2	2.5	2.7	3.8	1.7
Biodiesel Yield (%)	91.5	96.5	97.5	86	75.3	71.1	71.3
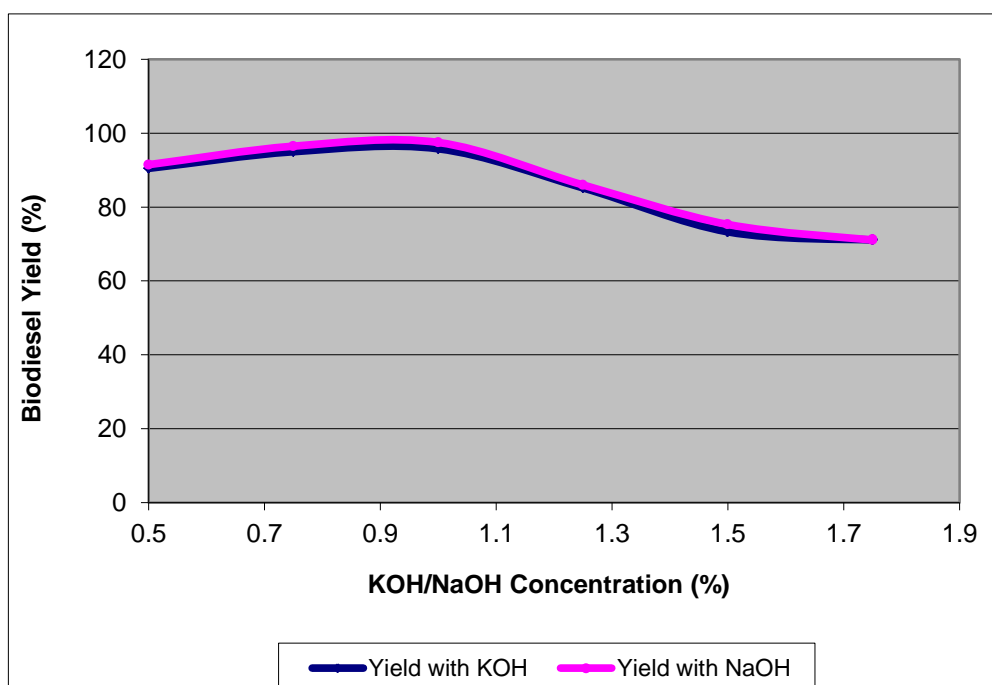
Figure 10: Effects of catalyst concentration on yield.

Three replicates of each of the laboratory transesterification experiments using different KOH concentrations, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0 % (by mass of

PVO and WVO), yielded average results presented in Table 4 and 5, representing three-run average results for experiment batches 1 to 7. From Table 4 and 5, different values of average PVO and WVO biodiesel yield, glycerol formed and losses recorded for the seven batches of the transesterification experiments are evident.

Similarly, 25.70, 21.10, 22.40, 32.80, 46.80, 46.60 and 71.30 g glycerol were formed with the respective yields of the biodiesel. The losses recorded in each run of the experiment were obviously some unreacted alcohol, residual catalyst, and emulsion removed during the washing stage of the production process. Results in Table 4 also revealed that increase in KOH concentration resulted in increase in biodiesel yield, only up to a certain concentration of KOH. Beyond this point, no further increase in biodiesel yield was achieved; hence an optimum concentration of the catalyst (KOH) exists. A plot of biodiesel yield against KOH concentration showed a peak biodiesel yield at 98 % with a corresponding KOH concentration of 1.0 % as evident in Figure 10. KOH concentration 1.0 % (in relation to PVO/WVO mass) can therefore be taken as optimum for KOH catalysed transesterification with ethanol under reaction conditions of 65º C temperature, 30 minutes duration and 20.0 % ethanol (by mass of PVO). A similar trend occurred with NaOH shown in Table 5 and Figure 10.

In summary, a maximum biodiesel yield of 98 % was obtained with KOH/NaOH concentration of 1.0 % under typical transesterification reaction conditions of 65º C temperature, 30 minutes duration and 20.0 % ethanol (by mass of PVO).

3.5.4 Purity of Alcohol

The effect of alcohol purity on yield for pure vegetable oil and waste vegetable oil using sodium hydroxide or potassium hydroxide are shown in Figures 11 and 12 below.
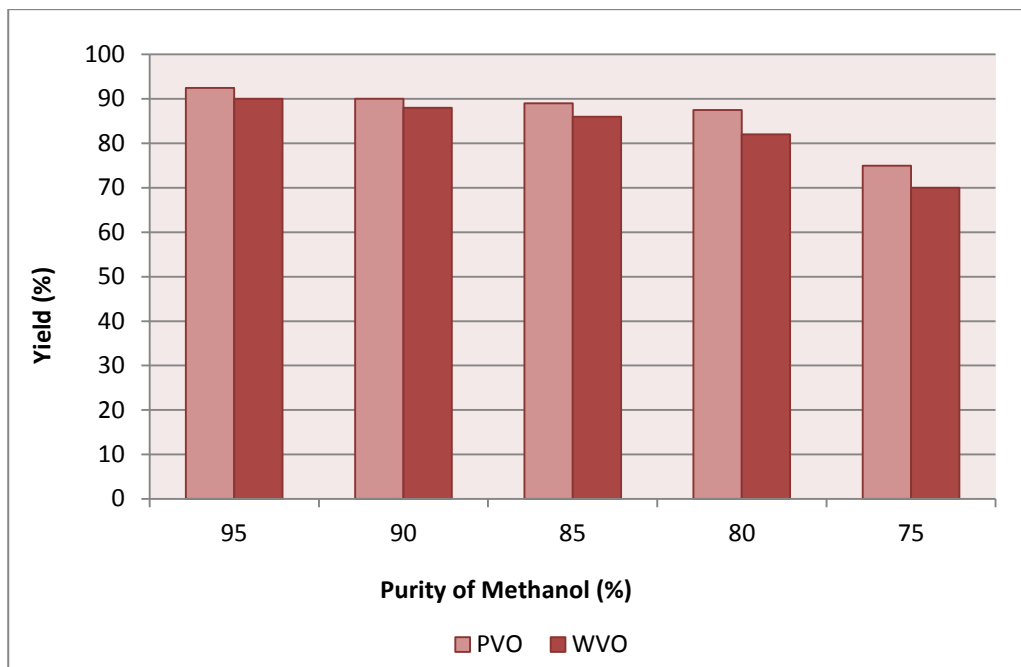
Figure 11: Effects of methanol purity on yield.
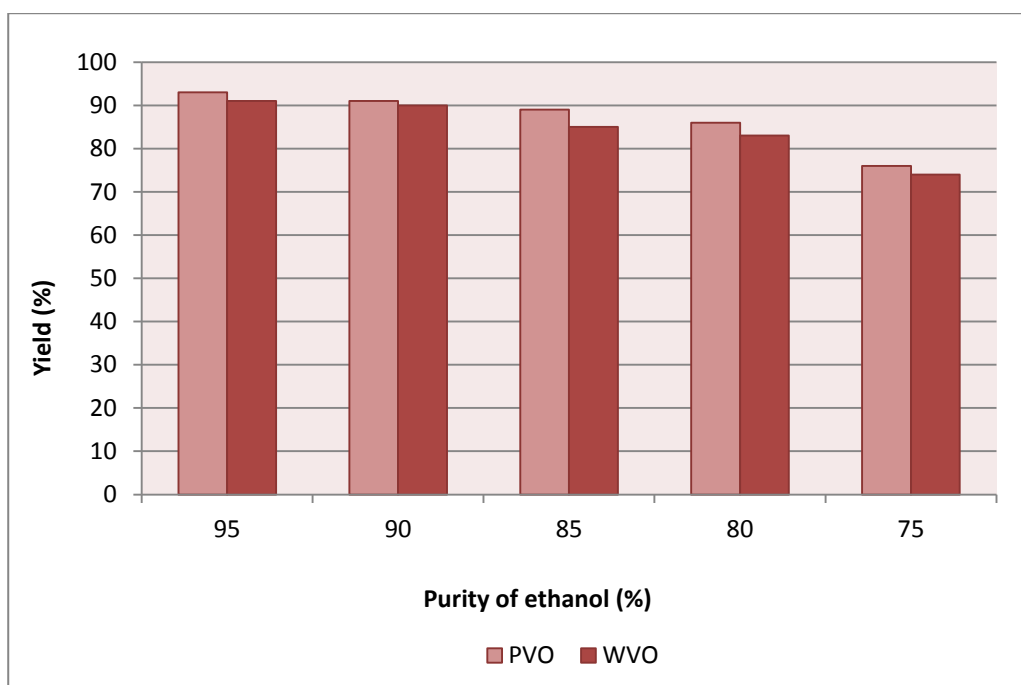
Figure 12: Effects of ethanol purity on yield.

A steady temperature of 65 $^{\circ}$C was used for this trial. This was carried out using NaOH and KOH catalysts respectively. WVO and PVO were also used as feed for

this trial. In addition, 99.9 % methanol and ethanol was used and this was diluted using water to 95 %, 90 %, etc. purity as required (see step by step method on experimental method for details). The experiment was then carried out for different purities shown on the graph and the yields were plotted against the purity. The purity was stopped at 75 % as above this level, the biodiesel batch contains water that can affect the progress of the transesterification reaction in each case.

According to Kusdiana and Saka (2007), it is strongly recommended that a pure methanol or ethanol be used for base catalyzed esterification reaction. This will enable a consistent quality in the biodiesel produced. If the alcohols used are contaminated, this will greatly affect the yield of the batch produced. Therefore, maintaining the purity of alcohol used must not be compromised, particularly where a local producer may vary on the range of feedstock that might be used. This will also ensure a safe operation without complexities. It will also enable the biodiesel quality to meet ASTM standards for biodiesel.

3.6 Comparison of Some ASTM Chemical Properties

As earlier stated, biodiesel and petroleum diesel vastly differ in their chemical compositions. These differences give biodiesel different physical and chemical properties. Part of the objective of this study is to compare approved ASTM chemical properties of petroleum diesel, to that of varying vegetable oils (PVO and WVO) as supported in the work of Mittelbach and Remschmidt (2005) and chemical properties of batch results generated during this study.

The first two columns of Table 6 below contains some chemical properties of petroleum diesel and sunflower oil ME (Mittelbach and Remschmidt, 2005) while the remaining columns labeled Trial 1 to Trial 9 represents some of the ASTM result gathered during the trial from different batches produced (refer to Appendix B: Laboratory test results).

Table 6: ASTM result comparism of petroleum diesel, sunflower oil ME and batch produced during investigation

	1	2	3	4	5	6	7	8	9	9	11	12
CHEMICAL PROPERTIES	**Units**	**Fossil Diesel**	**Sunflower Oil ME**	**Trial 1 PVO**	**Trial 2 PVO**	**Trial 3 PVO**	**Trial 4 PVO**	**Trial 5 WVO**	**Trial 6 WVO**	**Trial 7 WVO**	**Trial 8 WVO**	**Trial 9 WVO**
Density	Kg/m^3	835	835	895	895	829	837	811	821	857	863	843
Viscosity	Mm^2/s	2.7	4.2 - 4.4	5.4	4.9	4.6	6.3	4.4	4.3	5.3	5.1	4.7
Cloud Point	^{o}C	-15	0 - 3	1	2	-1	0	-1	1	-1	0	1
CFPP	^{o}C	-18	-3	-4	-4	-6	-5	-6	-5	-7	-7	-6
Flash Point	^{o}C	50 - 80	164 - 183	139	142	142	153	160	152	163	153	149
Water Content	%	-	-	0	0	0	0	0.002	0.05	0.006	0.008	0.007

PVO – PURE VEGETABLE OIL
WVO – WASTE VEGETABLE OIL

Even though biodiesel generally has higher viscosity (Demirbas and Demirbas, 2007), Table 6 above showed that viscosities obtained from column 1 to 9 were close to that on column 3. Biodiesel has higher cloud point and pour point compared to petroleum diesel; however the cloud point obtained from these trials were also close to that on column 3 as supported in the work by Mittelbach and Remschmidt (2005). Flash points were also close to column 3 results. Water content of PVO differed slightly from that of WVO because of the nature of both feeds.

In summary, this shows that biodiesel batches produced during this study are fairly acceptable. It therefore implies that it is possible for a producer in a developing economy to obtain close results if these recommended regimes are used.

3.6 Summary

From the discussions of the trends obtained at different trial conditions, we can conclusively say the following;

1. The best operating regime is between 55 ^{o}C to 65 ^{o}C. Further increase in temperature would not increase the product yield. From an energy conservation point of view, this means more cost to the entire process.

2. 99 % alcohol purity must be maintained in order to not jeopardize the quality of the batch produced.

3. As a rule of thumb, 30 minutes should be allowed before the washing of each batch can commence. This will enable a complete reaction with optimum yield to be achieved for each batch produced.

4. The best operating regime for concentration of catalyst weight per weight of oil is between 0.75 to 1 percent. Further increase in concentration of catalyst with regards to weight would not increase the product yield. This also provides a guide that has some cost implication.

In conclusion, to evaluate batch biodiesel options for developing economies with focus on base-catalyzed transesterification, these conditions must be adhered to Table 7.

Table 7: Summary of recommended viable regime

KEY CONDITIONS	BAD (Option 1)	GOOD (Option 2)	EXCELLENT (Option 3)
Reaction Time (minutes)	0 to 5	5 to 20	20 to 30 (or more)
Catalyst Concentration (%)	1.5 to 1.75	1.25	0.75 to 1.0
Reaction Temperature (^{o}C)	0 to 35	35 to 45	45 to 75
Quality of biodiesel	less than 50%	51 to 89	90-100%
Ease of Operation	Fair	Good	Very Good

Chapter 4

Equipment Design

Aim: Develop simplified small scale equipment that is inexpensive, easy to obtain, set up and operate.

4.1 Processor Design

According to Guy (2008), two types of processor design are generally used. The advantages and the disadvantage of each was also considered. They include;

    4.1.1   Appleseed design

    4.1.2   Cone tank design

4.1.1 Appleseed Design

Appleseed-type processor basically uses a hot water heater and some external wash tanks. With this design, the oil and water is heated, then washed and dried in separate tanks. A separate carboy container is usually used for mixing the methoxide. This was a popular, do-it-yourself style, because of the fairly simple design and the common availability of water heaters. Built properly, this type of processor will make quality fuel (Guy, 2008).

4.1.1.1 Advantages of Appleseed (Flat-Bottom) Processor

According to Guy (2008), the advantages of appleseed reactor are as follows:

1. The water tank is made from steel, which makes it very long-lasting.
2. Tanks made from steel are highly resilient to chemicals.
3. A built-in heater makes it easy to preheat the oil.
4. It can also be made predominantly fumeless.
5. It also does not require welding, contrast to processors made from steel barrels or from scratch.
6. There are free instructions about them on the internet.
7. The plans required are offered at a reasonable cost.

4.1.1.2 Disadvantages of Appleseed (Flat-Bottom) Processor.

According to Guy (2008), the disadvantages of appleseed reactors are as follows:

1. Processors are not transparent, which makes it difficult to see through the tank while processing. If there are challenges of glop or soaps, it cannot be detected. Observations can only be made via the sight glass.

2. Processors are also very difficult to clean if the user ends up making glop.

3. It does not have a sharp and conical base, as such separation and draining is difficult. Therefore, there is a possibility of having untapped glycerine in the tank, causing contamination in the fuel.

4. There might be a need for a separate heater to assist in pumping during the winter season.

5. In comparison to poly tanks which come in various sizes, tank sizes may be limited.

6. Unskilled producer can find it difficult to understand easy free designs available on the internet, if they do have access to the internet. Appleseed design requires good skill.

7. It demands a separate mist washing tank, which adds to the foot print area needed.

8. If the heating element is mistakenly switched on while the processor still contains the oil/methoxide mixture, the methanol can be ignited.

4.1.2 Cone Tank Design

Another way of making biodiesel is by using polyethylene cone-base tanks or processors (Guy, 2008). One tank is majorly used to prepare the methoxide while the other serves as the processor or mixer for the biodiesel. After washing the fuel, it can be dried inside the processor or in another external tank. This is a growing design for most manufacturers as the biodiesel, glycerine and water can be seen because they are transparent. This design of mixer when built properly, will always make a high-quality, ASTM- grade fuel (Guy, 2008). The advantages and disadvantages of cone tank design are shown below:

4.1.2.1 Advantages of Cone Bottom MDPE Processor

According to Guy (2008), the advantages of cone bottom MDPE (Medium-density polyethylene) processors are as follows:

1. This type of process enables you to see the level of fluid inside the tank without removing the lid. The user can look inside to see what is happening.
2. Conical bottom processors allow for better mixing and complete separation as compared to the flat-bottom wash tanks.
3. It is very easy to totally drain glycerine without any remains that can contaminate the fuel.
4. It is also very easy to bubble or mist in the same processor or mixer.
5. It uses a light weight tank.
6. MDPE tanks are very resilient to chemicals and they are extremely durable.
7. If a glop batch occurs, it is easier to clean out.
8. It is easy to build in a methoxide mixer into the main processor. Thus, all the mixing can be done in the cone bottom tank.
9. It is easy to make a spark-free mixing system for the methoxide tank.
10. This system can be made mostly fumeless, by ensuring the lid is sealed and adding a vent tube to a hose leading to the outside.

4.1.2.2 Disadvantages of Cone Bottom MDPE Processor

According to Guy (2008), the disadvantages of cone bottom MDPE processors are as follows:

1. These types of tank are rated 65 ^{o}C and will pose problems if the oil is overheated. Hence it is recommended to operate below 65 ^{o}C. Methanol starts evaporating at 65 ^{o} C, hence this temperature should not be exceeded.
2. There is basically no straight forward instruction for this type of processor.
3. Cone shaped processors may require a little more expertise if one decides to build from scratch.
4. Heating inside the tank with direct element is strongly discouraged.

4.2 Summarized Design, Selection and Essential Elements

From the comparison of the two designs, advantages and disadvantages, the cone bottom process type was selected. This was selected because the user requires minimum skill to eliminate some of the difficulties invoiced. Flat-base designs are difficult to use because of the disadvantages involved in it. A typical example of this is an industrial 200 litre drum. Even though they might be available easily, the fact that they are flat and not transparent makes it difficult for a user from a developing economy to use.

From the local survey, producer A was able to use Appleseed design because of his engineering background and industrial experience. As a result, it is recommended for a local producer to buy a cone-shaped processor as they are easy to handle during production. The investment required as a result is mainly the first cost involved.

To summarize the design, the following items are required based on selecting a cone shaped design using 30 litre as basis:

1. 30 litre volume cone bottom MDPE processor – Some designs do have a feed tank, processor and separating or wash tanks set up as one system. To minimize cost for small-scale, only the cone bottom processor will be used and this will also act as the separating/wash tank.

2. Processor stand.

3. Manual hand mixer – this will be used to create a batch mixing in the processor after methoxide is mixed with the oil (e.g. 3 minutes).

4. Fittings – Brass valves are recommended.

5. Reinforced PVC Hoses – This will be used to connect from the bottom of the processor into any collecting container.

6. 20 litres transparent paint buckets – Graduated ones are recommended if available.

7. 5 litre sized funnel.

A simplified design is represented in Figure 13.
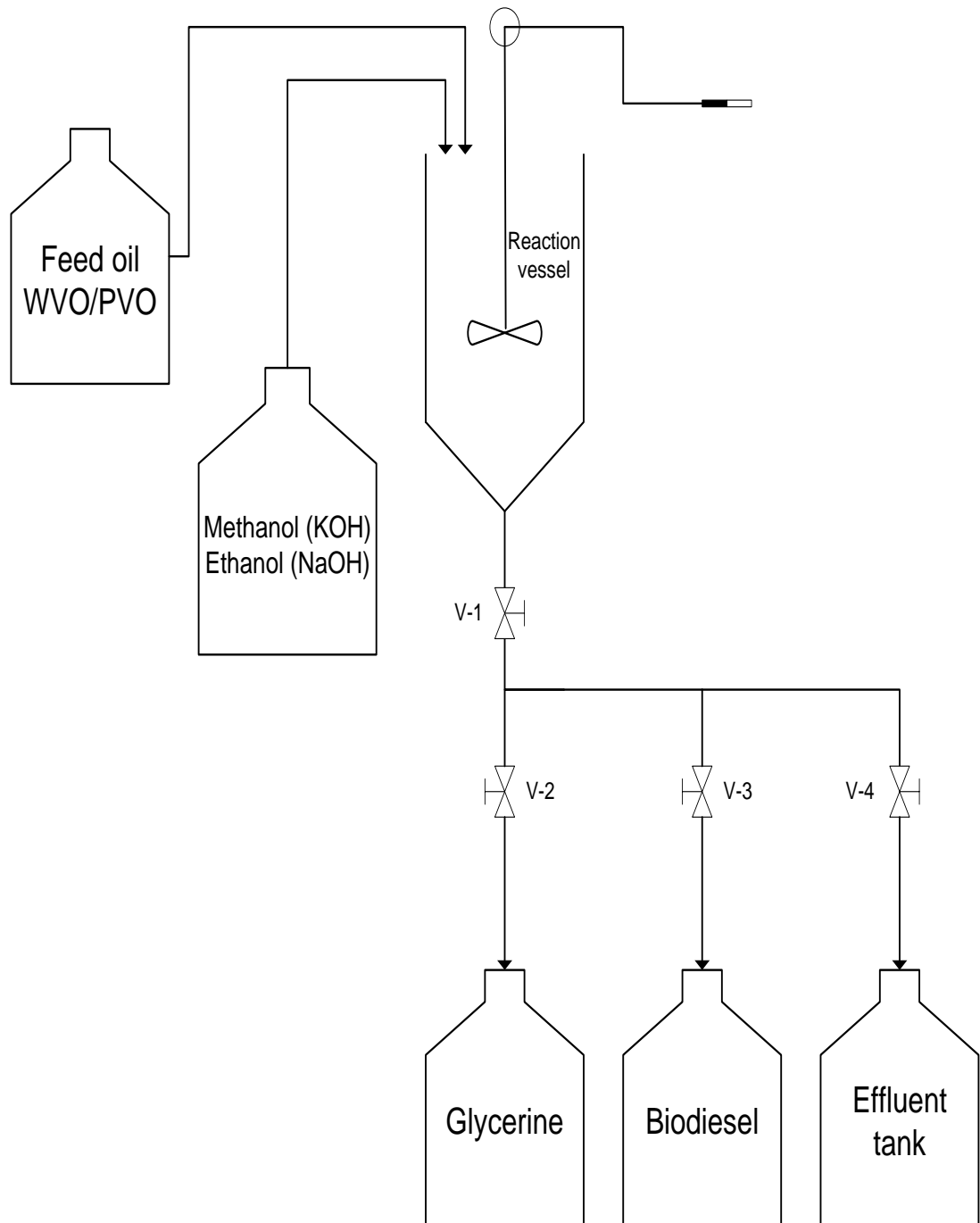
Figure 13: Simplified diagram for equipment design.

4.4 Conclusions and Recommendations

From this Chapter, the following conclusions and recommendations are made.

1. Even though a cylindrical drum or bucket may be easy to get, a cone shaped design is recommended as it makes the process of making biodiesel easy for a local producer.

2. The major investment to be made based on this design is the initial purchase of a 30 litre cone shaped processor or mixer.

3. A maximum temperature of 65°C should not be exceeded because of the strength of the MDPE. From earlier investigation on temperature, 65°C falls into the optimum temperature range for biodiesel production.

The recommended basic items for local producers are:

a) Cone bottom MDPE processor
b) Processor stand.
c) Manual hand mixer
d) Fittings
e) Reinforced PVC Hoses
f) Transparent graduated plastic buckets
g) Funnel

Chapter 5

Guidelines : Pre-treatment, Titration and Washing of Biodiesel

5.1 Testing Oil on Site

Fresh or unused oil still remain a vital source for biodiesel production. However, this is not feasible for developing economies and farmers to use because of the cost involved in it. It therefore implies that WVO will remain a vital focus for local producers and that the testing of feed for production needs to meet a minimum standard. Once a new source of used oil has been located, several questions about the oil need to be answered. Ask a responsible person what goes into their oil barrels. Is it mostly beef tallow from hamburger, etc. If so, it will have a high gel point and may turn rancid quickly. It is desirable to have oils mostly from fried foods, not beef tallow. Then find out how often they change their oil. If they are typically a busy restaurant i.e. open for 3 meals a day, and changes it less than every 7 to 10 days, tests are required to quantify the contaminants. Tests on used oil sample to determine how good or bad they are for proper use for a small-scale biodiesel production can be in the following ways:

- Visual test
- Titration test
- Water test: This is divided into simple and qualitative work test.

5.1.1 Visual Test

To test, first inspect it visually to see if there is anything obvious about the appearance, or sniff it to detect a strong smell that indicates that it is overused. The oil may range from golden in colour to fairly clear, to dark amber and quite dirty. In summary, the procedure is basically to pour a quart or a gallon into a clear jug with a lid to allow you to visually inspect it, then if it looks fine, you can do a titration test. If that passes, take the sample home and do a water test and make a mini-batch with it for your final test (Guy, 2008).

5.1.2 The Titration Test

The second test to do on a new source of used oil is a titration test. This is probably the most important test, since it will tell you how **"used"** the oil actually is. If it has been used for a long period, it will contain a lot of free fatty acids (FFAs), which is bad for your biodiesel production. This will be discussed in detail later in this Chapter.

5.1.3 Water Test

Any water present in the oil does not simply boil out while the fryer is in use (even though a fryer is running much hotter than the boiling point of water). Food particles and other conditions help retain small amounts of water in the restaurant oil, so one might usually get stuck with some water whenever they pick up their free cooking oil. Water in oil can cause you to make more soap when making your biodiesel. It can also result in making glop (a totally ruined batch) or an incomplete reaction, as compared to using drier oil. The drier the oil is from water, the better it is for use.

5.2 Simple Water Test

To test for water content, simply heat a small sample (a quarter cup) in a small pot, and see if it sputters or bubbles when it reaches the boiling point of water (100 $^{\circ}$C). It is advisable to stir while heating; otherwise it can build up a steam pocket and suddenly splash boiling oil all over the individual performing such an exercise. Note that all used oil will bubble and sputter. It is the amount of bubbling and sputtering that matters. Basically, if it really sputters and pops a lot, there is likely lots of water in it. If it sputters just a little, it is probably really good (containing little water). The best approach is to test various oils from several restaurants, and then compare, while working carefully and cautiously, and keep notes. If any oil does not sputter much, then that is probably the best of all the other options. In general, it is not easy to describe what is acceptable except by trial and error. This test gives us only a basic idea of the water content and a sample of oil should not be entirely ruled out on the basis of this test only (Guy, 2008).

5.3 Quantitative Water Test

There is also another way to measure the quantity of water in the oil. In brief, you weigh it, heat it to drive out the water, weigh it once more, and then perform the basic calculation. For one to perform a quantitative water test, an accurate scale that can measure weight precisely with a resolution of 0.1 g or better is required. For more accurate testing, the scale should have an upper capacity of about 500 g or more. If the sample is smaller, then top a capacity of 100 g is also acceptable (Guy, 2008).

5.3.1 The Procedure

To carry out this test, it is recommended to wear safety glasses (hot oil can sputter and erupt with steam pockets), a long-sleeved shirt, pants, and leather gloves (to handle hot containers). Hot oil also needs to be handled with care as it can cause serious burns. The procedure is as follows:

a) Find a microwavable container such as a glass jar, to put an oil sample in with good heating resistance at the operating temperature.

b) Weigh the empty container to the nearest tenth of a gram and record.

c) Take a 300 ml to 400 ml sample of oil and place it in your container. The sample should be a representative of all the oil to be reacted. It is recommended to shake the oil up a bit, and then take the required sample.

d) Weigh the sample in the container and record the value of the weight. Subtracting the weight of the container gives the actual weight of the oil. Record the oil weight (wet oil weight).

e) Heat the sample in a microwave oven until the oil reaches a temperature of 121 $^{\circ}$C. The sample should be stirred often while heating to avoid steam pockets from erupting hot oil all over. Checking of the temperature is best monitored by an infra-red thermometer.

f) Allow the sample to cool for 10 minutes or a little more. This allows any residual emulsified water to evaporate and it is safer to handle. Stirring during this time will help to ensure that all water escapes.

g) Weigh the sample again and record the weight. Subtract the weight of the container. This is the oil "dry weight." For accuracy, the whole sample needs to be heated to a point where all the weight stops going down on the weighing balance. It is also safe to make the assumption that if the sample has reached 121 ºC and there is no boiling, the water did evaporate.

h) The difference between the wet weight and dry weight is equal to the weight of the water that was in the original sample. Dividing the water weight by wet oil weight multiplied by 100 gives the percentage.

It is strongly recommended not to use oil with more than about 2 or 3 percent water, as it would be equivalent to more than 1gallon of water for every 50 gallons of oil to be processed.

5.4 Titration Tests for FFAs

Titration is a laboratory procedure that allows us to determine the concentration of an unknown reagent using a standard concentration of another reagent that chemically reacts with the unknown. This standardized solution is called the **titrant.** One needs to have a way to determine when the reaction of the biodiesel will be complete. This completion is referred to as the **end point** or more technically, as the **equivalence point.** When that end point is reached, all the unknown reagents have reacted with the standard titrant and some kind of chemical indicator solution will give this notification. In simple biodiesel terms, titration basically tests the presence and concentration of FFAs in waste restaurant fryer oil (Guy, 2008)

FFAs are a chemical component of the cooking oil chemically known as a triglyceride. A triglyceride has a glycerine molecule as its base, attached to three long-chain fatty acids. The more oil used, and the higher the temperature it reaches, the greater the chance that some of its fatty acids will break off the triglycerides and end up as FFAs. The more FFAs there are, the harder the oil is to process because these FFAs form soap in the biodiesel making process. The more the soap, the harder it is to wash. In addition, oil with a high FFA will not fully convert, meaning that a lot of undesirable and harmful components are left behind. The titration performs the

catalyst/free fatty acid reaction on a very small scale, which we basically use pH values to measure. Historically, chemists have figured out that when all the FFAs have been turned into soap, the pH of the solution will rise to a value of 8.5, which happens to be at the colour change point of phenolphthalein indicator. A homemade titrant made from the cooking spice turmeric can also be used. Turmeric indicator solution works the same as phenolphthalein. Phenol red can also be used, though it is slightly less accurate (Guy, 2008).

5.4.1 Why Titration is Necessary

Simply put, the titration analysis is used to determine the free fatty acids content of the used cooking oil so that you will know how much catalyst to add to your large batch to achieve a complete reaction. Methanol and vegetable oil will not react to make biodiesel by themselves, so catalyst was added to complete the reaction. Because the excess FFAs consume some of the catalyst and end up making soap, more catalyst should be added to sacrifice for the excess FFAs (Guy, 2008). If too much is added, it may result in more soap and risk a failed batch. Since the precise catalyst must be added, a titration test is done that measures the amount of FFAs in the oil. A titration test takes less than a minute to do and is relatively simple, even though at first it may seem complicated. The test is done by mixing and reacting a small sample of the WVO with an accurately measured catalyst or water reference solution (Guy, 2008).

5.4.2 How to Titrate

Although titration can be performed by different indicator selections, the best are phenolphthalein and turmeric. This titration description was done using turmeric as it is considered to be the best titrant, and can be made at home. These procedures have also been written for titrations using KOH.

5.4.3 Titration Kit List

Guy (2008), recommended some items required for this titration as follows:

     a) Isopropyl alcohol.

b) Indicator: pH meters are poor substitutes for a simple indicator solution. Meters for testing pH require meticulous maintenance and constant calibration using a standard solution to set the high end of the range and another to set the low end. Therefore, it is better to stick with the chemical indicator solution.

c) Catalyst: KOH or lye, 1 gram for titrations.

d) Empty 1 litre bottle: These are bottles used to store 1 litre of the titrating fluid in and to make a mini-batch in. New plastic or MDPE containers with tight-sealing lids are best.

e) Distilled water.

f) Eyedropper or syringes.

g) Graduated measuring container: Accuracy is important; hence graduated cylinders are perfect for this. Graduated cylinders are the most accurate as they are tall and narrow.

h) Mixing containers: When titrating, label one to use as the titration container that you do all the testing, label a second one for holding a small amount of the reference solution and label a third one to hold a small amount of the alcohol.

i) Rags and paper towels.

j) Scale: When mixing your titrating reference solution, you will need a scale that is accurate down to 0.1g or finer. The accuracy is important in other to avoid failed batches. The small scales that read up to around 200 g work best for this.

k) Wash bottles.

5.4.4 Preparing the Titration Reference Solution

The titration reference solution is a combination of distilled water and KOH (or lye). For simplicity, KOH will be used. Titrating fluid is the reference fluid when doing titrations. It is made by dissolving 1 g KOH into a 1 litre of distilled water. To make this solution, pour exactly 1 litre of distilled water into your container (which should be clearly labeled), then add exactly 1g of KOH. Put the lid on tightly and shake the

container until the KOH is completely dissolved. This quantity will last quite a while and a small amount of this fluid can be used many times over the course of several months (Guy, 2008).

Accuracy is important, hence if there are no accurate scales, there is another way accuracy can be achieved. First, measure out 10 g of catalyst and dissolve into this 1 litre of distilled water. Then take 100 ml of this water and mix with 900 ml distilled water.

5.4.5 Making the Titration Indicator Solution

Although phenolphthalein indicator can be used, turmeric indicator solution will be used because it is considered highly accurate and can be made with a cooking spice. Turmeric can be purchased at most grocery stores or health food stores. Here are the details of how to make this indicator:

- Thoroughly mix turmeric with 90 percent or better isopropyl alcohol in the following proportions: 1 part turmeric to 5 parts alcohol.
- Allow the mixture to settle until most of the turmeric has settled out.
- Decant the liquid into a dispenser bottle with an eyedropper, pipette, or similar device.

5.4.6 The Titration Procedure

This is the procedure for using turmeric as your indicator. Note that this may seem slightly different than other methods one may come across on the internet. In comparison, it should be the same, except one can use double the amount and then divide the results by 2, which gives a slightly more accurate reading (accuracy is important to avoid failed batches). One may use 4 times the normal amounts and then divide the result by 4, but using two times and dividing by two gives sufficient accuracy (Guy, 2008).

While using turmeric, one needs to be observant of any colour change, not a specific colour change. The titrant will start out mostly colourless, but slightly yellow. When it changes colour it may appear pink, purple, or red toned. As long as it changes

colour and holds that colour for 15 seconds or longer, that is all that matters. It will often lose the colour after 20 to 30 seconds, but that is okay. Do not look for solid colour, just a colour change all throughout the liquid. According to Guy (2008), the titration procedure is as follows:

a) Using the alcohol syringe or eyedropper, draw up 20 ml of alcohol into the syringe and dispense into the titration container. This does not have to be exact, as the alcohol is only a carrier.

b) Add roughly 5 or 6 drops of turmeric indicator solutions to the alcohol and swirl around well to mix.

c) Blank titration. This neutralizes any acid that may be in the alcohol, making the titration more accurate. Usually, it will take only a drop or two. If it starts going bad, it may take a dozen drops.

d) Fill one of the eyedroppers with some of the reference titrating fluid. Swirl the alcohol/turmeric mixture in the titration container, and then slowly begin to add some titrating fluid to the mixture, a drop at a time until the alcohol just starts to turn a permanent colour throughout, and then STOP. When this is done, next step is to perform the test on the trial sample.

e) Using the other oil eyedropper, add to the alcohol exactly 2 ml of the oil to be titrated. Warm oil (about 38 $^{\circ}$C) is best, as it will dissolve in the alcohol more easily.

f) To warm the oil and alcohol mixture further, place the solution into a microwave oven and microwave until the first bubble appears (5 to 10 seconds), then stop. Note that this step is not absolutely necessary.

g) Swirl the solution to mix the oil and alcohol together. The mixture will be a murky yellow, but the exact colour is not the important just yet.

h) Next step is to fill the titration eyedropper with exactly 5 ml of titrating fluid and start adding it, about ¼ ml at a time, into the titration container while swirling the mixture constantly. Keep swirling and adding drops until the entire solution changes colour and lasts for 15 seconds or more while swirling. Keep swirling all the time, as it will often turn colour, then back to yellow, until you have added enough to fully neutralize the FFAs.

i) Observe how many milliliters it took and record the number. Since double the amount is being used, divide this number by 2. Write this final number down too, as this is the titration number.

j) To ensure accuracy, wipe the titration container out, and then repeat the test once or twice. Use the average reading from these tests as your final number. This repetition is vital for accuracy.

Example: If the above steps are followed and 2 ½ ml of titrating fluid was used, then divide that by 2, which will give a final acid number of 1 ¼. That is the number to be used in order to determine how much lye (NaOH) to add to a larger batch.

The titration should be done with the same catalyst that will be used to make the biodiesel. If lye will be used, also use that to make your lye/water reference mixture. If KOH will be used, use a gram of that to make a water/KOH mixture instead. Simply put, all that needs to be remembered is 20 ml alcohol, 5-6 drops indicator, 2 ml oil, 5 ml titrant.

5.4.7 How to Use the Titration Information

The titration will give us a number (technically called **acid value** or **acid number AN**). It is known that the free fatty acids will consume some of the catalyst during the biodiesel-making process, so this is compensated by adding a specific amount of catalyst to overcome the free fatty acids so that the rest of the catalyst can continue the biodiesel reaction (Guy, 2008)

For every 1 ml titration result (that is, the acid number), an extra 1 g of lye (on top of the base amount) for each litre of oil/FFA that is reacting is required. This is to compensate for the side reaction caused by the FFA content. This acid value or acid number can also be known as the **Titration Number (TN).**

5.4.8 Simple Calculation of the Required Alcohol and Catalyst

To calculate the amount of NaOH or KOH to use, people generally use either the KOH/NaOH calculator that is common these days on the internet. This usually will eliminate the possibility of making a mathematical mistake and ruining a batch because of that.

Recommended Methanol Quantity

According to Guy (2008), the required litre of oil is multiplied by a factor of 0.22 which gives you the required volume of methanol that must be used. Example;

Volume of methanol for 10 litres of oil = 10 * 0.22 = 2.2 litres of methanol.

For this study, a factor of 0.25 was used during the trials which is equivalent to dividing the required litres of oil by 4. Example,

Volume of methanol for 10 litres of oil = 10 * 0.25 = 2.5 litres of methanol

Using Lye (NaOH):

A basis of 5 g of NaOH is generally required against 1litre of PVO (Guy, 2008). Hence if 5 litre of oil is used, then 25g of NaOH will be used.

5 litres of oil = 5 * 5g = 25 gram of NaOH

If a waste vegetable oil (WVO) is used, an extra gram of NaOH is required for every TN. This is simply to eliminate the free fatty acids in that oil. So if the final TN is 1.5 ml, this is added to the base amount of 5, giving a total of 6.5. This means that 6.5 grams of NaOH is required per litre. Example;

If TN = 1.5 ml for 5 litres of oil to be used,

For 1 litre of oil = 5 g + 1.5 g = 6.5 gram of NaOH

For 5 litres of oil = 5 * 6.5 g = 32.5 gram of NaOH (Assuming 99% purity)

Using KOH:

A basis of 7 g of KOH is generally required against 1litre of PVO (Guy, 2008). Hence if 5 litres of oil is used, then 35 g of KOH will be used.

5 litres of oil = 5 * 7g = 35 gram of NaOH

If a waste vegetable oil (WVO) is used, an extra gram of KOH is required for every TN. This is simply to eliminate the free fatty acids in that oil. So if the final TN is 1.5 ml, this is added to the base amount of 7, giving a total of 8.5. This means that 8.5 grams of KOH is required per litre. Example,

If TN = 1.5 ml for a 5 litres of oil to be used,

For 1 litre of oil = 7 g + 1.5 g = 8.5 gram of KOH

For 5 litres of oil = 5 * 8.5g = 42.5 gram of KOH (Assuming 99% purity)

In conclusion, this means that an extra 10 gram of KOH is used for the same quantity of feed volume to make biodiesel. This variation and how it impacts cost will be discussed more in Chapter 6

5.5 What is Considered Good Oil

If your titration results are in the range of 0 to 0.3ml, this is considered good oil. From 3 ml to 6 ml is considered poor but usable. Over 6 ml is getting questionable and should be avoided until one gains more experience. Average restaurant oil will require about 2 ml to 3 ml on the titration, while really bad fast–food grease can take 10 ml or more, which is completely unusable with a transesterification process. Using oil this bad requires first processing with an esterification, which involves an acid pretreatment followed by a normal transesterification. An esterification adds a lot of work and complexity to the whole process, and this is beyond the scope of this study. It is strongly recommended to use oil with a titration value under **2 ½ or 3 ml** (Guy, 2008)

It is important to note that the titration test recommended in this work is for quick approach. For an even more accurate titration test, or upgrading the test equipment, standard titration equipment may be used.

5.6 Washing a Biodiesel Batch

After biodiesel is made, the pH usually ranges between 8.0 and 9.0. It is usually good to have the pH about 6. This is done by washing the biodiesel to remove remaining catalyst, alcohol and impurities. The biodiesel produced has impurities that settle out into the glycerol layer, including unfiltered particulates, methanol and glycerine. Some sources encourage using unwashed biodiesel because washing biodiesel is a time-consuming process. However, some alcohol, catalyst and soap remain suspended throughout the biodiesel after the transesterification is complete (Guy, 2008)

5.6.1 Reasons for Washing Biodiesel

- To remove unreacted alcohol, catalyst and soap remains from the batch.
- To remove catalyst that can attack engine components.
- Unwashed biodiesel is caustic and may damage engine components. This also implies that the washing reduces the pH to a neutral value of about 6.
- Some molecules of soap may be formed during production. Hence, washing helps remove the soap as it will reduce fuel lubricity and cause injector coking and other deposits.

5.6.2 Washing Techniques

According to Guy (2008), there are several common techniques for washing biodiesel. This includes agitation washing, mist washing and bubble washing. The process of washing biodiesel involves mixing it with water. Water is heavier than biodiesel and absorbs the excess alcohol, catalyst and soap suspended in the fuel. After washing and settling, the water and the impurities in the water can be drained from the bottom of the container. Several wash cycles are generally needed. The first water drained off will be clear. Excess catalyst in the biodiesel will form soap when mixed with water, and it takes a while for the soap to settle out. Depending on the method used, it takes roughly the same volume of batch in water to wash off the biodiesel batch (Guy, 2008). Refer to washing techniques on Chapter 2.

5.6.3 Biodiesel Wastewater Treatment

In Journey to forever (1999), the washing of biodiesel always leaves waste water that needs to be accounted for with developing economies in focus. This water contains high levels of CODs which will cause more organic pollutants in water. **Chemical oxygen demand (COD)** is defined as the quantity of a specified oxidant that reacts with a sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. COD is expressed in mg/L O_2. COD is often measured as a rapid indicator of organic pollutant in water. The treatment of wastewater from the biodiesel production process is vital, so as to discourage contamination of the local environment, rivers and surroundings with biodiesel wastewater. Treatment of biodiesel wastewater is beyond the scope of this study.

5.6.4 Drying the Washed Biodiesel

After the biodiesel is washed, it should be dried until it is crystal clear. Letting the biodiesel stay uncovered in a sunny location for a few days can do this (this is very suitable for a local producer particularly in a summer season), or it may be heated to about 50 ^{o}C for a few hours. Another popular technique is re-circulating the biodiesel from the bottom of the drying tank through a shower head or spraying above the top of the open tank. This increases contact with air and will dry the biodiesel in about an hour, depending on the humidity of the air. Reacted, washed and dried biodiesel may be used in any diesel engine. It should have a pH of close to 7, or chemically neutral and it should have no methanol left in it. There is presently an **advanced approach** to drying washed biodiesel which is beyond the scope of this work. This can be investigated for future research work.

For the purpose of this research work, a simple approach of using water with beakers and container was used for the washing. The water was then drained off the biodiesel mixer after some time. This may not be the most ideal approach but would be sufficient for a local producer with little expertise and experience.

Chapter 6

Economic and Cost Analysis

Objective: The aim of this Chapter is to identify how equipment, feed oil, catalyst and chemicals used will affect the cost of biodiesel production for a developing economy.

6.1 Cost of Equipment, Feedstock, Catalyst and Chemical

6.1.1 Cost of Equipment and Kit:

The cost of equipment focuses on items like cone bottom processor, processor stand, manual stirrer or mixer, valves and fittings, reinforced PVC hoses, transparent graduated buckets, titration kit and funnel. These are considered fixed costs and will require a once-off investment by the local producer even though a life span of 24 months may be used before changing or servicing any of the items. The quantity of feed used as a basis for this evaluation is 30 litres. A market survey cost is shown in Table 8 below:

Table 8: Survey cost of recommended equipment for a local producer

Item	Material Description	Quantity	Unit Cost	Total Cost
1	Cone bottom MDPE processor (30 Litre)	1	1 500.00	1 500.00
2	Processor Stand	1	150.00	150.00
3	Manual Stirrer or mixer	1	30.00	30.00
4	Fittings	2	200.00	400.00
5	Reinforced PVC hoses (2 metre)	2	100.00	200.00
6	Transparent graduated buckets	5	80.00	400.00
7	Titration Kit	1	300.00	300.00
8	Funnel (5 litre)	1	100.00	100.00
9	**Total**			**R 3 080.00**

It is true that the main aim of this study is to explore a simplified approach for production of biodiesel for developing economies. However, there are certainly costs involved as these equipment are required. Comparing the survey cost on Table 8 to standard equipment used by highly skilled users, this amount is affordable for a local producer. Removing item 1 from the table and replacing it with a cheap 30 litre bucket might be cheap, but a local producer may experience difficulties separating the biodiesel from glycerine after transesterification.

6.1.2 Cost of Oil Feedstock:

This cost varies based on the nature and source of oil used. The scope of this study was limited to pure vegetable oil and waste vegetable oil. The WVO sources varied from restaurant oil, and domestic used oil. Table 9 shows the various cost of feed oil.

Table 9: Cost of feed oil

Item	Material Description	Quantity (L)	Unit Cost	Total Cost
1	Pure Vegetable oil	10	13.00	130.00
2	WVO 1 - Restraunt oil	10	4.00	40.00
3	WVO 2 - Canola oil	10	2.00	20.00
4	WVO 3 - Domestic oil	10	-	-

Cost of PVO vegetable oil is the most expensive as this is industrially prepared. The canola and restaurant oil were cheaper than PVO because they are already used and require titration before being an acceptable feed for biodiesel production. A good titration number will also determine if a batch will be used to avoid making glop. Domestic WVO were obtained free from homes but is the most difficult to get as most people dispose of them after use.

6.1.3 Cost of Catalyst and Methanol:

Two most common catalysts used were KOH and NaOH. The availability and simplicity involved in handling them makes them the best choice. NaOH is generally much more difficult to dissolve than are KOH flakes. The main advantage NaOH has is that it is cheaper and purer than KOH, so even less of it is required. This is true as

it takes 5g of NaOH versus 7g of KOH required for a litre of feed oil. Table 10 below shows the unit cost of the required catalysts.

Table 10: Cost of catalyst required for 1 litre of feed oil

Item	Material Description	Quantity of Catalyst Required for 1L of Oil (gram)	Unit Cost/gram	Total Cost	
1	NaOH – Industrial	5	R 0.12	R	0.60
2	NaOH - Chemically pure	5	R 0.16	R	0.80
3	KOH – Industrial	7	R 0.14	R	0.98
4	KOH - Chemically pure	7	R 0.20	R	1.40

However, for this study the industrial grade KOH and NaOH were used because both are affordable and easily accessible for base catalyzed transesterification. The cost of methanol required for three feed stock samples is also shown in Table 11 below;

Table 11: Cost of Methanol required for PVO, WVO 1, and WVO 2

Feed PVO/WVO 1/WVO 2 (Litres)	Feed KOH (g)	Feed NaOH (g)	Methanol Required for PVO (L)	Cost of PVO feed		Cost of Methanol	
10	70	50	2.5	R	130	R	25
20	140	100	5.0	R	260	R	50
30	210	150	7.5	R	390	R	75
40	280	200	10.0	R	520	R	100
50	350	250	12.5	R	650	R	125
60	420	300	15.0	R	780	R	150
70	490	350	17.5	R	910	R	175
80	560	400	20.0	R	1 040	R	200
90	630	450	22.5	R	1 170	R	225
100	700	500	25.0	R	1 300	R	250

6.2 Varying Options and Related Cost

6.2.1 Varying Cost of Feed Oil:

Based on the cost of feed oil as highlighted in Table 12, a comparism of the required amount of feed against the varying cost of PVO, WVO 1, and WVO 2.

Table 12: Cost comparism for PVO, WVO 1, and WVO 2 for varying feed oil

Feed (L)	Cost of PVO feed (R)	Cost of WVO 1 feed (R)	Cost of WVO 2 feed (R)
10	130	40	20
20	260	80	40
30	390	120	60
40	520	160	80
50	650	200	100
60	780	240	120
70	910	280	140
80	1040	320	160
90	1170	360	180
100	1300	400	200
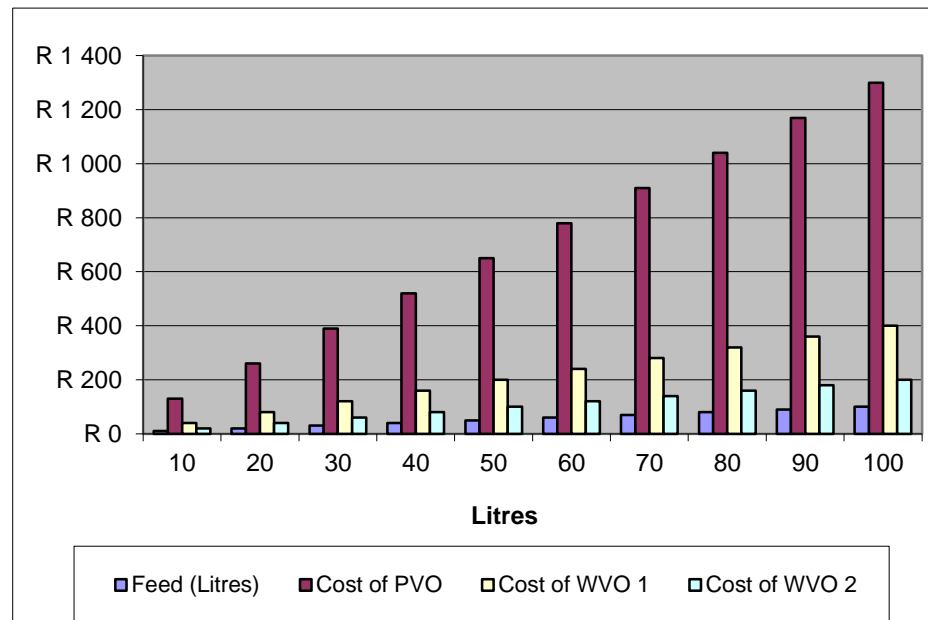
Figure 14: Cost comparism for using various feed oil.

Figure 14 is a summary of the cost of feed oil using PVO, WVO 1 and WVO 2 assuming the feed varies from 10 to 100 litres. We can deduce the following points from the chart;

a. The cheapest feed oil to use for biodiesel production is WVO 2 (used canola oil) followed by WVO 1 (restaurant oil).

b. PVO is the most expensive hence, it cannot be recommended for a user from developing economy. The cost of 100 litres of feed oil which will produce biodiesel at 99% conversion is equivalent to the cost of buying 100 litres of diesel which is about R1, 260.

c. The profit for using WVO 1 or WVO 2 will be beneficial to developing economy users.

6.2.2 Cost of Producing Biodiesel Using PVO, WVO 1, WVO 2, KOH and NaOH

Appendix K, L and M are tables used to calculate the cost of producing biodiesel from start to finish at different feed oil volumes. The cost of PVO, WVO 1 and WVO 2 were used for this calculation and the volume of feed was varied from 10 to 100 litres. The charts below (Figure 15, 16, and 17) summarize the cost of using different feed oil.
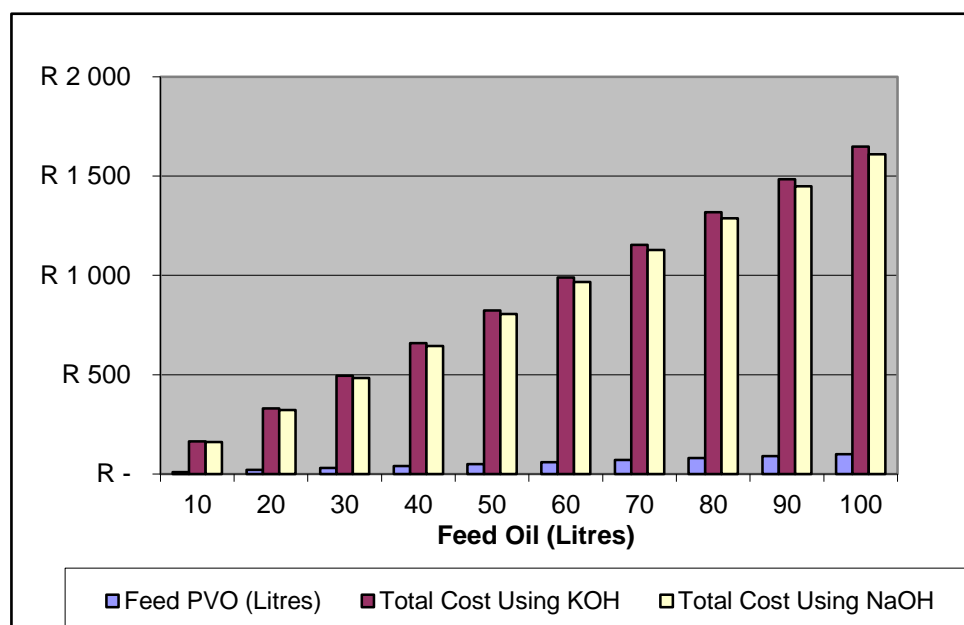
Figure 15: Cost of producing biodiesel using PVO, KOH, and NaOH.
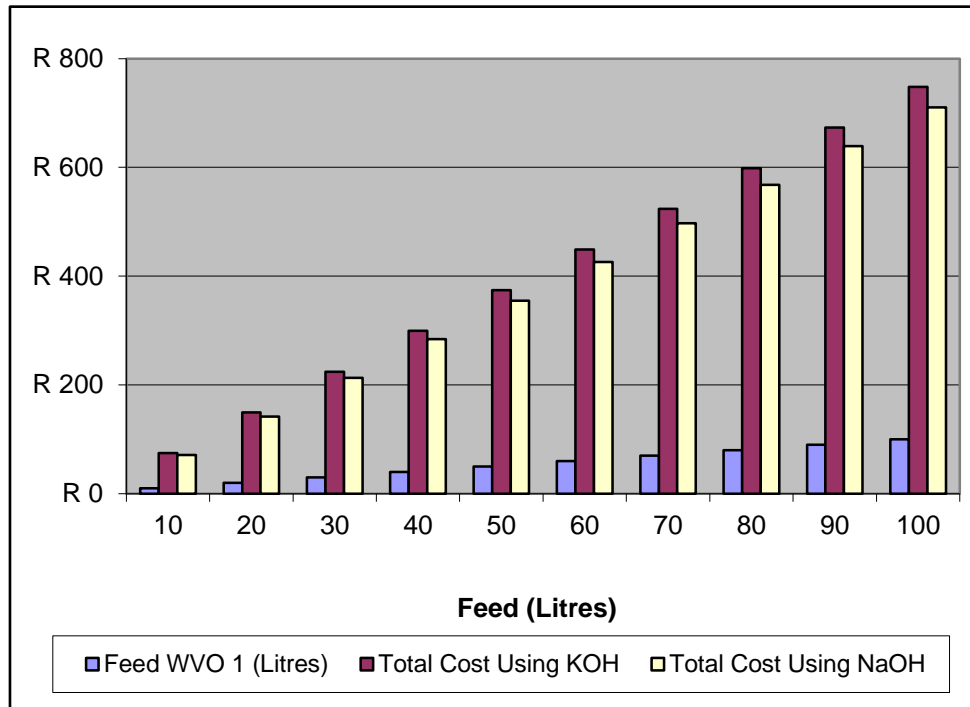
Figure 16: Cost of producing biodiesel using WVO 1, KOH and NaOH.
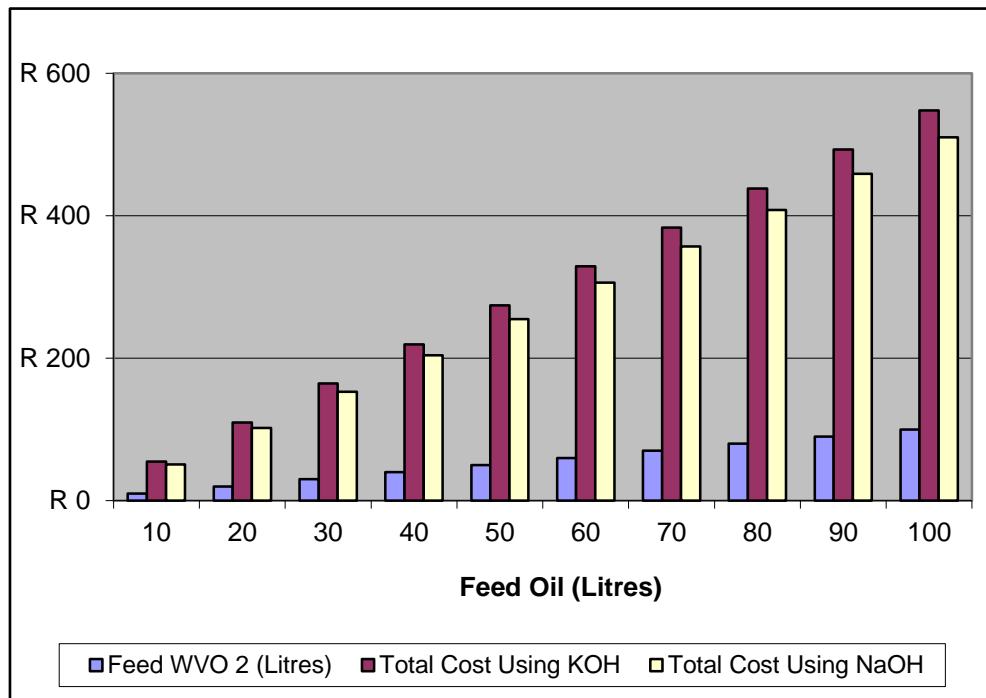
Figure 17: Cost of producing biodiesel using WVO 2, KOH, and NaOH.

The charts above were taken from appendix K, L and N. This summarizes the cost of producing biodiesel either using KOH or NaOH. It clearly takes into consideration the quantity in gram required of catalyst, methanol, cost of methanol, cost of KOH and NaOH. Varying parameters are feed oil quantity, total cost using KOH and NaOH assuming 99% yield.

In summary,

a. Charts showed that WVO 1 and WVO 2 gives the most cost affordable option for making biodiesel from start to finish.

b. The fixed cost involved is the cost of the equipment needed which is a once off purchase, except for future service.

c. These feed oils were mainly restaurant oil and industrial waste canola oil. More affordable feed oil may be used, as long as the cost remains affordable for a local producer.

Chapter 7

Conclusions and Recommendations

Conclusions

From the above study, the following conclusions were made by the author:

    a. Biodiesel is currently produced by small and medium enterprises in Southern Africa. However, this study will encourage local producers from developing economies to embark on biodiesel production on a small scale without complexities.

    b. The summary in Chapter three must be adhered to for a local producer to successfully produce biodiesel either using PVO or WVO.

    c. A cone shaped design for a mixer is most suitable to be used, as it makes separation of biodiesel and glycerine easy to separate.

    d. It was concluded that the cost of producing biodiesel for a local producer is affordable using WVO but the initial expense is still required for the equipment and kit.

    e. All WVO used by local producers from developing economies should undergo pre-treatment before use, as this will avoid making gloop or a batch that cannot be used.

    f. It was concluded that using a catalyst concentration between 0.75 % to 1 % and reaction temperature of 45 $^{\circ}$C to 75 $^{\circ}$C, quality biodiesel can be achieved.

    g. As a rule of thumb, 30 minutes should be allowed for the washing of each biodiesel batch.

Recommendations

Based on the findings of this study, the following recommendations are made by the author:

    a. As a rule of thumb, 30 minutes should be allowed for the washing of each biodiesel batch.

    b. Always use alcohol with good purity for biodiesel production (industrial grade alcohol is acceptable).

c. It may be necessary to explore other possible designs besides cone shaped, that could be used for developing economies to produce biodiesel.

d. A more extensive feasibility study should be conducted to explore the possibility of using a wider range of WVO for biodiesel production as it relates to developing economies.

e. Biodiesel should be washed and dried before use to remove unreacted materials that could cause damage to engines during use.

References

Alamu, O.J., Waheed, M.A., and Jekayinfa, S.O, 2007. Optimal Operating Conditions for the Production of Biodiesel from Palm Kernel Oil, unpublished Ph.D. thesis, Mechanical Engineering Department, Ladoke Akintola University of Technology, Ogbomoso, Nigeria.

Biodiesel Education, 2004, Available at: http://www.me.iastate.edu/biodiesel, (Accessed June 2012).

Bender, M. 1999; Economic feasibility review for community-scale farmer cooperatives for biodiesel. *Bioresource Technology* 70: 81 – 87.

Beer, T., Grant, T., year unknown, *Comparison of Transport Fuels*, Australian Greenhouse Office.

BP Statistical Review of World Energy, June 2012. Available at: http://www.bp.com/statistical review (Accessed 14 January 2013).

Colucci, J.A., et al. (2005). Biodiesel from an Alkaline Transeterification Reaction of Soybean Oil Using Ultrasonic Mixing. *Journal of American Oil Chemists' Society* 82: 525-530.

Canakci M, Van Gerpen J. Biodiesel production via acid catalysis. *Transactions of the ASAE* 42: 1203-1210

Demirbas A., and Demirbas I., 2007. Importance of rural bioenergy for developing countries. *Energy Conservation and Management.* 48: 2386-2398.

Fangrui Ma., and Milford A.H, 1999. A review of biodiesel production. *Bioresource Technology 70*: 1-15.

Freedman, B., Pryde, E.H., Mounts, T.L., 1984. Variables affecting the yields of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists' Society* 61: 1638–1643.

Friedrich, S., 2003, A world wide Review of the commercial production of Biodiesel.

Fukuda Hl, Kondo A., and Noda H., 2001. Biodiesel fuel production by transesterification of oils 1: 405-416.

Guy, P., 2008. Do it yourself guide to biodiesel, Berkeley, CA. Ulysses Press.

Haas, M.J., 2005. Improving the economics of biodiesel production through the use of low value lipids as feedstock vegetable oil soapstock. *Fuel processing technology* 35: 1087 − 1096.

Journey to Forever, 1999, Biodiesel, Available at: http://journeytoforever.org/biodiesel, (Accessed July 2012).

Kusdiana, D., and Saka, S., 2007-12-20 "Biodiesel fuel for diesel fuel substitute prepared by a catalyst free supercritical methanol", (Accessed 23 January 2012).

Knothe, G., and Steidley, K.R., 2005. "Kinematic viscosity of biodiesel fuel component and related compounds: influence of compound structure and comparison to petroleum diesel fuel components", Fuel Volume, 1059-1065.

Kulkarni MG, Gopinath R, Meher LC, Dalai AK 2006. Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification. *Green Chemistry 8*: 1056–62.

Kumar, G.R, 2011. Kinetic studies of base-catalyzed transesterification reaction of non-edible oil to prepare biodiesel*: The effect of co-solvent and temperature*. 25 (7): 2826 – 2832.

Leung DYC and Guo Y., 2006. Transesterification of neat and used frying oil: optimization for biodiesel production. *Fuel Process Technology 87:* 883–90.

Ma, F., Clements, L.D., and Hanna, M.A., 1999. "The effects of catalyst, free fatty acids and water on transesterification of beef tallow", *Transactions of the ASAE* 41: 1261-1264.

Manaka, A., 2006, South African Bureau of Standards – Chemical and Mining Standards, personal communication via email. Available at: http://www.sabs.co.za (Accessed April 2013).

Mittelbach, M., Remschmidt, C., 2005, Biodiesel - the Comprehensive Handbook, 2nd Edition, Martin Mittelbach, 332.

Mudge, S.M., Pereira, G., 1999. Stimulating the biodegradation of crude oil with biodiesel preliminary results. *Spill Science and Technology Bulletin* 5: 353–355.

Nitske, W.R., Wilson, C.M., 1965: Rudolf Diesel: Pioneer of the Age of Power, University of Oklahoma Press, 318.

Prankl, H., 2002: High Biodiesel quality required by European Standards. *European Journal of Lipid Science and Technology* 104: 371 – 375.

South African Grain Information Service, 2006, Available at: www.sagis.org.za (Accessed March, 2013)

SAPIA 2006, South African Petroleum Industry Association, Available at: www.sapia.co.za (Accessed March, 2013)

Tyson, K.S., Bozell, J., Wallace, R., Petersen, E., Moens, L., 2004, Biomass Oil Analysis − Research Needs and Recommendations, National Renewable Energy Laboratory, US Department of Energy.

Wilson, M., 1993. Soybeans by the tankful. Prairie Farmer (November), 10 − 11, 20.

Worldwatch Institute, June 2006, Biofuels for Transportation Report: Global Potential and Implications of Energy and Agriculture. London, Earthscan.

Zhang, Y., Dubé, M., McLean, D., Kates, M., 2003. Biodiesel production from waste cooking oil: 2. *Economic assessment and sensitivity analysis. Bioresource Technology* 90: 229–240.

Appendices

Appendix A: Sample Standard Results Performed at Engen Refinery

ENGEN REFINERY LABORATORY
P.O. Box 956
Durban
4000
TEL: (031) 4603911
FAX: (031) 4603385

CERTIFICATE OF QUALITY

DATE OF APPROVAL   10/01/11 11:37:3   TANK NUMBER:
SAMPLE NUMBER: 824373   PRODUCT: BIO DIESEL

TEST	UNITS	RESULT	LOWER LIMIT	UPPER LIMIT	TEST METHOD
Appearance (Haze)		>4			D4176
CFPP	°C	-4			IP309
Cloud Pt	°C	17			D2500
Colour		<1.0			D1500
Density @ 20°C	kg/L	0.8858			D4052
Flash PMCC	°C	55			D93
Pour Point	°C	0			D6749
Viscosity @ 40°C	cSt	7.944			D445
Hyd / Proc Fuel	%	100			
Severely Hydroprocessed	%	NIL			

COMMENTS: _____

CHIEF CHEMIST [redacted]   DATE: 10 JAN 2011

                                  10/01/11   11:38:26AM

Appendix B: Laboratory ASTM Test Results

Test Approach: Production of biodiesel using KOH, PVO and Methanol at Ideal Conditions (Trial 1)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	4		D4176	
CFPP	-4	^oC	IP309	
Density @ 20°C	0.8955	Kg/l	D4052	
Cloud Point	1	^oC	D6749	
Flash PMCC	139	^oC	D93	
Viscosity @ 40°C	5.4	cSt	D445	
Sulphur	2	ppm	D5453	
Product Yield	98	%	-	
Ease of operation	2	-	-	2 representing easy operation
Colour (visual check)	1	-	-	1 representing light yellow
Water Content	0	%		

Test Approach: Production of biodiesel using NaOH, PVO and Methanol at ideal conditions (Trial 2)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	4	-	D4176	
CFPP`	-4	^oC	IP309	
Density @ 20°C	0.8955	kg/l	D2624	
Cloud Point	2	^oC	D6749	
Flash PMCC	142	^oC	D93	
Viscosity @ 40°C	4.9	cSt	D445	
Sulphur	1.8	ppm	D5453	
Product Yield	98	%	-	
Ease of Operation	2	-	-	2 represents easy operation
Colour (Visual Check)	1	-	-	1 represents light yellow
Water Content	0	%		

Test Approach: Production of biodiesel using KOH, PVO and Ethanol at Ideal Conditions (Trial 3)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	5	-	D4176	
CFPP	-6	^{o}C	IP309	
Density @ 20°C	0.8287	kg/l	D2624	
Cloud Point	-1	^{o}C	D6749	
Flash PMCC	142	^{o}C	D93	
Viscosity @ 40°C	4.6	cSt	D445	
Sulphur	1	ppm	D5453	
Product Yield	98	%	-	
Ease of Operation	2	-	-	2 represents easy operation
Colour (Visual Check)	1	-	-	1 represents light yellow
Water Content	0	%		

Test Approach: Production of biodiesel using NaOH, PVO and Ethanol at Ideal Conditions (Trial 4)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	4	-	D4176	
CFPP	-5	^{o}C	IP309	
Density @ 20°C	0.8366	kg/l	D2624	
Cloud Point	0	^{o}C	D6749	
Flash PMCC	153	^{o}C	D93	
Sulphur	1.4	ppm	D5453	
Viscosity @ 40°C	6.3	cSt	D445	
Product Yield	98	%	-	
Ease of Operation	2	-	-	2 represents easy operation
Colour (Visual Check)	1	-	-	1 represents light yellow
Water Content	0	%		

Test Approach: Production of biodiesel using KOH, Methanol, and Overused WVO at Ideal Conditions (Trial 5)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	5	-	D4176	
CFPP	-6	^{o}C	IP309	
Density @ 20°C	0.811	kg/l	D2624	
Cloud Point	-1	^{o}C	D6749	
Flash PMCC	160	^{o}C	D93	
Sulphur	1	ppm	D5453	
Viscosity @ 40°C	4.41	cSt	D445	
Product Yield	<70	%	-	
Ease of Operation	1	-	-	1 represents difficult operation
Colour (Visual Check)	1	-	-	1 represents light yellow
Water Content	0.002	%	-	

Test Approach: Production of biodiesel using NaOH, Methanol, and Overused WVO at Ideal Conditions (Trial 6)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	5	-	D4176	
CFPP	-5	^{o}C	IP309	
Density @ 20°C	0.821	kg/l	D2624	
Cloud Point	1	^{o}C	D6749	
Flash PMCC	152	^{o}C	D93	
Sulphur	1	ppm	D5453	
Viscosity @ 40°C	4.34	cSt	D445	
Product Yield	<70	%	-	
Ease of Operation	1	-	-	1 represents difficult operation
Colour (Visual Check)	1	-	-	1 represents light yellow
Water Content	0.05	-	-	

Test Approach: Production of biodiesel using KOH, Methanol and WVO (fried chips) oil at Ideal Conditions (Trial 7)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	5	-	D4176	
CFPP	-7	^{o}C	IP309	
Density @ 20°C	0.8566	kg/l	D2624	
Cloud Point	-1	^{o}C	D6749	
Flash PMCC	163	^{o}C	D93	
Sulphur	0	ppm	D5453	
Viscosity @ 40°C	5.34	cSt	D445	
Product Yield	90	%	-	Based on feed used
Ease of Operation	2	-	-	2 represents easy operation
Colour (Visual Check)	1			1 represents light yellow
Water Content	0.006	%	-	

Test Approach: Production of biodiesel using NaOH, Methanol and WVO (fried chips) oil at Ideal Conditions (Trial 8)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	5	-	D4176	
CFPP	-7	^{o}C	IP309	
Density @ 20°C	0.8633	kg/l	D2624	
Cloud Point	0	^{o}C	D6749	
Flash PMCC	153	^{o}C	D93	
Sulphur	0	ppm	D5453	
Viscosity @ 40°C	5.12	cSt	D445	
Product Yield	90	%	-	Based on feed used
Ease of Operation	2	-	-	2 represents easy operation
Colour (Visual Check)	1			1 represents light yellow
Water Content	0.008	%	-	

Test Approach: Production of biodiesel using KOH, Methanol and WVO (fried fish) oil at Ideal Conditions (Trial 9)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	5	-	D4176	
CFPP	-6	^{o}C	IP309	
Density @ 20°C	0.8433	kg/l	D2624	
Cloud Point	1	^{o}C	D6749	
Flash PMCC	149	^{o}C	D93	
Sulphur	1	ppm	D5453	
Viscosity @ 40°C	4.66	cSt	D445	
Product Yield	90	%		Based on feed used
Ease of Operation	2	-	-	2 represents easy operation
Colour (Visual Check)	2	-	-	2 represents pitch
Water Content	0.007	%	-	

Test Approach: Production of biodiesel using NaOH, Methanol and WVO (fried fish) oil at Ideal Conditions (Trial 10)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	5	-	D4176	
CFPP	-6	^{o}C	IP309	
Density @ 20°C	0.8633	kg/l	D2624	
Cloud Point	0	^{o}C	D6749	
Flash PMCC	152	^{o}C	D93	
Sulphur	2	ppm	D5453	
Viscosity @ 40°C	4.88	cSt	D445	
Product Yield	90	%		Based on feed used
Ease of Operation	2	-	-	2 represents easy operation
Colour (Visual Check)	2	-	-	2 represents pitch
Water Content	0.004	%	-	

Test Approach: Production of biodiesel using KOH/NaOH with Methanol at 35°C temperature (Trial 11)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	5	-	D4176	
CFPP	-2	°C	IP309	
Density @ 20°C	0.7663	kg/l	D2624	
Cloud Point	-1	°C	D6749	
Flash PMCC	150	°C	D93	
Sulphur	2	ppm	D5453	
Viscosity @ 40°C	5.12	cSt	D445	
Product Yield	<60	%	-	Based on feed used
Ease of Operation	1	-	-	1 represents difficult operation
Colour (Visual Check)	1	-	-	1 represents light yellow
Water Content	0.1	%	-	

Test Approach: Production of biodiesel using KOH/NaOH with Methanol at 45°C temperature (Trial 12)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	5	-	D4176	
CFPP	-6	°C	IP309	
Density @ 20°C	0.7922	kg/l	D2624	
Cloud Point	-1	°C	D6749	
Flash PMCC	140	°C	D93	
Sulphur	2	ppm	D5453	
Viscosity @ 40°C	6.22	cSt	D445	
Product Yield	<90	%	-	Based on feed used
Ease of Operation	2	-	-	2 represents easy operation
Colour (Visual Check)	1	-	-	1 represents light yellow
Water Content	0.009	%	-	

Test Approach: Production of biodiesel using KOH/NaOH with Methanol at 55°C temperature (Trial 13)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	4	-	D4176	
CFPP	-6	°C	IP309	
Density @ 20°C	0.8965	kg/l	D2624	
Cloud Point	0	°C	D6749	
Flash PMCC	145	°C	D93	
Sulphur	0	ppm	D5453	
Viscosity @ 40°C	5.22	cSt	D445	
Product Yield	95	%		Based on feed used
Ease of Operation	2	-	-	2 represents easy operation
Colour (Visual Check)	1	-	-	1 represents light yellow
Water Content	0.001	%	-	

Test Approach: Production of biodiesel using KOH/NaOH with Methanol at 65°C temperature (Trial 14)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	4	-	D4176	
CFPP	-6	°C	IP309	
Density @ 20°C	0.8755	kg/l	D2624	
Cloud Point	-1	°C	D6749	
Flash PMCC	137	°C	D93	
Sulphur	1	ppm	D5453	
Viscosity @ 40°C	5.1	cSt	D445	
Product Yield	98	%	-	Based on feed used
Ease of Operation	2	-	-	2 represents easy operation
Colour (Visual Check)	1	-	-	1 represents light yellow
Water Content	0	%	-	

Test Approach: Production of biodiesel using KOH/NaOH with Methanol at 75°C temperature (Trial 15)

TEST	RESULTS	UNITS	TEST METHOD	COMMENTS
Appearance (Haze)	4	-	D4176	
CFPP	-6	^{o}C	IP309	
Density @ 20°C	0.8833	kg/l	D2624	
Cloud Point	-1	^{o}C	D6749	
Flash PMCC	141	^{o}C	D93	
Sulphur	0	Ppm	D5453	
Viscosity @ 40°C	4.31	cSt	D445	
Product Yield	98	%	-	Based on feed used
Ease of Operation	2	-	-	2 represents easy operation
Colour (Visual Check)	1	-	-	1 represents light yellow
Water Content	0	%	-	

Appendix C: Laboratory equipment for measuring of Haze/Appearance (D4176)

Appendix D: Laboratory equipment for measuring Cold filter plugging point CFPP (IP 309)
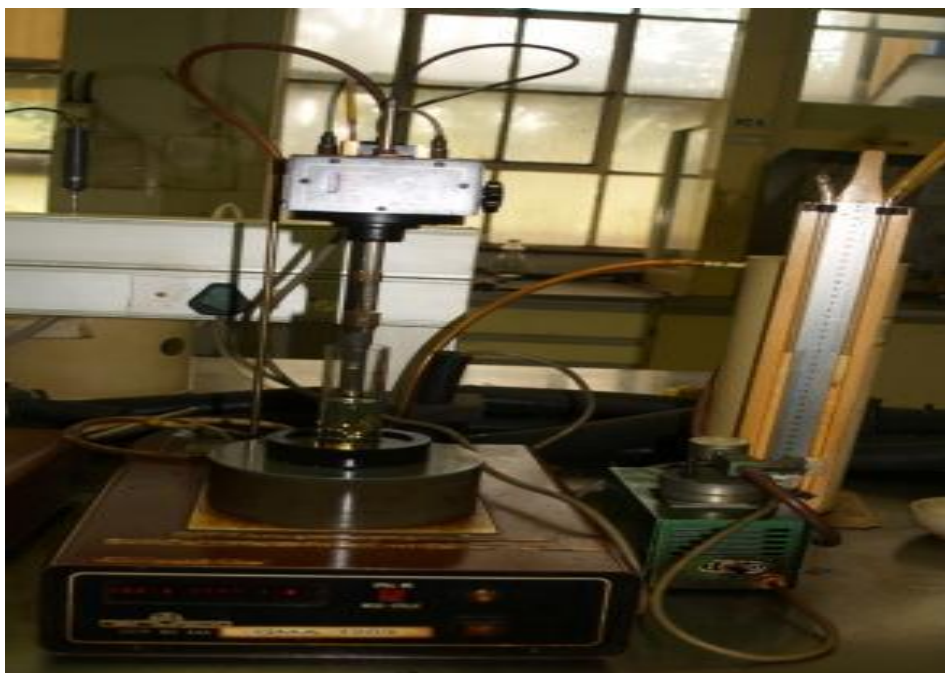
Appendix E: Laboratory equipment for measuring density (D4052)

Appendix F: Laboratory equipment for measuring cloud point (D6749)

Appendix G: Laboratory equipment for measuring Flash point (D93)

Appendix H: Laboratory equipment for measuring sulphur (D5453)

Appendix I: Laboratory equipment for measuring viscosity (D445)

Appendix J: Laboratory equipment for measuring water content (D6464)

Appendix K: Total cost for producing up to 99% biodiesel yield using KOH, NaOH and PVO

	NaOH	KOH	PVO/L	Methanol/L						
Factors	R 0.12	R 0.14	R 13.00	R 10.00						
Item	Feed PVO (Litres)	Feed KOH (g)	Feed NaOH (g)	Methanol Required for PVO (L)	Cost of PVO feed	Cost of Methanol	Cost of KOH used	Cost of NaOH used	Total Cost for 95-99% Biodiesel Yield Using KOH (ZAR)	Total Cost for 95-99% Biodiesel Yield Using NaOH (ZAR)
1	10	70	50	2.5	R 130	R 25	R 10	R 6	R 165	R 161
2	20	140	100	5.0	R 260	R 50	R 20	R 12	R 330	R 322
3	30	210	150	7.5	R 390	R 75	R 29	R 18	R 494	R 483
4	40	280	200	10.0	R 520	R 100	R 39	R 24	R 659	R 644
5	50	350	250	12.5	R 650	R 125	R 49	R 30	R 824	R 805
6	60	420	300	15.0	R 780	R 150	R 59	R 36	R 989	R 966
7	70	490	350	17.5	R 910	R 175	R 69	R 42	R 1 154	R 1 127
8	80	560	400	20.0	R 1 040	R 200	R 78	R 48	R 1 318	R 1 288
9	90	630	450	22.5	R 1 170	R 225	R 88	R 54	R 1 483	R 1 449
10	100	700	500	25.0	R 1 300	R 250	R 98	R 60	R 1 648	R 1 610

Appendix L: Total cost for producing up to 99% biodiesel yield using KOH, NaOH and WVO 1

	NaOH	KOH	WVO 1/L	Methanol/L						
Factors	R 0.12	R 0.14	R 4.00	R 10.00						
Item	Feed WVO 1 (Litres)	Feed KOH (g)	Feed NaOH (g)	Methanol Required for PVO (L)	Cost of WVO 1 feed	Cost of Methanol	Cost of KOH used	Cost of NaOH used	Total Cost for 95-99% Biodiesel Yield using KOH	Total Cost for 95-99% Biodiesel Yield using NaOH
1	10	70	50	2.5	R 40	R 25	R 10	R 6	R 75	R 71
2	20	140	100	5.0	R 80	R 50	R 20	R 12	R 150	R 142
3	30	210	150	7.5	R 120	R 75	R 29	R 18	R 224	R 213
4	40	280	200	10.0	R 160	R 100	R 39	R 24	R 299	R 284
5	50	350	250	12.5	R 200	R 125	R 49	R 30	R 374	R 355
6	60	420	300	15.0	R 240	R 150	R 59	R 36	R 449	R 426
7	70	490	350	17.5	R 280	R 175	R 69	R 42	R 524	R 497
8	80	560	400	20.0	R 320	R 200	R 78	R 48	R 598	R 568
9	90	630	450	22.5	R 360	R 225	R 88	R 54	R 673	R 639
10	100	700	500	25.0	R 400	R 250	R 98	R 60	R 748	R 710

Appendix M: Total cost for producing up to 99% biodiesel yield using KOH, NaOH and WVO 2

	NaOH	KOH	WVO 2/L	Methanol/L						
Factors	R 0.12	R 0.14	R 2.00	R 10.00						
Item	Feed WVO 2 (Litres)	Feed KOH (g)	Feed NaOH (g)	Methanol Required for PVO (L)	Cost of WVO 2 feed	Cost of Methanol	Cost of KOH used	Cost of NaOH used	Total Cost for 95-99% Biodiesel Yield using KOH	Total Cost for 95-99% Biodiesel Yield using NaOH
1	10	70	50	2.5	R 20	R 25	R 10	R 6	R 55	R 51
2	20	140	100	5.0	R 40	R 50	R 20	R 12	R 110	R 102
3	30	210	150	7.5	R 60	R 75	R 29	R 18	R 164	R 153
4	40	280	200	10.0	R 80	R 100	R 39	R 24	R 219	R 204
5	50	350	250	12.5	R 100	R 125	R 49	R 30	R 274	R 255
6	60	420	300	15.0	R 120	R 150	R 59	R 36	R 329	R 306
7	70	490	350	17.5	R 140	R 175	R 69	R 42	R 384	R 357
8	80	560	400	20.0	R 160	R 200	R 78	R 48	R 438	R 408
9	90	630	450	22.5	R 180	R 225	R 88	R 54	R 493	R 459
10	100	700	500	25.0	R 200	R 250	R 98	R 60	R 548	R 510