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Development and validation of in-process control test kits for biodiesel production

By

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MASTER OF TECHNOLOGY (CHEMISTRY): PRODUCT AND PROCESS DEVELOPMENT

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DECLARATION

I, Pumza Oscarine Fibi 20303485, hereby declare that this treatise for the degree of Master of Technology (Chemistry): Product and Process development is my own work and that it has not previously been submitted for assessment or completion of any postgraduate qualification to another University or for another qualification.

P. Fibi

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This is dedicated to my children…

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List of Abbreviations

FAME – Fatty acid methyl esters

WHW – Weight heat weight

SANS – South African National Standard

B100 – 100 % biodiesel

B20 – 20 % biodiesel, 80 % diesel

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PART A

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ABSTRACT

The production of biodiesel from vegetable oils is not a new technology; it has been around since the 1950's and both the research in terms of the different feedstock that can be used and the production of biodiesel has since been gaining momentum as there needs to be a new, sustainable and domestic alternative to petroleum fuels. These petroleum fuels pose enormous threats to the environment and therefore need to be replaced as they are mostly contributing to climate change and global warming not to mention the frequent price hikes which are crippling the South African economy. Biodiesel production using vegetable oils seems to be and is the future and a law has recently been passed which sanctions the production of biofuel locally.[1] South African fuel producers will instigate obligatory blending of fossil fuel with biofuel as the country moves to encourage investment in its biofuels sector. The production of biodiesel locally and the blending of biodiesel with other petroleum products will reduce the country's dependence on imported fuel.

The already established petrochemical companies like BP, Sasol and Engine are therefore mandated to purchase these biofuels if and when the biofuels meet the required South African National Standard (SANS) 1935 requirements. This is then where the challenge comes as most of these growing biofuel companies cannot afford to purchase testing equipment.The growing companiesthen discover upon completion of the biofuel manufacturing process that their product does not meet the required standard specification. The failuretranslates to a financial loss as the final product can possibly not be reworked. The aim of the project is then to assist these companies who are manufacturing biofuel, by providing them with in-house biofuel process methods which will allow for early detection, should there be a need to redo a step in the process and not wait until the completion of the production process. These in-house process-testing methods will range from pH determination, titration tests which will determine the soap content and the percentage free fatty acid content, water determination, density and visual testing. It is not cost-effective for these biodiesel manufacturers to send their samples for outsource testing as evidently the results obtained would be out of specification hence the need to provide these biodiesel manufacturers with in-house analytical testing techniques that will aid in monitoring of the biodiesel production.

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Chapter 1

1.1 Introduction

In South Africa, restaurants and other food outlets usually traded their used cooking oils to street vendors who re-used it to fry their food. Afterwards the waste oils were commonly just thrown away. The discarding of used and untreated waste cooking oil resulted in the environment being polluted. One of the ways to treat the waste oil was to convert it to biodiesel. [2] This conversion of used and waste oil to biodiesel not only saved the environment from being polluted, however,alternative and renewable fuel which will benefit the economy tremendously was made available.

The escalating fuel prices coupled with the risks imposed on the ozone layer by fossil fuel emissions also led the world to contemplating of coming up with alternative, renewable and green methods of producing fuel. [3]The source from which this fuel was derivedwas not only vegetable oil but microalgae and animal matter as well and it was termed biodiesel or B100. [4]

Biodiesel is also referred to as FAME (fatty acid methyl esters). It is not only currently used as a diesel fuel additive, but it is also marketed as green industrial degreasing solvents; as diluents for pigments, paints, and coatings, and for military engine fuel applications. [5]

It is an advantageous alternative to fossil fuel because of its biodegradability, bio renewable nature, very low sulphur content and toxicity, low volatility or flammability and higher cetane number. [6, 7]Due to its oxidative stability, biodiesel has good transport and storage properties. It is either used as is (B100) or is blended in different ratios with the fossil fuel, for example B2, B5 and B20 are fuels with a concentration of 2 %, 5 % and 20% biodiesel respectively, mixed with diesel.

There are various ways of synthesizing biodiesel namely; acid catalysis, enzymatic conversion, solid catalysis, non-catalytic conversion techniques and base catalysis or transesterification. Following is a brief discussion of each method.

(a) Acid catalysis. This method is carried out if the oil used has a high percent free fatty acid content. This technique employs a strong acid usually concentrated sulphuric acid. Sulphuric acid acts as a protonating catalyst and as a dehydrating

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agent. [8]Methanol and sulphuric acid are premixed in relative mole ratios in a separate reactor. An appropriate amount of oil is heated separately and fed into the methanol: acid reactor. The reaction reaches completion after 4 hours or more. Soap formation will not be a problem in this technique as there are no alkali metals in the reaction mixture. This technique is however not suitable for industrial processing as it is very slow. [9, 10, 11]

(b) Enzymatic conversion. This technique makes use of enzymes as a catalyst. These enzymes can either be in solution or immobilized onto a support material allowing the use of fixed-bed reactors. The reaction takes from four to fourteen hours to reach completion and is performed at 35 – 45 ^{0}C. This technique is not viable economically, due to the high cost of the enzymes.[10, 11, 12]

(c)Solid catalysis. This technique is also referred to as heterogeneous catalysis i.e. the catalyst used is immiscible with the alcohol and it can be re-used as it stays in the reactor. This process employs fixed-bed reactors. The final product does not require water washing and the yield is generally high. This type of technique requires operation under high pressure and temperature.[13]

(d) Non-catalytic conversion techniques. The technique uses only methanol at a very high temperature and pressure to convert oil into biodiesel. It requires a high ratio of alcohol to oil. The reaction is quite rapid taking about three to five minutes to reach completion. The energy consumption resulting from the use of this process is higher compared to the other conventional processes. [10, 13]

The above techniques of synthesizing biodiesel were not used in this study. The one technique used is the one mentioned below.

(e) Base catalysis or transesterification. The process of making biodiesel from used or commercial oil is known as transesterification and it is achieved by adding methanol to a triglyceride such as vegetable oil. A catalyst which has to be alkaline is required so as to increase the rate of the chemical reaction between the methanol and the oil. Potassium hydroxide or sodium hydroxide is a much more effective catalyst for this reaction. Methanol and ethanol are used commercially because of their low cost and their physical and chemical advantages.[6, 7,10]

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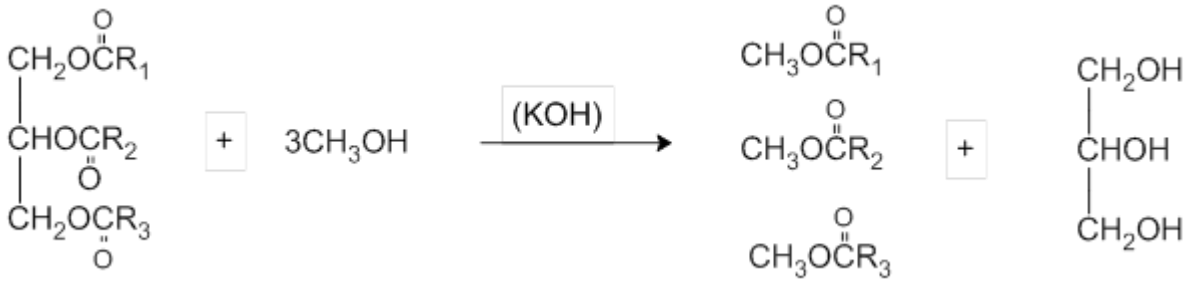
Potassium hydroxide or sodium hydroxide is easily dissolved and react quickly with triglycerides with the aid of an alcohol. Transesterification, also referred to as alcoholysis produces fatty acids and glycerine. The pH of the biodiesel is measured periodically because for biodiesel to form the pH should be above 10. The glycerine given out as a by-product is important because of its various uses in the pharmaceutical, food and cosmetic sectors.[5, 14] It is beneficial to the manufacturing or production sector as well as it can be turned into biogas.

The reaction is represented as follows:



Triglyceride Methanol Mixture of fatty esters Glycerine

Scheme 1.1: Transesterification process. [7, 27]

R1, R2 and R3 are long chain hydrocarbons, commonly referred to as fatty acids. In the presence of the catalyst, the alcohol molecule will be able to break the fatty acid chains, resulting in two different products, glycerine and a mixture of fatty acid esters. Stochiometrically, when the reaction takes place, for every mole of triglycerides reacting, 3 moles of alcohol are used. [15] A higher molar ratio of alcohol is usually used for maximum ester production.

Scheme 1.1 only illustrates the overall transesterification reaction. Three consecutive and reversible reactions are believed to occur. These reactions are illustrated in Scheme 1.2 below:

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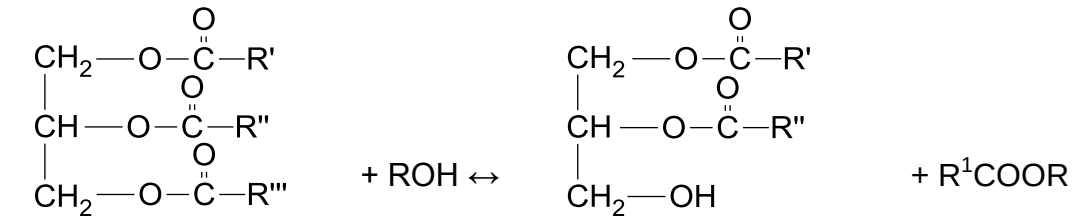
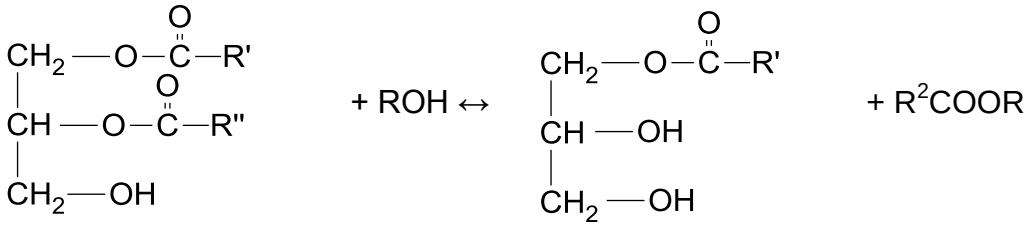
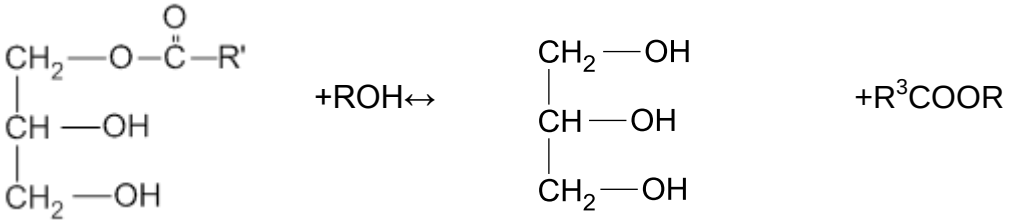


(Triglycerides) (Diglycerides) (Biodiesel)



(Diglycerides) (Monoglycerides) (Biodiesel)



(Monoglycerides) (Glycerol) (Biodiesel)

Scheme 1.2: Chemistry of transesterification. [27]

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Biodiesel is made from vegetable oils or triglycerides which consist of three long chain fatty acid molecules joined by a glycerine molecule. Triglycerides or oil may need pre-treatment if the percentage free fatty acid content is too high (refer to Table 1.1). Esterification is a process which employs sulphuric acid, a dehydrating agent and a catalyst, to lower the percentage free fatty acid content in the oil by causing a reaction between the carboxylic acids present in the oil with an alcohol to form esters. See equation 1.1 below:

$$RCO_2H + R`OH \leftrightarrow RCO_2R` + H_2O \qquad \text{Eqn. 1.1}$$

The process of synthesizing biodiesel via the transesterificaton process makes use of an alkaline catalyst which could either be sodium hydroxide or potassium hydroxide to break off the glycerine molecule. The reaction is carried out in a reactor with a controlled heat source applied. The transesterification process combines each of the three fatty acid chains with a molecule of methanol thus creating fatty acid methyl esters. Upon the reaction being completed, two products are formed, biodiesel and glycerine which is a by-product. The contents are poured from the reactor into a separating funnel. Glycerine sinks to the bottom and is separated or drained out. Biodiesel is then washed and dried (refer to Figure 1.1 below for the transesterification process flow chart).

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The process flow chart of biodiesel is shown in **Fig.1.1**

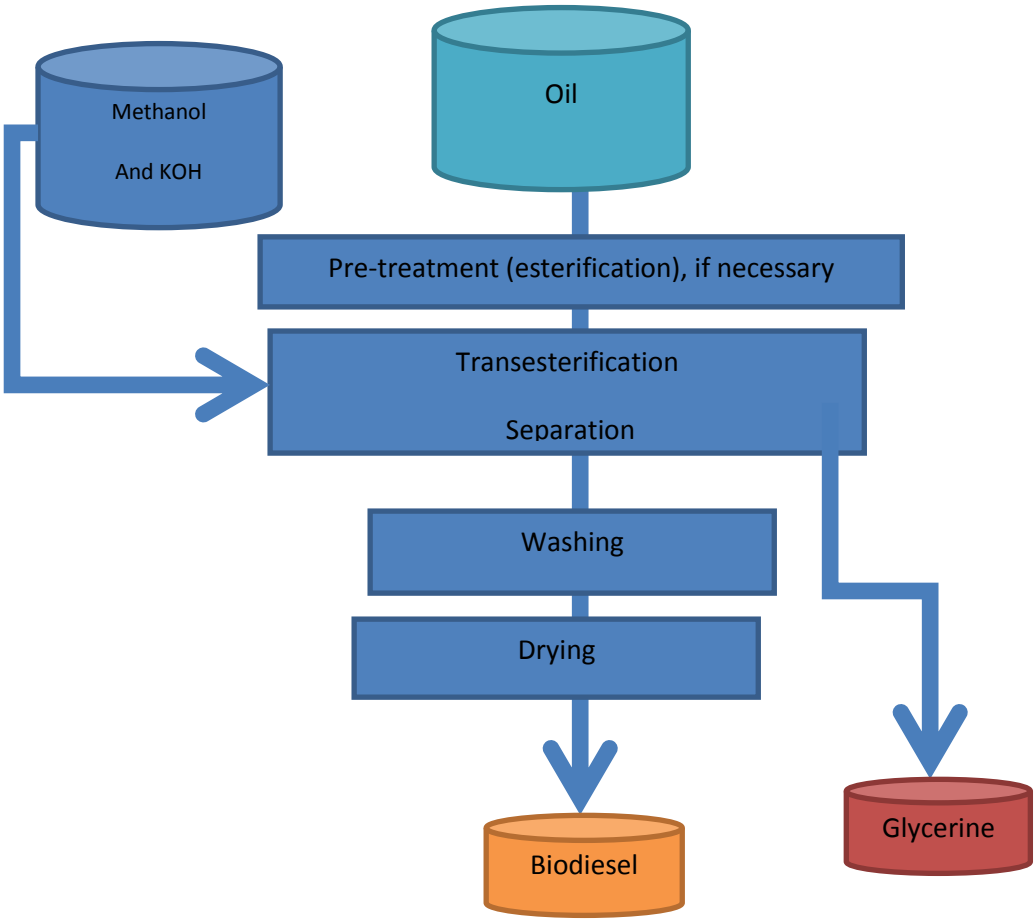

Fig. 1.1: Flowchart illustrating the transesterification process of biodiesel

Table 1.1: Percentage free fatty acid and the quality of the oil

Percentage free fatty acid content (%)	**Quality of oil**
0 - 5	Good oil
5 – 10	Average oil (needs to be treated i.e. it will require the esterification step
12	Bad oil (cannot be used)

The production of biodiesel to be used as alternative fuel is a greatly welcomed innovation due to its benefits economically and environmentally. However, with every new technique there arepros and cons; biodiesel is not different from the other methods. The following are the advantages and disadvantages of biodiesel.

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1.2aBenefits of biodiesel

Biodiesel is good for the environment as it is derived from renewable resources.[3, 16] It has lower emissions compared to petroleum diesel and it is less toxic. It does not contain sulphur or aromatics. [3, 17]Its usage results in a significant decrease of carbon monoxide, particulate matter and unburned hydrocarbons.The lower emissions result in cleaner air which contributes positively to people's health.The biodiesel reduces the reliance on the crude oil imports, something that will contribute significantly to the domestic economy through job creation. [17]It yields a high level of combustion quality during compression ignition which is measured by the cetane number. It has a higher cetane number compared to petroleum diesel fuel. Biodiesel is an oxygenated fuel containing about 11 % of oxygen. The high oxygen content results in complete combustion. [3, 17]

1.2b Disadvantages of biodiesel

The one major disadvantage of the biodiesel is the fact that it takes directly from the food industry. The availability of the agricultural feedstock needed to produce it might be constrained. [7, 18]The kinematic viscosity of biodiesel is higher than that of diesel fuel. This affects fuel atomisation during injection and requires modified fuel injection systems.Biodiesel is hygroscopic, meaning it absorbs water easily.Contact with sources of humidity should be avoided.[19]

1.3 Variables affecting the transesterification reaction

The parameters that affect the reaction are as follows; type of oil, temperature, amount of alcohol, type and amount of catalyst, reaction time and mixing. Each of the parameters is individually discussed below.

1.3.1 Types of oil

There is quite a variety of pure oils to make use of as far as the production of biodiesel is concerned, oils from sunflower, canola, peanut, sesame seed, corn and hemp can be used. Used oil from the food industry is also made use of, however, because it has been heated a number of times through frying, it may need to be pre-treated first before the transesterification process is done. The quality of the oil used is determined by calculating its percentage free fatty acid content (refer to Table 1.1). The lower the percentage free fatty acid content, the higher the quality of the oil. The

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higher the percentage free fatty acid content, the higher the soap content that will be produced. Soap may lead to difficulties in the reaction and separation of products.

1.3.2 Temperature

It is well known through literature that higher temperatures speed up the reaction thereby shortening the reaction time. Furthermore, higher ester yields would be obtained as a result of the reaction carried out under higher temperatures. However, if the reaction temperature is higher than the boiling point of the alcohol, the alcohol would evaporate resulting in a lower yield. The optimum temperature for the transesterification reaction has been found to be between 50 and 60^{o}C.[13]

1.3.3 Methanol/ oil molar ratio

The methanol/ oil molar ratio is one of the most important factors that can affect the production and percentage yield of FAME. The amount of methanol used is relevant to the amount of oil used. Methanol should amount to 20 % relative to the oil. The optimum methanol to oil ratio when sunflower oil is transesterified using potassium hydroxide is 6:1. [20]

1.3.4 Type and amount of catalyst

The purer the reagent used in the production of biodiesel i.e. the catalyst, the higher the yield that will be obtained. [20] However, if the catalyst used is of lesser quality, it must be used in a greater quantity. For an example, if 5 g of pure potassium hydroxide is sufficient to synthesise about 1000 mL of oil, then about 10 g of less pure potassium hydroxide will be required to achieve the same yield and to completely convert all of the fatty acids.

The type of catalyst also plays a role.[20] Different catalysts will require different concentrations regardless of the fact that they might belong in the same group as in the case of sodium hydroxide and potassium hydroxide. If the amount of catalyst is more than the optimum amount required, the yield of methyl esters will decrease due to the formation of soap. The higher amounts of catalyst will also increase the viscosity of the reagents.

1.3.5 Reaction time

The conversion rate of the triglyceride to an ester increases with the reaction time. The ester yield will be low if the reaction time is not long enough. Part of the oil will

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be left unreacted. The optimum reaction time for the production of biodiesel when heat is used is an hour. [20]

1.3.6Mixing

Mixing is quite crucial for any homogeneous reaction. The reaction will only occur in the interface between the methanol and the oil in the absence of a mixing device. The mixing for these experiments has been done by means of an electric stirrer and stirrer bar. In production however, overhead mixers will be used to ensure complete mass transfer between the used oil and the methanol / catalyst mixture. [20]

1.4Washing and testing of biodiesel

It is most important for the biodiesel to be tested before, during and after the reaction is completed. Once the reaction is completed, the biodiesel- glycerol mixture is poured into a separating funnel. The two components separate due to their different densities. The glycerol settles at the bottom and the biodiesel floats at the top. Once the glycerol layer is drained out, the biodiesel is intensely cleansed or washed as it contains some impurities which are free glycerol or soap, residual catalyst, water and unreacted alcohol.

Before washing, it is important to first recover the methanol through a vacuum distillation process so it does not end up in the wastewater and goes down the drain thereby polluting the environment. After recovering the methanol, the biodiesel is washed with warm water because most of the impurities are highly soluble in water. Water also helps retards the formation of emulsions and prevents the precipitation of saturated fatty acid esters.

Dry washing can also be performed on the biodiesel. The advantage of dry washing is that no water is used, something that eliminates any problems with wastewater sewage. Magnesol or D-Sol is amongst the commercial brands that may be used.

1.5 Characteristics of biodiesel

Quality standards are important and they are prerequisites for the commercial use of any fuel product. [17]Due to the large variety of vegetable oils that can be used for biodiesel production, specifications for biodiesel require particularly close attention. Numerous biodiesel standards are currently available in a number of countries. EN

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14214 is in force in the European Union and ASTM D 6751 in the United States of America. South Africa currently uses SANS 1935 Automotive diesel fuel standard. [17]

Explained below are the important biodiesel characteristics for this particular project which are water content, acid value, ester content, density and free and total glycerol content.

Water content- biodiesel or fatty acid methyl ester is hygroscopic. It can absorb water during storage resulting in the product not meeting the specification requirements. The presence of water in biodiesel will result in the formation of biological products and the reverse reaction, turning the biodiesel to free fatty acids. It is therefore imperative that biodiesel be stored with a drying agent. [19] The water content in biodiesel should not exceed 0.05 % (m/m). Refer to Table 1.2 below.

Acid value – It measures the amount of mineral acids and free fatty acids contained in a fuel sample. The high fuel acid will result in the corrosion in the engine and other parts of the vehicle and engine deposits.[19] According to SANS 1935 the value obtained for this characteristic should not exceed 0.5 mg KOH, refer to Table 1.2 below.

Ester content – This characteristic is measured using gas chromatography. It is an indication of how well the triglycerides have been converted to form biodiesel. A 3/27 test was used in this study to determine if complete conversion from triglyceride to biodiesel was reached. If triglycerides are not completely converted, biodiesel will not form and therefore the specification requirements will not be met.[19] The minimum amount of the ester contents after the completion of the transesterification process is 96.5 % (m/m), refer to Table 1.2 below. To determine ester content quantitatively, a gas chromatography would be employed as the 3/27 test kit determines complete conversion of triglycerides to fatty acid methyl esters (FAME) qualitatively.

Density – This parameter is indicative of the quality of biodiesel. The higher the density measurement the poorer the quality of biodiesel. Density can have an effect on fuel consumption.[19]The specification requirement for this characteristic is 860 – 900 kg/m^3, refer to Table 1.2.

Free and total glycerol contents–this characteristic is indicative of the free and bound glycerol content. Glycerol is given out as a by-product during the synthesis of

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biodiesel. Thorough washing of the biodiesel should result in obtaining very low levels of glycerol. According to the SANS 1935,free glycerol and total glycerol contents in biodiesel should not exceed 0.02 % (m/m) and 0.25 % (m/m) respectively. The presence of this impurity will result in deposit formation on valves and injectors.[19] Glycerol is a by-product of biodiesel production. An access amount of glycerol in the final biodiesel product will result in fuel separation, transportation problems and storage complications. [21]

1.5.1 Table of characteristics

The following Table 1.2 shows other important biodiesel characteristics. The characteristics highlighted on Table 1.2 will be investigated making use of the biodiesel test kits.

Table1.2: Characteristics of biodiesel generally tested as specified in SANS1935 [14]

Property	**Test method**	**Limits**		**Units**
		Min	**Max**	
Ester content	EN 14103	96.5	-	% (m/m)
Density, at 15^0C	ISO 3675, ISO 12185	860	900	kg/m^3
Kinematic viscosity at 40^0C	ISO 3104	3.5	5.0	mm^2/s
Flash point	ISO 3679	120	-	^{0}C
Sulfur content	ISO 20846, ISO 20884	-	10.0	mg/kg
Carbon residue (on 10 % distillation residue	ISO 10370	-	0.3	% (m/m)
Cetane number	ISO 5165	51.0	-	-
Sulfated ash content	ISO 3987	-	0.02	% (m/m)
Water content	ISO 12937	-	0.05	% (m/m)

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Table1.2 (continued)

Total contamination	EN 12662	-	24	mg/kg
Copper strip corrosion (3 hours at 50^0C)	ISO 2160	-	No.1	Rating
Oxidation stability, at 110^0C	EN 14112	6	-	Hours
Acid value	EN 14104	-	0.5	mg KOH
Iodine value	EN 14111	-	140	g I/100 g
Linolenic acid methyl ester	EN 14103	-	12	% (m/m)
Content of FAME with ≥4 bonds		-	1	% (m/m)
Methanol content	EN14110	-	0.2	% (m/m)
Monoglyceride content	EN 14105	-	0.8	% (m/m)
Diglyceride content	EN 14105	-	0.2	% (m/m)
Triglyceride content	EN 14105	-	0.2	% (m/m)
Free glycerol	EN 14105, EN 14106	-	0.02	% (m/m)
Total glycerol	EN 14105	-	0.25	% (m/m)
Group I metals (Na + K)	EN 14108, EN 14109	-	5.0	mg/kg
Group II metals (Ca + Mg)	EN 14538	-	5.0	mg/kg
Phosphorous content	EN 14107	-	10.0	mg/kg
Cold filter plugging point (CFPP) Winter/Summer	EN 116	-	-4/+3	^{0}C

1.6 Validation of biodiesel test kits

The aim of the project is to develop and validate biodiesel test kits to be used as quality checks by growing biodiesel producing companies. These companies run at a loss as they are unable to purchase equipment for testing their biodiesel during synthesis. Money is then lost through sending samples which do not meet the specification requirements for outsource testing, something which should have been detected prior sendingthe samples. The test kits which will be developed will assist these companies and reduce poor quality costs. The test kits will consist of the following kits; water test kit, density test kit, soap test kit, percentage free fatty acid

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test kit and the 3/27 methanol test kit. These test kits will be used in-process i.e. before, during and after the synthesis of biodiesel. When all the specifications are met upon using the test kits, the biodiesel may be sent to outsource laboratories for more advanced testing which will include the determination of the fatty acid methyl esters (FAME) content using gas chromatography.

With any method or test kit that is developed, the most important aspect is validation. Validation ensures that the method is working and it is suitable for its intended purpose. [13]It also ensures that the results obtained will be reliable and are accurate. Validation with regards to the project will not entail the 8 steps of validation as published by the USPharmacopeia; however, it refers to testing. This project was validated through performing replicates of runs.

Validation and verification of any method is based on running a series of tests. From the results obtained from the tests, a statistical study is done and graphs plotted. The data collected from all the tests will determine whether the methods are suitable for use. Validation is a process of proving that a procedure or method is working as expected and the intended results are achieved.[22]

The aspects of validation as stated in literature [22]areas follows:

(a) Selectivity/ specificityof an analytical method as its ability to measure accurately an analyte in the presence of interference. [22]

(b) Accuracy is how close the results are to the true value. [22]

(c) Precisionwhich refers to the degree of closeness between the measured values. The values or measurements obtained during a series of tests and under the same test conditions should remain the same or similar. [22]

(d) Repeatability, reproducibility these aspects refer to a variation in measurements. A measurement is deemed repeatable when the variation between the sets of results is low. Reproducibility refers to the degree of agreement between observations or measurements. Both these aspects are usually reported as the standard deviation.[21]

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(e) Robustnessof and analytical method is a measure of its capacity to remain unaffected by small but deliberate variations in method parameters and provides an indication of its reliability during normal usage. [22]

(f) Ruggedness is measure of reproducibility test results under the variation in conditions normally expected from laboratory to laboratory and from analyst to analyst. [22]

Not all the aspects of validation are relevant to this study. The results obtained from the analysis ofbiodiesel employing some test kits will be compared to instruments to check for the aspect of accuracy and precision.For some test kits results which will not be compared to any particular instruments, the aspect of repeatability and reproducibility will be looked at. The percentage free acid test was performed five times for an example.

1.7 Biodiesel in South Africa

Kerosene and diesel will in future be replaced by biodiesel as it is found to be more competent, economical and a cleaner alternative. Biodiesel is the fuel of the future due to its copious benefits to the environment, economy, human health, along with the reduction of dependence on foreign oil. [23] The Department of Energy had issued reports on the blending of biodiesel which will be made mandatory at the beginning of October 2015. [38]

Producing biodiesel in South Africa is relatively and significantly cheaper than buying diesel. For industries that rely solely on diesel fuel like agriculture, transport, construction and shipping, their production of own biodiesel is an attractive alternative that makes great economic sense. Farming input costs for an example have abruptly ascended over the years. The revenue on the other hand for the produce has been on a steady decline. The decline is due to a number of factors and none of which the farmer can control. [24]

The farmer, through manufacturing his own biodiesel, is able to bring down his cost of fuel used. Industries that manufacture their ownbiodiesel for transport fuel can cut down on fossil fuel costs. [24]

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The production of biodiesel does not only benefit the businesses, it ensures that jobs are protected and also created. In rural areas for an example, biodiesel production will prevent the influx of jobless people into urban areas something that will give rise to more informal settlements. The Department of Minerals and Energy (DME) has identified biodiesel as a major contributor for job security on the farms. [24]

The South African government has decided to actively endorse the biodiesel production practice, by exempting small biodiesel producers from all fuel tax and road accident levies if they produce up to 300 000 litres of biodiesel per year. The government has offered refunds and incentives for biodiesel even in cases where more than 300 000 litres of biodiesel is produced per year. Such governmental policies which are in the form of incentives and subsidies ensure a growing market for biodiesel in South Africa. [24]

Used vegetable oil is often looked at for use as the feedstock, but supply is usually infrequent and rarely available in sufficient quantities out of the cities. This then eliminates the usage of used vegetable oil in sectors that are centred out in rural areas like agriculture and mining sectors. Used cooking oil contains high free fatty acid content and neutralizing the free fatty acid content adds to operating costs. Used cooking oil then becomes a feasible option if it is received at a very low cost or for free. Currently a litre of used oil is selling for about R6.Taking that cost into account, biodiesel should therefore cost not more that R10 per litre.

Alternatively, sunflower seeds are used as feedstock. Sunflowers are South Africa's most extensively grown feedstock. Cotton seeds, soya and canola are grown in fairly small amounts as feedstock for biodiesel production in the Eastern Cape and Free State. [24]

The production of biodiesel from sunflower seeds ensures a steady and constant supply of feedstock. Feedstock and raw material contribute to about 80 percent of the manufacturing cost while transport costs are the second biggest contributor.

A dominant issue of biodiesel production is land as large tracks are required. The land is often acquired from communities who are economically and socially susceptible, and whose land occupancy is not formal or insecure, something which impacts negatively the poorest who reside in the particular lands.[25, 26] That however

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can be prevented by allowing the land occupants benefit from the wealth and allow them to partake and be responsible for the biofuel feedstock plantations.

Another dominant issue of biodiesel production is its threat to the food sector and as such, in South Africa, there are areas where the production of biodiesel is not permitted. In some areas in the Eastern Cape sorghum is currently looked at as the biodiesel feedstock instead of maize. With the many political issues around the production of biodiesel, it is also believed that South Africa has ample and underutilized space making it more than capable of producing sufficient amounts of alternative crops without any infringement towards the food sector and its relative laws.

1.8 Instrumentation

The South African National Standard (SANS) requires the use of more accurate equipment in testing the quality of biodiesel as not all the biodiesel characteristics can be determined using the tests kits developed in this study. Some of the instruments used to determine biodiesel characteristics are mentioned below.

1.8.1 Cold flow analyser

The cold flow analyser (Fig. 1.2) determines two temperature measurements; the temperature at which the biodiesel starts to crystalize which is the cloud point and the temperature at which the biodiesel melts after it has been frozen which is the freezing point. Samples need to be dried before proceeding with the analysis as excess water might interfere with the results. The extra drying option is available for highly hygroscopic samples.

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Fig. 1.2 Cold flow analyser instrument

1.8.2 Anton Paar Viscometer

A viscometer is an instrument used to measure the viscosity and density of a liquid. The process works by injecting a biodiesel sample to be measured into the instrument sample tube. The Anton Paar viscometer is a rotational viscometer. The software measures the density reading based on the torque required to rotate a disk or bob inside the sample cell at a known speed.

1.8.3 Flash Point (Mini Flash FLPH)

The flash point is an instrument that measures the temperature at which the air or vapour above the surface of the liquid is flammable or makes a spark in the presence of the two electrodes with a potential. Itdetermines the temperature at which the fuel ignites when exposed to a flame. The flash point for biodiesel is higher compared to the diesel which makes it an even safer option for transport purposes.

1.8.4 Mini Scan IR Xpert

The Mini Scan IR Xpert measures the IR spectrum and from the spectrum obtained the software deduces the cetane value or number which is the measure of the fuel capacity. The higher the cetane number, the better as it affects engine performance

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parameters like combustion, stability, noise, stability, emissions of carbon monoxide and hydrocarbons.

1.8.5 Karl Fischer(KF) Coulometer

The KF Coulometer determines the amount of water present in a sample. According to the South African National Standard (SANS) 1935, the water content in biodiesel should not exceed 0.05 %. High water content will give rise to corrosion of fuel and injector pumps, fuel lines and some other important parts of the vehicle.

1.9 Biodiesel test kits

The following biodiesel test kits were developed and validated:water test kit, soap test kit, 3/27 Test kit, percentage free fatty acid test kit and density test kit. The following is a discussion of how each of these test kits is utilized.

1.9.1 Water test kit

The presence of water in the oil gives rise to numerous problems during the production of biodiesel like poor reactions and high soap content. As clear as the oil might be and seem one cannot assume that it is anhydrous hence the many quantitative and qualitative water tests that have been developed. We will be looking at the weight heat weight (WHW) [37]test for water (Fig. 1.3). It is important to get rid of excess water in biodiesel as well as it can accelerate the growth of microorganism clusters and also result in the rotting of the filters in the system. Refer to Table 2.2for the test requirements.

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Fig. 1.3: Instrumentation for weight heat weight (WHW) water test kit

1.9.2 Percentage free fatty acid (FFA) Test Kit

The purpose of this test is to check the amount of free fatty acids present in oil before proceeding with the reaction. It is an indication of the quality of the oil at hand and if there is any pre-treatment of the oil required. It can also be used on the finished biodiesel to determine acidity and to find out if there are any un-reacted free fatty acids present. The requirements for this test kit (Fig. 1.4) are summarized in Table 2.2.

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Fig. 1.4: Apparatus and reagents for the percentage free fatty acid test kit

1.9.3 The 3/27 Methanol Test Kit

This test is an indication of how well the oil has been converted to biodiesel. If the oil is not converted well the fuel may not perform well in diesel equipment and it may not comply with the ASTM standard for biodiesel. When performing the test, the biodiesel sample should dissolve completely in methanol resulting in a homogeneous and clear solution. Refer to Table 2.2 for the test requirements. Pictured below (Fig. 1.5) is the 3/27 Test kit.

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Fig. 1.5: Apparatus and reagents for the 3/27 test kit

1.9.4 Soap Test Kit

The purpose of this kit is to determine both qualitatively and quantitatively the presence of soap in biodiesel. Soap can plug fuel filters, gum up fuel tanks, leave engine deposits and cause plenty of other problems. There are two types of soap test kits, a visual test kit (Fig. 1.7 and Fig. 1.8) and a titration test kit (Fig. 1.6). Ideally, a visual test should be performed first to avoid wasting chemicals on a titration. Refer to Table 2.2 for test requirements.

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Fig. 1.6: Apparatus for the soap test kit (titration)

Fig. 1.7: Soap test kit (visual)

Fig. 1.8: Phenolphthalein drops soap test kit

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1.9.5 Density Test Kit

The aim of this kit (Fig. 1.9) is to determine the density of the biodiesel. Density is an important biodiesel parameter that impacts greatly on the biodiesel quality. For biodiesel, the density is generally higher compared to diesel. Refer to Table2.2 for the requirements of this test kit.

Fig. 1.9: Apparatus and instrumentation for the density test kit

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Chapter 2

2.1 Methods and Materials

The following are the detailed methods of how each of the test kits work. Table 2.1 shows the list of reagents and chemicals required for the synthesis and testing of biodiesel and Table 2.2 shows the consumables list of the biodiesel test kit. Pure sunflower oil was purchased from a local grocery shop and the used oil was obtained from a local restaurant.

Table. 2.1: List of reagents and chemicals used during the synthesis and testing of biodiesel

Reagent	**Grade**
Potassium hydroxide	AR
Methanol	AR
Isopropyl alcohol	AR
Phenolphthalein indicator	AR
Sulphuric acid	AR
Hydrochloric acid	AR
Bromocresol green	AR
Copper sulphate	AR

AR- analytical reagent

Table. 2.2: Consumablesrequired for biodiesel test kits

No.	**Test kit**	**Requirements**
A	Percent free fatty acid test kit	• Phenolphthalein Indicator • Potassium hydroxide [0.1M] • Iso-propanol • Dropper • Burette • Burette stand • Pipettes (1ml and 10 ml) • Conical flasks *(3 flasks) • Volumetric flask (500 ml) (for making

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Table 2.2 (continues)

		up the 0.1 M potassium hydroxide)
B	3/27 test kit	• Vials with caps • Measuring cylinder • Syringe • Methanol
C	Water test kit	• A Scale • Hot Plate • Thermometer • 150 ml Glass Beaker • Stirrer Bar
D	Soap test kit (visual)	• A glass Jar with lid • Water
E	Soap test kit (titration)	• Measuring cylinder • 250 ml beaker • Magnetic stirrer • Stirrer bar • 1 ml Pipette • Iso-propanol • Bromophenol blue • 0.01 M hydrochloric acid
F	Density test kit	• Hydrometer • 100 ml measuring cylinder • Thermometer

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2.1.1 Water test kit procedure

An empty glass beakerwas pre-weighed and the mass recorded. The glass beakerwas charged with about 50 g of the oil sample and again the massrecorded (wet weight). The oil was heated for about an hour and then allowed to cool. A desiccator was used for storing the sample so as to avoid the sample from absorbing moisture from the atmosphere. Ideally the experiment should be carried out in a closed room with controlled atmospheric condition. The glass beaker with the sample was again weighed and the mass again recorded (dry weight) (Eqn. 2.1). From the masses obtained the percentage water content or ppm water(Eqn.2.2) was determined making use of the following formula:

% water = ((wet weight – dry weight)/ wet weight x 100) Eqn. 2.1

ppm water = multiply the % water by 10000 Eqn. 2.2

2.1.2 Percentage free fatty acid test kit procedure

Apotassium hydroxide solution [0.1 M]was made up (note: solution has a shelf life of 3 months). The solution (50 mL)was poured into a burette. The oil was pipetted into a conical flask the oil(1 mL). Isopropyl alcohol(10 mL) was added to the conical flasktogether with the phenolphthalein indicator(2-3 drops)with the aid of a dropper. The solution was titrated until a permanent pink colour which lasted for about 30 seconds was reached and the volume of the titrant used was recorded.Eqn. 2.3 was used to calculate the percentage free fatty acid content.

Calculate the percentage free fatty acid using the following formula:

Percentage free fatty acid = titrant (mL) x 0.75 Eqn. 2.3

For the purpose of using the test kit in the field, it was simplified further. Instead of making use of a burette in carrying out titrations, medicinal droppers were used (one drop = 0.061 mL) and instead of using a conical flask a glass bottle may be used.

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2.1.3 3/27 Test kit procedure

Abiodiesel (3 mL) samplewas added to a test vial together withmethanol (27 mL). The vial was closed and shaken for about 15 minutes.The vial with contents was allowed to sit for about 5 minutes. The vial was held at a 45 degree angle and it was observed if there was any un-dissolved oil. Test complied when there was no visible layer of unreacted oil at the bottom of the vial.

2.1.4 Soap test kit procedure (visual test kit)

A glass jar was filled half way full with distilled water and then the rest of the jar was filled with biodiesel. The jar was capped and shaken violently for about 45 seconds and then it was allowed to stand for about an hour. Test complied when the water at the bottom was as clear as it was initially added. If the water at the bottom was cloudy, then it meantsoap levels were still high. The biodiesel needed to washed some more.

Simplifying this test kit further for use in the field, phenolphthalein indicator drops were used. Refer to Fig.1.7. About three drops were added on the biodiesel waste water wash. The presence of soap would be indicated by the change of the waste water from colourless to pink. The biodiesel is clean if the water after the addition of phenolphthalein indicator drops remains clear and colourless.

2.1.5 Soap test kit procedure (titration test kit)

Iso-propanol (100 mL) was added into a 250 mL glass beaker and placed on a magnetic stirrer. To the iso-propanol, the biodiesel (12 mL) sample was dissolved in which was equivalent to 10 g biodiesel sample. About 10 – 20 drops of bromophenol blue were added. The mixture turned blue to bluish green. With the use of a 1 mL glass pipette, measured amounts of hydrochloric acid solution were added until the mixture changed colour to yellow. The amount of hydrochloric acid used was recorded and the amount of soap (ppm) present in biodiesel was calculated. The calculation wasas follows (Eqn.2.4):

Soap content = B x 0.01 x c / 1000 x w Eqn.2.4

Where B= titre (mL)

c = base constant (KOH = 320.56, NaOH =304.4)

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w = mass of biodiesel in g

2.1.6 Density test kit procedure

The biodiesel sample was heated to about 40 ^{o}C. A glass cylinder was filled with adequate sample for the hydrometer to float in it.A thermometer was inserted inside the glass cylinder to measure the temperature of the biodiesel. The hydrometer was then inserted and it was allowed to stabilize. The reading where the hydrometer intersects with the top meniscus of the biodiesel was recorded. That was to measure the specific gravity of the biodiesel.

Density is dependent on the temperature. In order to get a correct reading, the temperature of the sample to be measured should be as per specification requirements (40^{o}C).

2.2 Synthesis of biodiesel

A sample of the oil was taken and the percentage free fatty acid content determined. Ideally the FFA content should be below five percent and if it was above, the oil would have to be pre-treated through a process known as esterification (see Eqn. 1.1). With the FFA content within required specification, the oil is heated up to 100 ^{o}C to get rid of excess water. The temperature of the oil was brought down to between 55 – 60 ^{o}C and a methoxide solution was prepared and added drop-wise into the oil. Methanol amounted to 20 % of the oil batch size with the potassium hydroxide amounting to 1 % by weight of the oil.

The process, termed transesterification required an hour to reach completion. The completion of the reaction or process was confirmed by measuring the pH of the reaction. For biodiesel to form, the pH had to be above 10. Another method was to perform a 3/27 test which would be an indication of whether all triglycerides were converted to form biodiesel. With the results from both tests meeting the specification requirements, a step that followed was the separation step as two products were formed; biodiesel and glycerine which was a by-product (see Scheme 1.1). The contents of the reaction were added into a separating funnel. Glycerine was drained out and the biodiesel was washed several times with warm water and dried through heating.

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Chapter 3

3. Results and Discussion

The following results were obtained during the validation of the biodiesel test kits developed.

3.1 Percentage free fatty acid test kit validation

The percentage free fatty acid content of pure oil is expected to be lower compared to that of used oil as it is pure. Used oil will generally have to be treated through a process known as acid esterification before the synthesis of biodiesel. Used oil is expected to contain high carboxylic acid content due to the fact that it has been in use and it has been subjected to high temperatures from frying and contaminants like food particles and water. Should acid esterification be required it is important to ensure that the oil is completely dry as the acid might react with the water first causing the reaction not to occur as readily.

According to literature and as mentioned previously good oil has a percentage free fatty acid content that is in the range 0 – 5 %, with the bad oil having a percentage free fatty acid content in the range 5 – 10 %. Analysis and validation were carried out using both pure and used oil. The results obtained concurred with the literature. The percentage free fatty acid content of pure oil was lower compared to the percentage free fatty acid of used oil.

The following were the results obtained and were validated statistically.Table 3.1 shows the percentages of free fatty acid content results obtained from analysing both the pure and used oil. The results were as expected; the percentage free fatty acid content of used oil was higher compared to that of pure oil.

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Table 3.1: Percentage free fatty acid results

#	Percentage free fatty acid content (pure oil)	Percentage free fatty acid content (Used oil)
1	0.15	0.68
2	0.23	0.56
3	0.15	0.53
4	0.19	0.60
5	0.15	0.56
mean	0.17	0.59
SD	0.0335	0.0569
t	2.776	2.776
Uncertainty	0.0416	0.0706
LL (95 %)	0.13	0.51
UP (95 %)	0.21	0.66

The Thompson Tau method [38] was used to check for outliers from the results obtained. The results acquired from the analysis of pure oil had no outliers, however for the used oil results, one outlier was detected (0.68),and however it was not significant. An F-test was used to determine the variability between the two sets of results.There was no evidence of the two samples being significantly different, p = 0.165 (p›0.0001)

The variability among the percentage free fatty acid measurements of the pure and used oils was found to be statistically equal (F test, p=0.165), therefore the T-test was used to further validate the results.

The T-test showed that there is a significant difference between the percentages free fatty acid contents of the pure oil and used oil. The p value was found to be 6.68E-07 (T-test, p<0.0001), the acid content for used oil was proved to be higher compared to that of pure oil.

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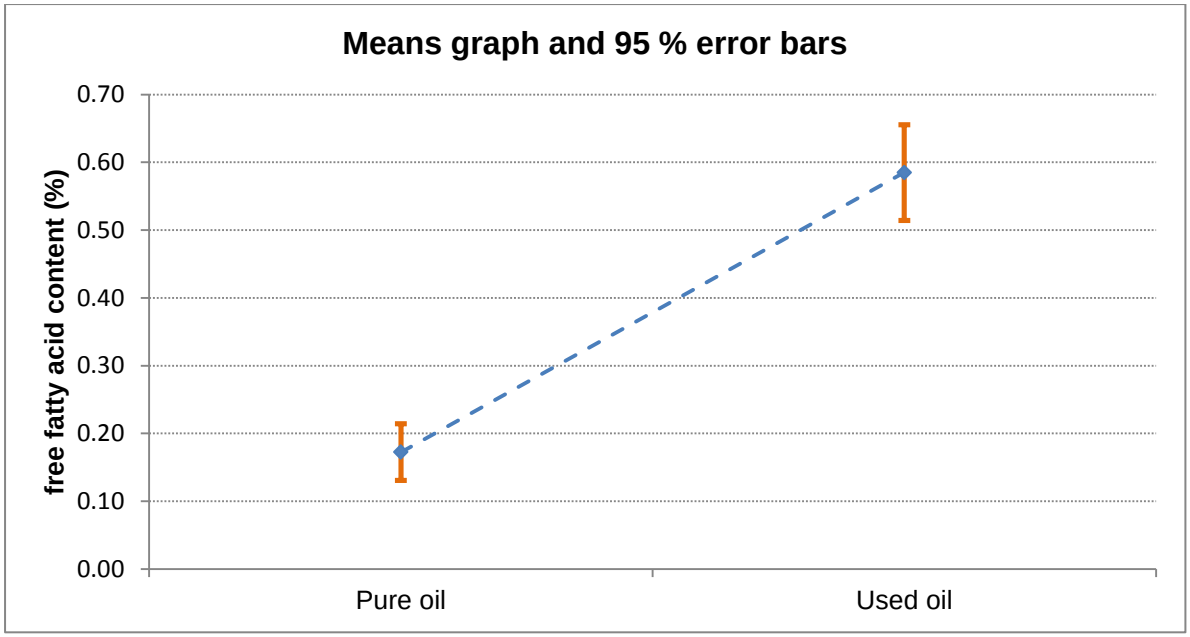

Fig.3.1: Percentage free fatty acid test kit validation.Means graph of pure and used oil and 95 % error bars

Fig. 3.1 illustrates the variability of percentage free fatty acid obtained from analysing pure oiland that obtained from used oil.Fig.3.1 clearly indicates the vastness of the difference between the two types of oil as the error bars do not overlap with each other.

3.2 3/27 test kit validation

Biodiesel was synthesized through the transesterification process using both pure and used oil. As means of developing and validating the 3/27 test kit, samples were taken at different time intervals throughout the reaction. The following were the observations.

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Fig. 3.2a:triglycerides observation (pure oil)

Fig. 3.2b: triglyceridesobservation (used oil)

Figures3.2aand b: Samples were tested at 0 min before the reaction was carried out i.e. before the methoxide was added into the oil. Sample on the left (Figure3.2a) was performed on pure sunflower oil and that on the right was done on used cooking oil (Figure3.2b).

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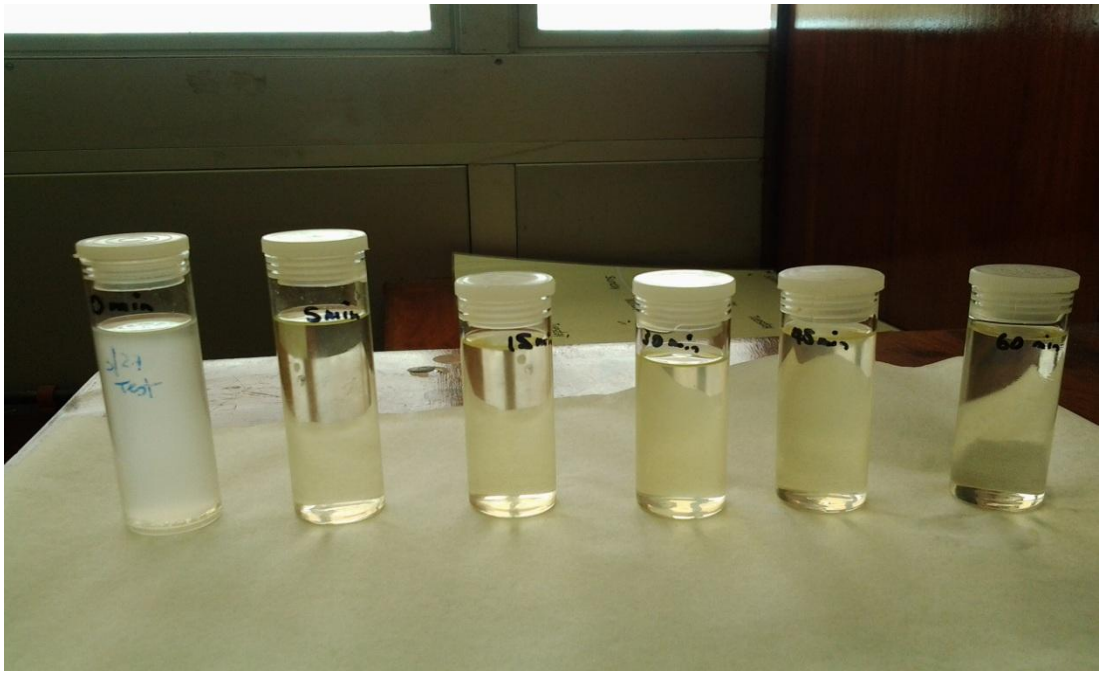

Fig. 3.3:3/27 Test kit validation (pure oil). Left to right are samples taken at different time intervals from 0-60 minutes.

Fig. 3.4: 3/27 Test kit validation (used oil). Left to right are samples taken at different time intervals from 0-60 minutes.

Figures3.3 (pure oil) and 3.4 (used oil) shows the samples taken at different intervals at 0, 5, 15, 30, 45 and 60 min respectively and tested for complete conversion of the

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oil to form triglycerides. As the reaction progresses the test sample gets clearer i.e. the sample dissolves completely in methanol. At 5 minutes it was evident that the reaction had almost gone to completion. There were just very few unreacted triglycerides or unreacted oil which formed little droplets at the bottom of the vial. Refer to Figure3.5. On the used oil, there were no visible droplets; the sample taken at 5 min was cloudier compared to the rest of the samples as the reaction progressed.

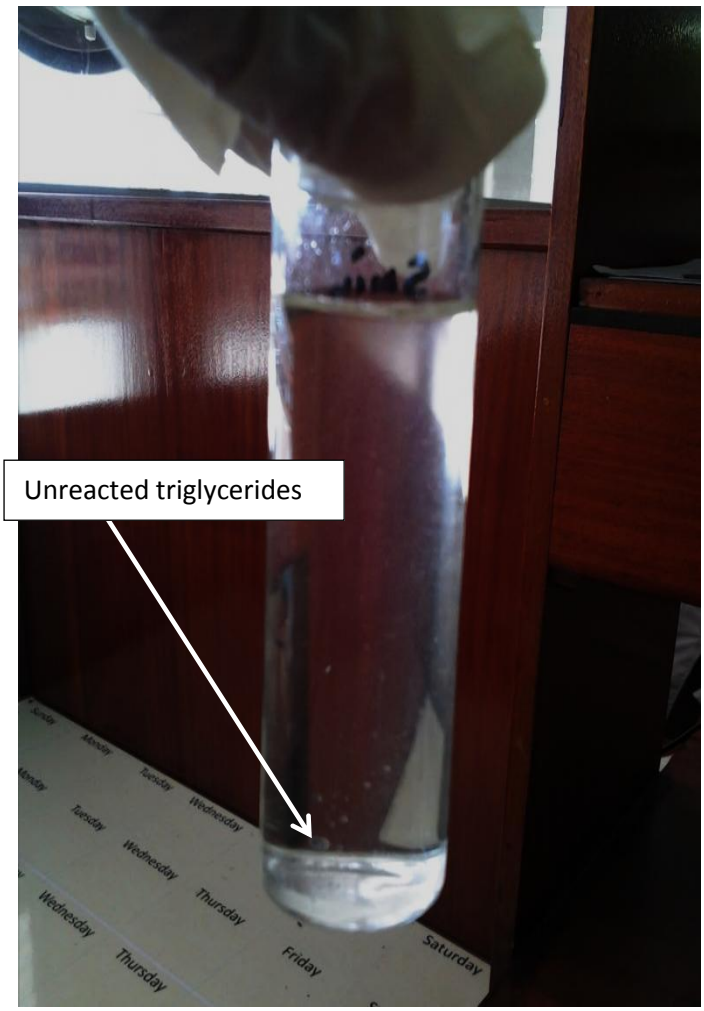

Fig. 3.5: Sample tested at 5 min. A minute amount of triglycerides or oil was still not reacted.

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The pH of the reaction was also tested as the reaction proceeded.

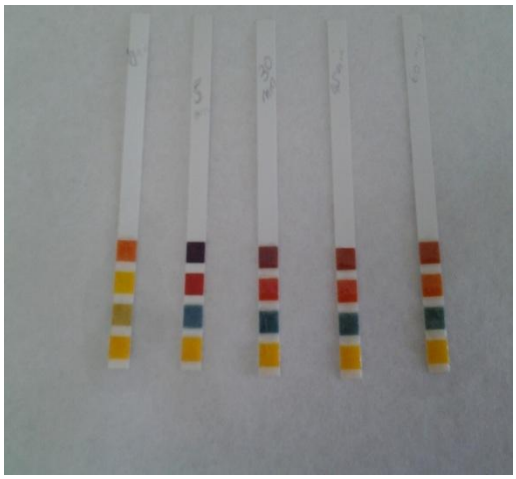

Fig. 3.6:pH measurement (pure oil)

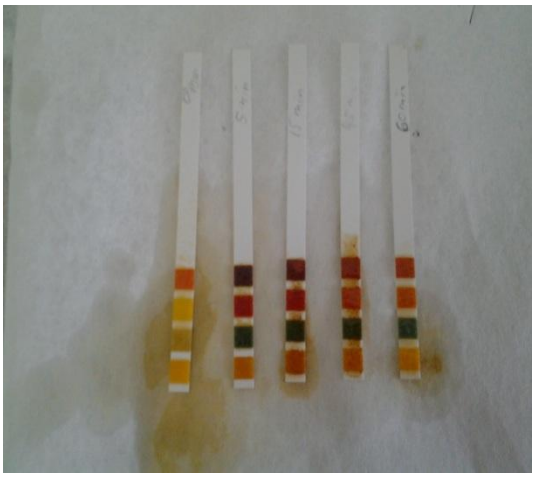

Fig. 3.7:pH measurement (used oil)

The pH was measured at 0, 5, 30, 45 and 60 min intervals. Comparing the pH strips (Figures 3.6 and 3.7) to the standard; the reaction goes from a pH of about 14 at 5 min to a pH of about 10. The pH of the oil at 0 minutes before the addition of methoxide was found to be about 6. For the biodiesel to form the pH of the reaction should be about 10 and above.

3.3 Soap test kit validation (visual)

After the process of synthesizing biodiesel, the final product needs to be washed to get rid of impurities such as soap, glycerine and excess methanol. A series of tests were performed to provide enough evidence of how much washing is required in purifying biodiesel. To determine the purity of biodiesel after each wash, the pH of the waste water wash was measured. The following results were obtained from biodiesel synthesized using used oil. Biodiesel gets cleaner with each wash, as illustrated in Figure3.8. The first water wash will exhibit a milky colour with a high pH measurement reading of about 10 due to the presence of soap and as it is washed the waste water wash will be clear i.e. the same as before the wash.

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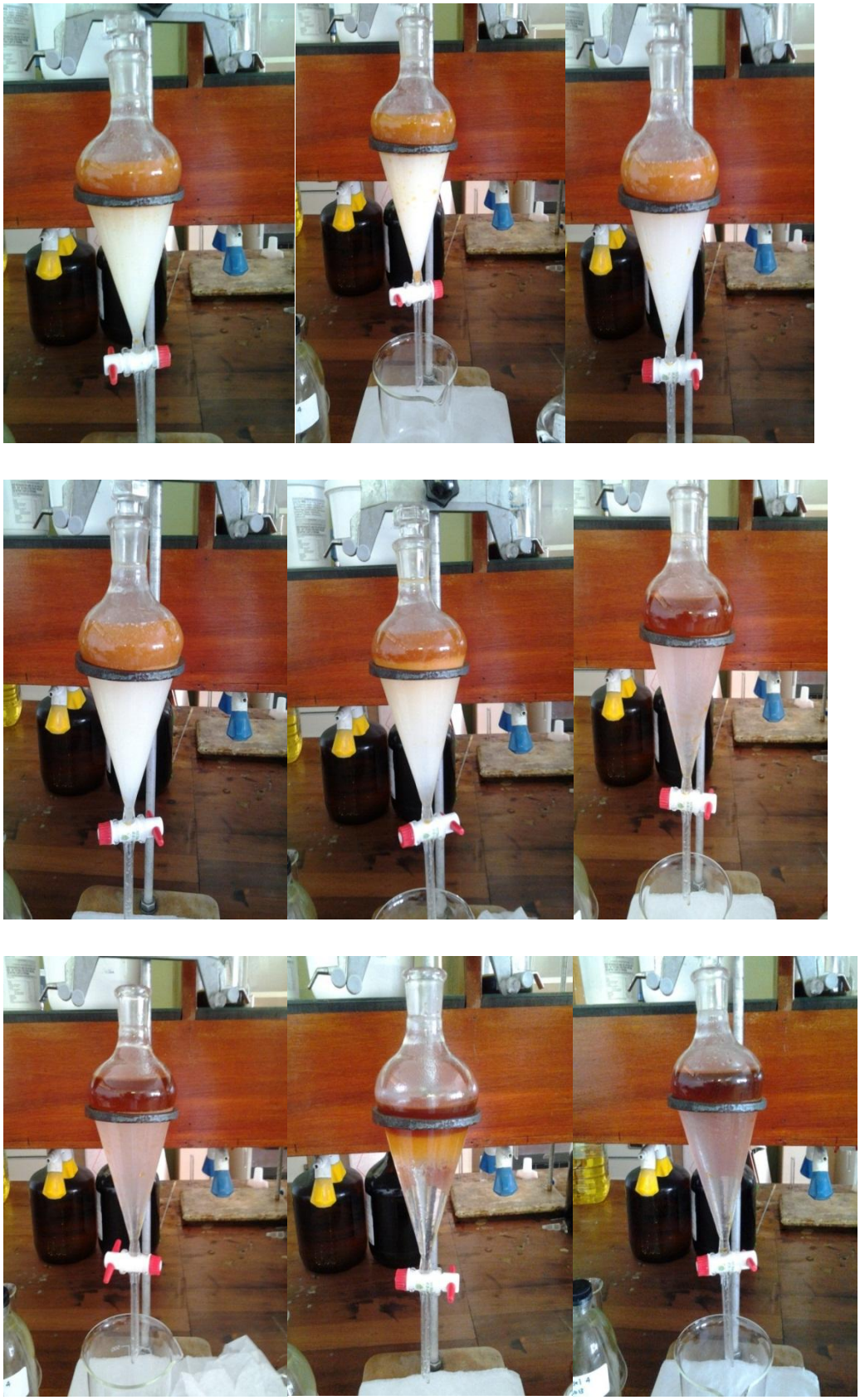

Fig. 3.8: Biodiesel soap test validation. The visual observation of the change in the waste water after each wash.

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The pH of the water before(pH 7.2) and after each biodiesel wash was measured. With the soap test, the idea was that the pH of the water after washing the biodiesel should be the same as that of the water before washing the biodiesel. The following graph (Figure 3.9) illustrates thatwith every wash, the biodiesel gets cleaner and the water less basic as evident in the pH measurement of the water obtained after thoroughly washing the biodiesel which was about 7.3.

3.3.1 Validation of soap test kit (Anova statistical analysis) - firstdetermination

Figure 3.9 was fitted with a linear model which fitted the set of results perfectly with a correlation of 0.97. Analysing the results statistically using ANOVA, a *p* value of 1.95E-09 was obtained ($p<0.0001$) proving that there is a decrease in the soap content. The soap content decreases with an average of -0.18 with every wash.

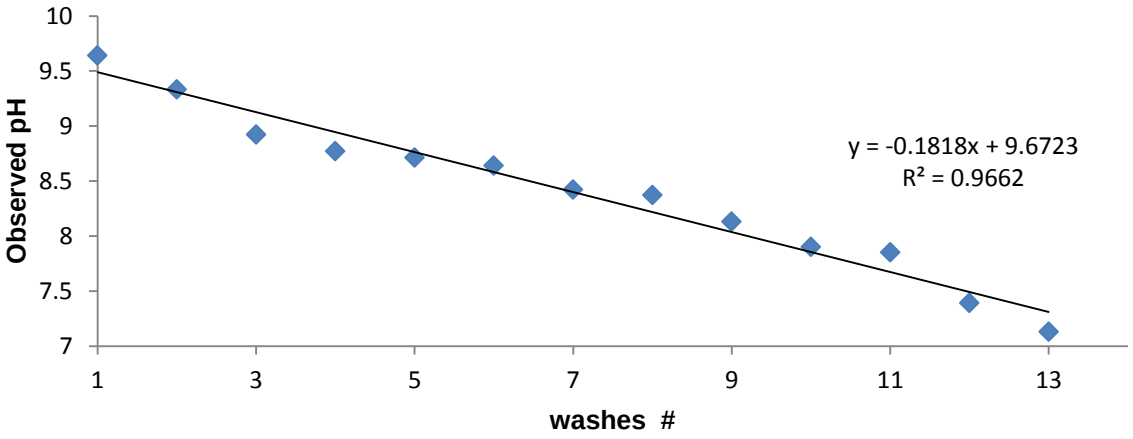

Fig. 3.9: Validation of the biodiesel soap test (visual)-first determination

3.3.2 Validation of soap test kit (Anova statistical analysis) - the second determination

Figure 3.10 shows the results obtained during the validation of the visual soap test kit. The linear model fits perfectly with a correlation of 0.96. Analysing the results

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statistically using ANOVA, it is proven that the soap content decreases with every wash, *p* value was equal to 3.93E-09 ($p<0.0001$). The soap content decreases with an average of -0.26 %.

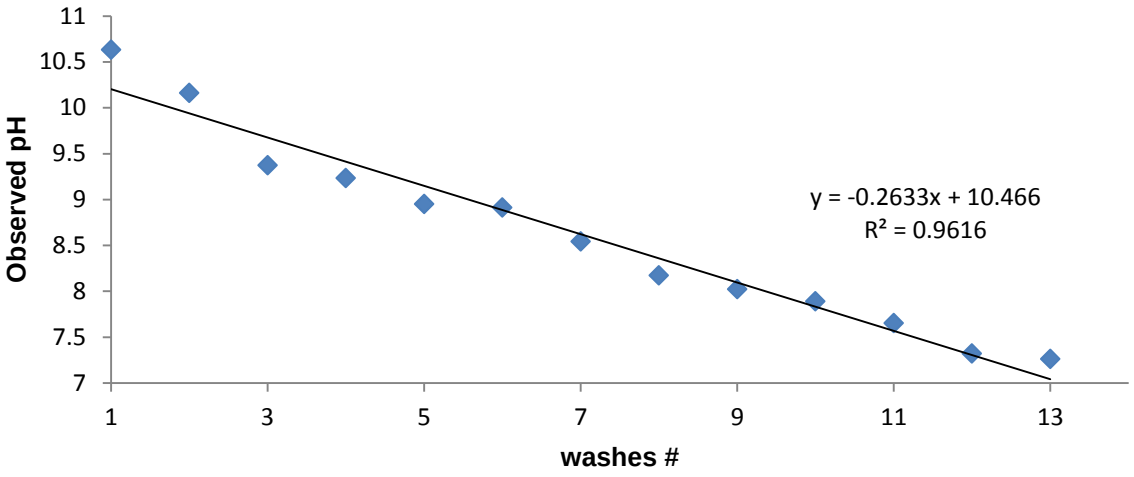

Fig. 3.10: Validation of the biodiesel soap test (visual)-second determination

3.3.3 Validation of soap test kit (Anova statistical analysis) – the third determination

The validation graph of the visual soap test kit is shown in Figure 3.11

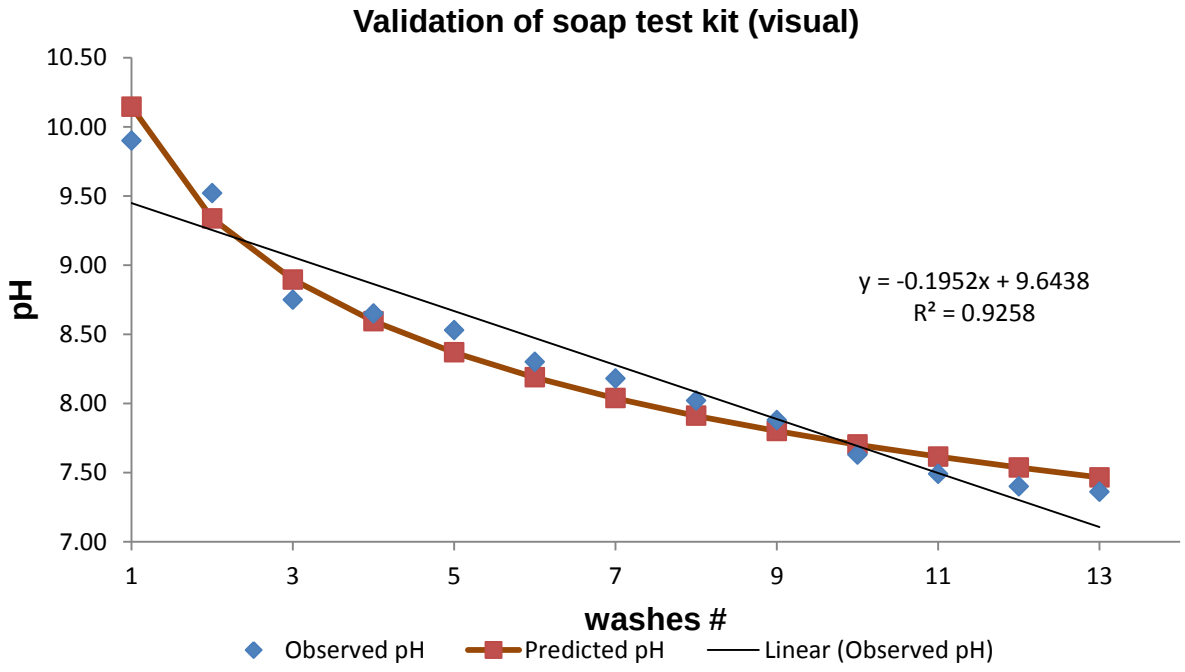

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Fig. 3.11: Validation of the biodiesel soap test- third determination

The linear model fitted on the graph was not a perfect fit as evident on the correlation equalling 0.93. The log of both the pH and of the washes was taken to obtain a better straight line from the results obtained. The correlation of 0.97 was then obtained after the log of both parameters was taken. Refer to Figure3.12.

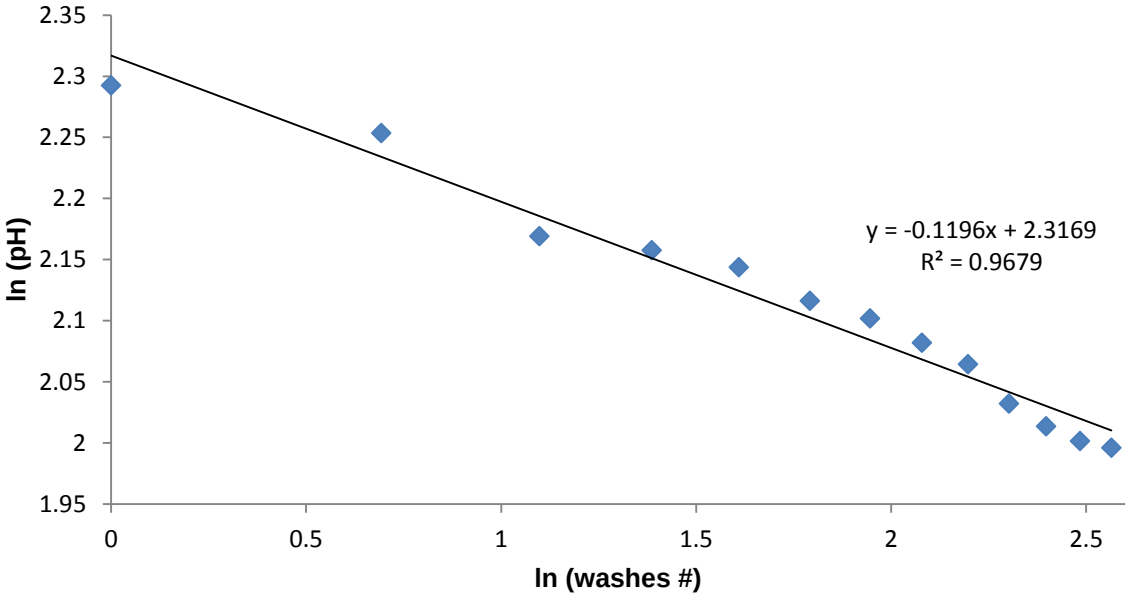

Fig. 3.12: Validation of the biodiesel soap test (visual)-(log parameters)

Using ANOVA to further validate the results proved that the soap content decreases with an average of -0.12 % with every wash. The p value was found to be 1.44 E-09 ($p<0.0001$).

3.4Soap test kit validation (titration)

A titration method for the soap test kit was also validated as follows. A sample of the biodiesel was titrated after each wash to determine the soap content. The results obtained were shown in Figure3.13.

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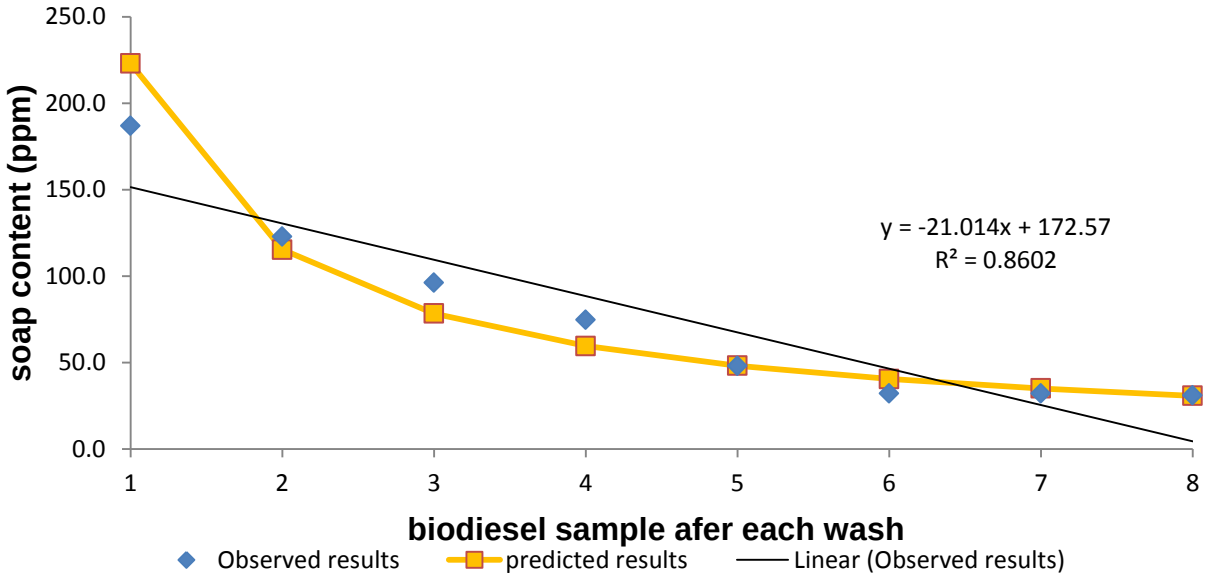

Fig. 3.13: Validation of the biodiesel soap test (titration)

When fitting a linear model on the results obtained, the model was not a perfect fit as the correlation obtained was 0.86. A power model was used which proved to be a better fit with a correlation of 0.94. Refer to Figure3.14.

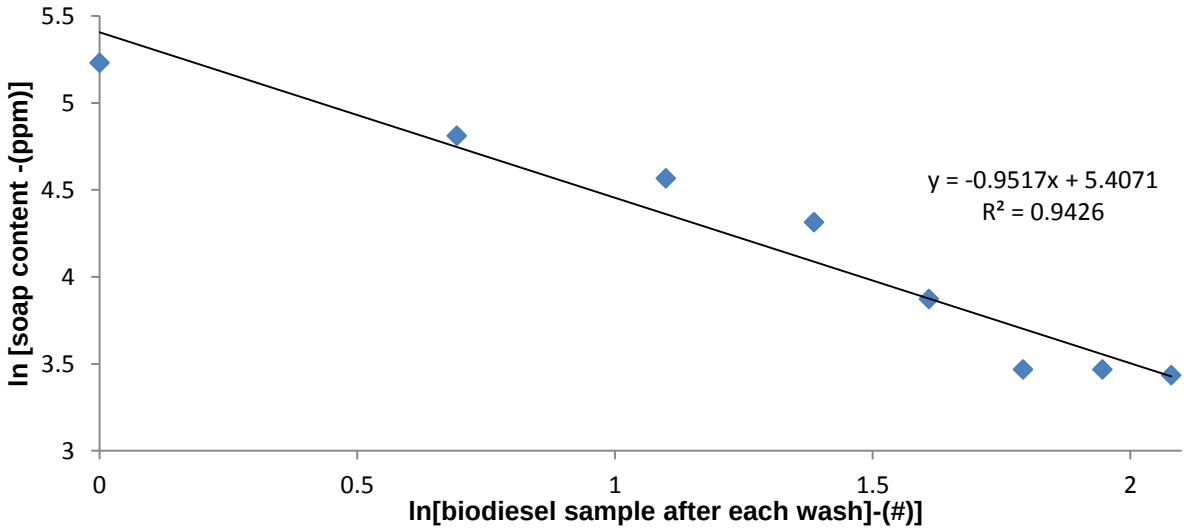

Fig. 3.14: Validation of the biodiesel soap test (titration) – (power model)

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Further validating results using ANOVA; it was proved that the soap content in biodiesel decreased with every wash by an average of -0.95 %. The *p*-value was significantly low, p = 6.05 E-05 (p<0.001) proving that there was a decrease in soap content.

The soap test kit was simplified further. The waste water washes were tested for the presence of soap using filter papers impregnated with the phenolphthalein indicator.Shown in Figure 3.15a.

Filter paper strips impregnated with the phenolphthalein indicator were developed.

Fig. 3.15a: Filter paper strips impregnated with phenolphthalein solutionindicator

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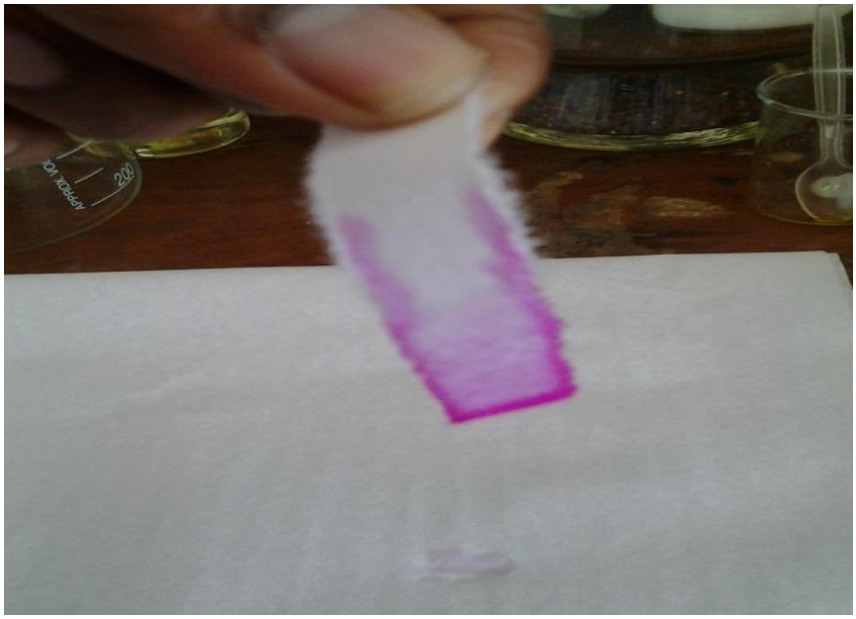

Fig. 3.15b: Testing forthe presence of soap using filter paper strips impregnated with phenolphthalein indicator solution.

The method was however found to be inaccurate as it only detected thoroughly the presence of soap in greater amounts, a 0.1 M potassium hydroxide solution was used as a comparison. A red litmus paper was also used and it was also found to as inaccurate. The presence of soap was only detected clearly on the first biodiesel waste water wash as evident on the first litmus paper stripshown in Figure 3.16.

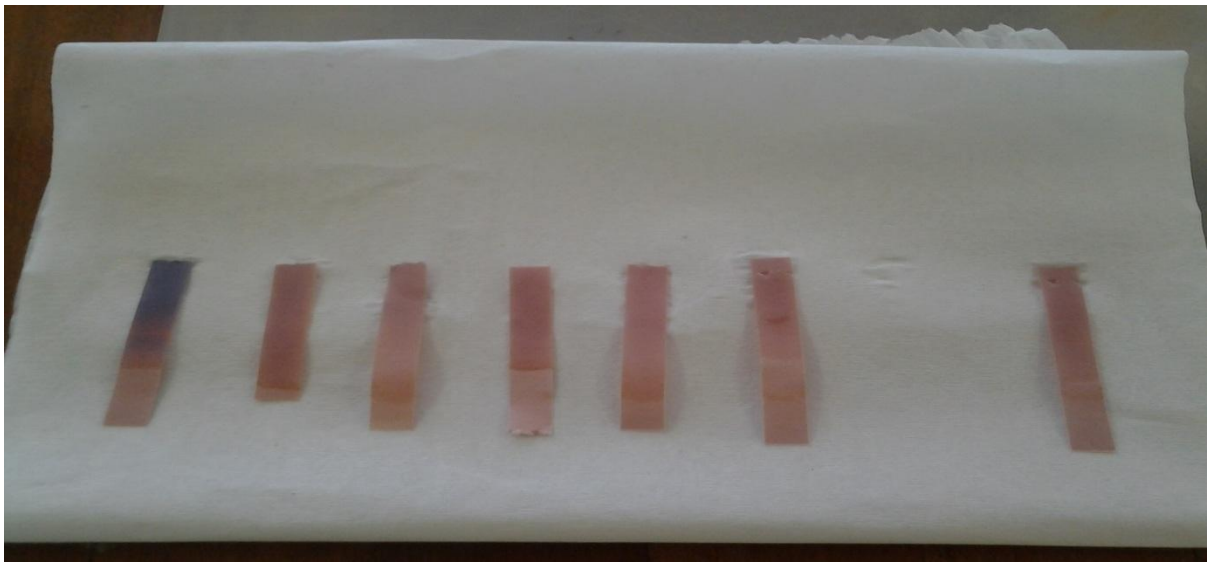

Fig. 3.16: Testing for the presence of soap using red litmus paper

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Phenolphthalein indicator drops were poured directly into the waste water wash. This method was found to be more accurate in detecting the presence of soap compared to the above litmus paper methods. The method detected the presence of soap up until the fourth wash whereas with the litmus paper, soap was only detected clearly and only on the first wash illustrated in Figure3.17.

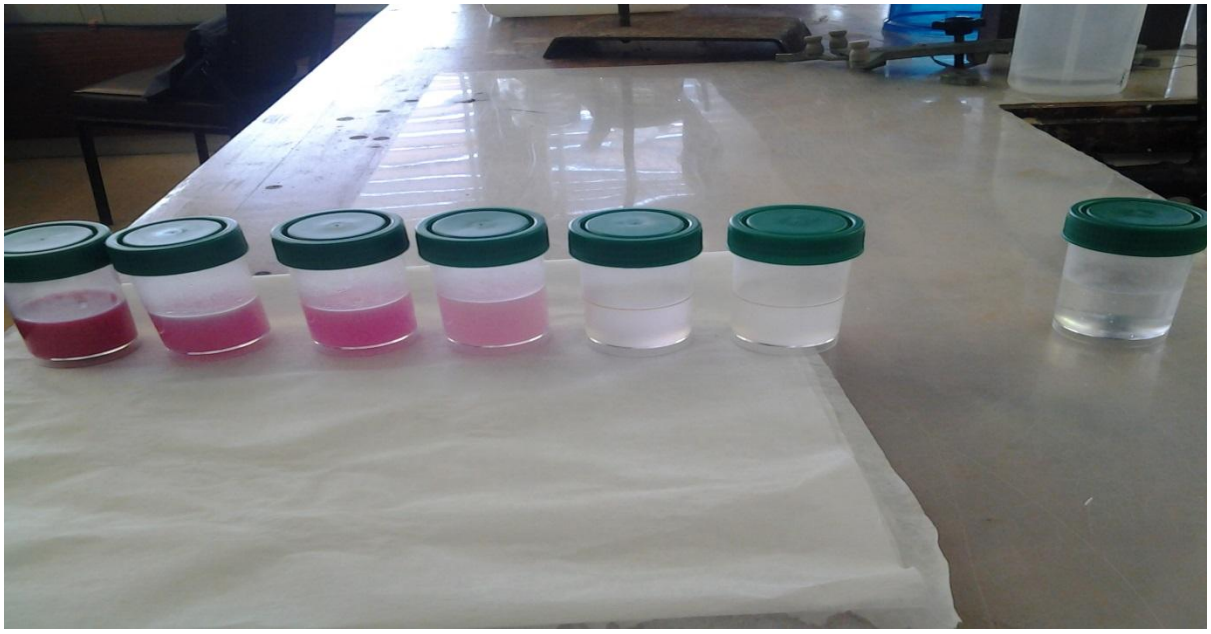

Fig. 3.17: Testing for the presence of soap in biodiesel waste water washes using phenolphthalein indicator solution drops

Comparing the litmus paper soap content determination method to the above soap content determination method by directly adding the drops of phenolphthalein indicator, the colour change of the waste water from colourless to pink was detected up until the fourth wash, whereas with the litmus paper, the presence of soap was only detected on the first wash. The direct addition of phenolphthalein drops to the waste water wash was therefore the most accurate and preferred test method.

3.5 Density test kit validation

The density measurement of biodiesel is relative to its quality. The hydrometer apparatus was validated by comparing its readings to those obtained using a viscometer. Summarized in Table 3.2.

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Table 3.2 Density results obtained from using a viscometer and a hydrometer

Viscometer	Biodiesel 1	Biodiesel 4	Biodiesel 2	Biodiesel 3
1	0.8765	0.8743	0.8786	0.8927
2	0.8766	0.8743	0.8785	0.8933
3	0.8767	0.8743	0.8785	0.8933
4	0.8766	0.8742	0.8785	0.8935
5	0.8767	0.8742	0.8785	0.8935
6	0.8766	0.8742	0.8785	0.8935
Mean	0.8766	0.8743	0.8785	0.8933
SD	7.528E-05	5.477E-05	4.082E-05	0.0003098
t	2.571	2.571	2.571	2.571
Uncertainty	7.901E-05	5.749E-05	4.285E-05	0.0003252
LL(95%)	0.8765	0.8742	0.8785	0.8930
UL(95%)	0.8767	0.8743	0.8786	0.8936

Hydrometer	Biodiesel 1	Biodiesel 4	Biodiesel 2	Biodiesel 3
1	0.875	0.873	0.875	0.885
2	0.876	0.872	0.876	0.895
3	0.875	0.872	0.878	0.893
4	0.874	0.872	0.879	0.895
5	0.875	0.873	0.879	0.893
6	0.874	0.872	0.875	0.894
Mean	0.875	0.872	0.877	0.893

The first two batches of biodiesel (biodiesel 1 and 4) are from the same source which is pure sunflower oil and biodiesel 2 and 3 are biodiesel obtained from used oil. The fact that these bars overlap signifies the fact that there is no significant difference in the average density.

With the hydrometer mean results within the error bars, that signifies that there is no significant difference between the two density measuring devices. The hydrometer is as accurate as the viscometer.

The lower limit (LL) and upper limit (UL) are the 95 % confidence ranges. To validate the accuracy of the other instrument, the values that will be obtained should fall within the upper and lower limits as evident and illustrated in Figure 3.18.

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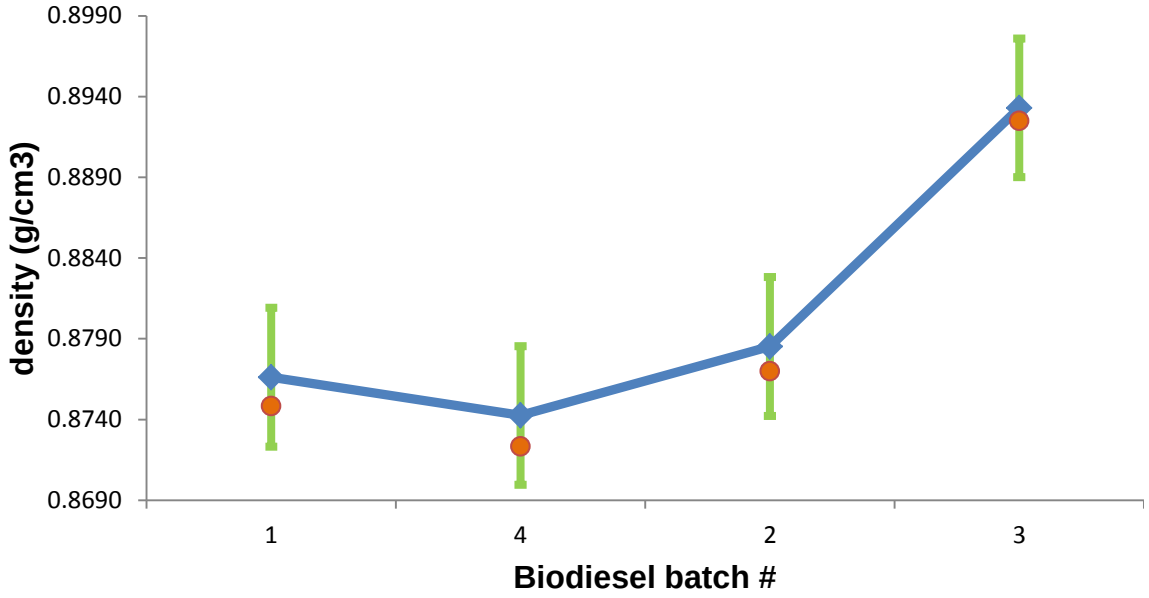

Fig. 3.18: Means graph and 95 % error bars of the density test kit validation. The comparison of the density results obtained using a hydrometer and a viscometer.

3.6 Water test kit

Tables 3.3 – 3.5 summarised the results obtained for the water test kit. The testing was performed on biodiesel samples using the weight heat weight method. Samples were taken at different time intervals; 5, 15, 30, 45,60 and 75 minutes. According to the SANS 1935 standard, the water content in biodiesel should be below 0.05 %.

Since the boiling point for water is 100 ^{0}C, heating the samples at that temperature ensured the evaporation of water from the sample. An hour proved to be sufficient as the results stabilized from 45 minutes to 75 minutes.

-

Table 3.3: Validation of water test kit - 1

Time (min)	mass of beaker + sample	% water
0 (initial mass)	160.9958	
5	160.5368	0.286
15	160.4938	0.027
30	160.4780	0.010
45	160.4779	0.000
60	160.4778	0.000
75	160.4778	0.000

Table 3.4: Validation of water test kit - 2

Time (min)	mass of beaker + sample	% water
0 (initial mass)	167.2016	
5	167.0599	0.085
15	167.0539	0.004
30	167.0495	0.003
45	167.0329	0.010*
60	167.0325	0.000
75	167.0324	0.000

Table 3.5: Validation of water test kit - 3

Time (min)	mass of beaker + sample	% water
0 (initial mass)	169.642	
5	169.1481	0.292
15	169.1353	0.008
30	169.1124	0.014*
45	169.1122	0.000
60	169.1122	0.000
75	169.1122	0.000

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A graphical representation of the results tabulated in Table 3.3 was as follows

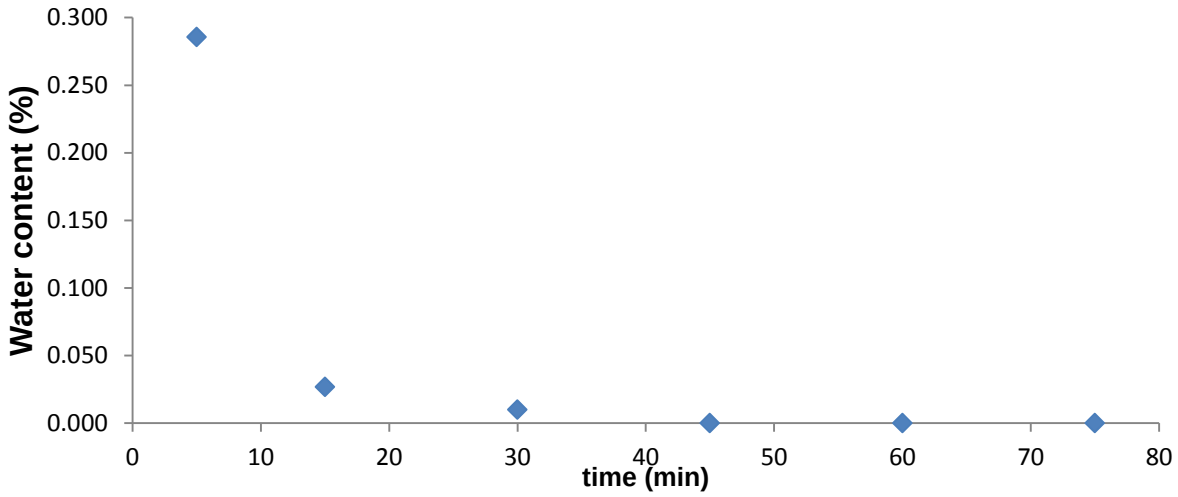

Fig. 3.19 Validation of the water test kit

A sharp decrease in water content as the sample is heated was evident. Except for an outlier on Table 12 and 13, which could have been due to the sample gaining moisture from the environment as biodiesel is hygroscopic, an hour was proved to be sufficient in getting rid of excess water from biodiesel after it has been washed.

Another simplified method for checking for the presence of water in biodiesel was to add anhydrous copper sulphate (about 1 g). Copper sulphate does not dissolve in biodiesel, however if there is a bit of water present, the anhydrous copper sulphate which settles at the bottom of the flask will change colour from whitish blue to a strong blue colour. Illustrated in Figures3.20 and 3.21.This copper sulphate kit does not form part of the WHW water test kit; it is extra information.

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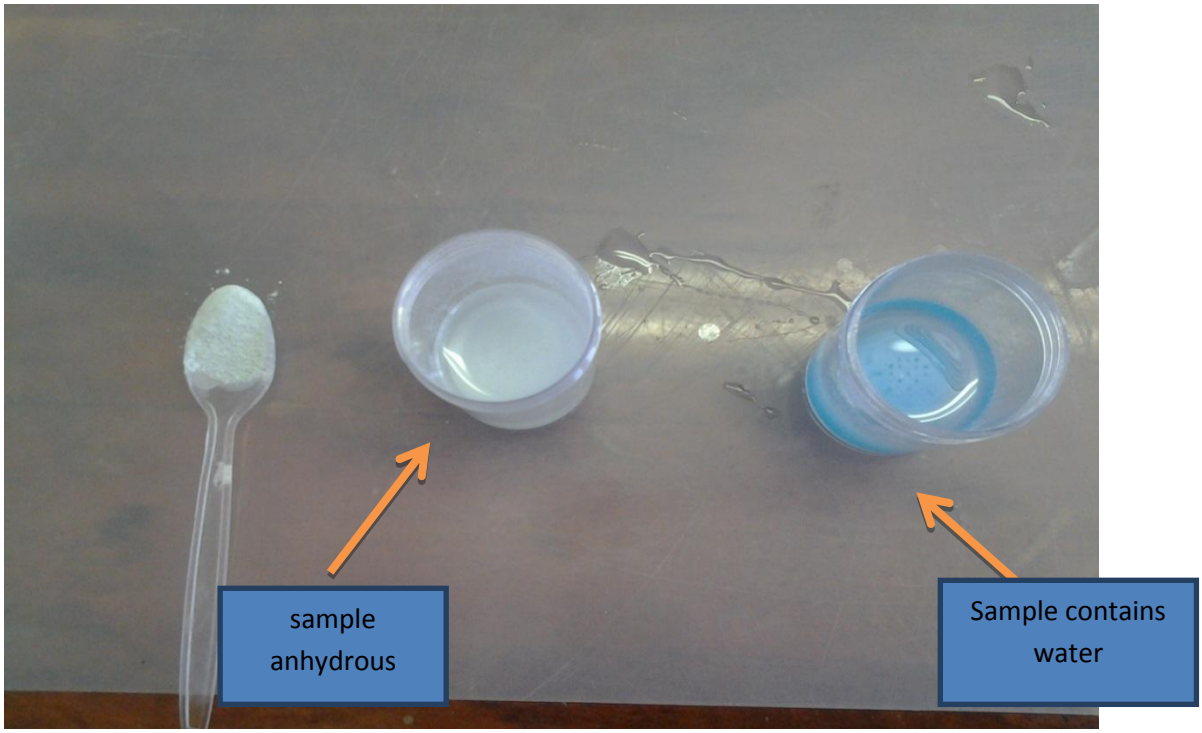

Fig. 3.20: Testing for the presence of water in a biodiesel sample using anhydrous copper sulphate

Fig. 3.21: Visual observation of biodiesel samples tested for the presence of water using anhydrous copper sulphate

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Chapter 4

4.1 Conclusion

The biodiesel test kits that were developed were found to be effective as the results produced were accurate, repeatable and reproducible. The water test kit was validated using hydrous biodiesel and the weight heat weight method. The results obtained were as expected. Heating a hydrous sample at 100 ^{0}C will result in the evaporation of moisture. As the biodiesel is hygroscopic, the sample would have to be stored with a drying agent after getting rid of the excess water. The drying agent could make the biodiesel usage difficult and possibly cause damage to the vehicle should it be decanted with the biodiesel. Filters would have to be used to ensure that when pumping out biodiesel, the drying agent does not also get pumped out into the vehicle. The objective with the water test kit was achieved.

The Weight Heat Weight (WHW) test kit was found to be effective. The water test kit was again simplified further. Another way of detecting the presence of moisture in a sample was through employing anhydrous copper sulphate. With this method, the indication of the presence or absence of water was observed through the change in colour of the anhydrous copper sulphate once added onto the sample. This method would be used after drying the sample as a control check.

A series of tests were performed during the validation of the Soap test kit (visual test) as no instruments were used to compare with. The results obtained were found to be repeatable and reproducible. As there were no fancy apparatus for these methods, an individual who has no chemistry background would be able to carry out the experiments with ease. The second soap test kit which is a titration was used to confirm what was observed on the visual soap test.

The visual soap test kit was found to be important as it prevents the biodiesel manufacturer from wasting chemicals on a titration test. Comparing both the qualitative and the quantitative methods for soap determination in biodiesel, the results obtained were in agreement. When cloudy water was observed during the biodiesel wash, the results were backed up as the titration test showed a high soap content.

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A series of tests were also performed during the validation of the 3/27 test kit. This method proved that an hour was sufficient for biodiesel synthesis. Taking the pH measurements of the sample during biodiesel syntheses was found to be effective. If the pH of the reaction was below 10 then the 3/27 test would not comply as for biodiesel to form, the pH should be above 10. The 3/27 test kit was found to easy to perform and the results obtained were conclusive.

The density test kit made use of a hydrometer. The results obtained were compared to results obtained employing a viscometer instruments. The closeness in results highlighted the accuracy of the hydrometer. The hydrometer was proved to be as effective as the viscometer in density measurements.

The ease of use of the test kits was a major aspect as it was the aim of the project i.e. to develop and validate simple biodiesel test kits to be used by growing biodiesel manufactures who do not afford to purchase fancy and expensive equipment.

The biodiesel test kits were successfully developed and validated and the objective of the project was met.

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PART B

FINANCIAL REPORT ON STUDY

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Project Business plan and marketing strategy

Submitted by:

Pumza Fibi

DATE COMPLETED: DECEMBER 2013

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FINANCIAL EXECUTIVE SUMMARY

A study was carried out which aimed to develop and validate biodiesel in-house test kits for use by the growing biodiesel manufacturers. The intention behind developing and validating the test kits was to assist these companies economically by minimizing poor quality costs (PQC). These test kits were to be a means of detecting irregularities and out of specifications before the finished product was sent elsewhere for quality testing. This financial report entails the marketing strategy and the breakdown of production and operation costs.

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A. Introduction

Biodiesel is a vegetable oil or animal fat based diesel fuel which consists of long chain alkyl esters. A study was carried out on the development and validation of in-house biodiesel process test kits. The study was done so as to assist growing biodiesel producing companies with their manufacturing process and testing. It was aimed at helping these companies reduce costs of sending a defective product for outsource testing i.e. for them to be able to determine before, during and after the process if the product complied to indicated specifications.

With the increase in the demand of biodiesel, commercial production offers a unique opportunity that may be financially profitable. Biodiesel is currently selling at about 1.6 % less compared to diesel. However, like in any other business venture; a business plan which is solid is a crucial tool. Marketing is one of the fundamental steps in drafting a business plan as it communicates the value of a product to a customer with the intention of selling.

A.1 Market Mix Elements

Market mix is a combination of elements used to market a product. These elements allow a business to combine all marketing tools in order to sell a product. Market mix elements consist of what is called the 4 P's i.e. Product, Place, Price and Promotion.

(i) Product: The product for this particular research is the biodiesel test kits. A good product markets itself as it provides benefits for the customer. The biodiesel test kits have been validated and thereby proven that they are suitable for the intended purposes which are to test for water, density, % free fatty acid content, soap content etc.

(ii) Place: A place is where one can expect to find the customer and consequently where the sale is realized. In this case the focus will be on the growing biodiesel manufacturer's production site. The intention will be to demonstrate to them how the test kits work. Marketing of the test kits may even be centralized i.e. organize a venue and invite all potential customers to the biodiesel test kits exhibition. This strategy will not only save time, however, it will also reach out to a wider and potential market.

-

(iii) Price: Price refers to the pricing strategy. Price refers to the cost of each test kit.

(iv) Promotion: Promotion includes such things as advertising and public relations and it is closely linked to sales. The function of promotion is to affect the customer behaviour in order to close a sale. The focus will be on advertising, hosting workshops that will demonstrate the easy use and relevancy of the biodiesel test kits.

A.2 Market Place

Market place is concerned with various methods of transporting and storing goods, and then making them available for the customer. Getting the right product to the right place at the right time involves the distribution system. A number of local companies that are in need of these simple biodiesel test kits will be identified. The test kits will be packed and sent to the companies after marketing the test kits through demonstrations held at suitable venues. The choice of distribution will depend on a variety of circumstances.

There are three main channels of distribution[iii]and are as follows:

(i) From the manufacturer to the wholesaler, from wholesaler to the retailor and then to the consumer;

(ii) from the manufacturer to the retailor and then to the consumer; and

(iii) from the manufacturer direct to the consumer.

All three channels would be carefully viewed and the one that works best would be implemented. Factors affecting the choice of the distribution channel are the perishability of the product, the monetary value of the product, and the technical nature of the product. In view of the biodiesel test kits, they are durable, they do not cost much and they are not highly perishable in nature therefore a long distribution channel may be considered. However, due to the technical nature of the test kit, it would be best to supply the test kits directly to the companies so as to strengthen customer relation and credibility.

-

A.3 Cost elements

The biodiesel test kits are not expensive. All six test kits amount to roughly R2643.85 (Refer to Table. A). For highly advanced companies, advanced test kits may be purchased, for an example the Sandy Brae water test (Fig. A) kit may be used which costs about R 3900.00. A viscometer (Fig. B) may also be used in the place of a hydrometer and it costs about R20 000.00.

Again for highly advanced entities, samples may be sent to SANS approved laboratories for fatty acid methyl ester (FAMEs) as well as free and bonded glycerine and overall glycerine content determination in biodiesel.Table A illustrates rough figures of how much the test kits combined cost.

Table A: Biodiesel test kit cost calculation

Item	Cost (Rand)
• **% free fatty acid test kit:**	
0.1 M KOH (1L)	190.00
Medicinal dropper (3)	20.60
250 ml bottles (3)	80.00
Calculator	75.60
• **3/27 test kit**	
Vials and caps (30)	160.90
• **Soap test kit (quantitative)**	
0.01M Hydrochloric acid	230.00
Bottles (5)	120.75
Medicinal dropper (3)	20.60
250 ml bottles	80.00
Bromophenol blue Indicator solution (10 ml)	190.75
Calculator	75.60

-

Table A (continues)

• **Soap test kit (visual)**	
Phenolphthalein indicator solution	90.00
20 ml plastic bottles	10.00
• **Water test kit**	
Hot plate	326.62
250 ml beaker (3)	240.85
Weighing Balance	501.29
Calculator	75.60
• **Density test kit**	
100 ml measuring cylinder	25.99
Hydrometer (0.800-0.900)	128.70
Total Costs	2643.85

Fig. A Sandy Brae water test kit[i]

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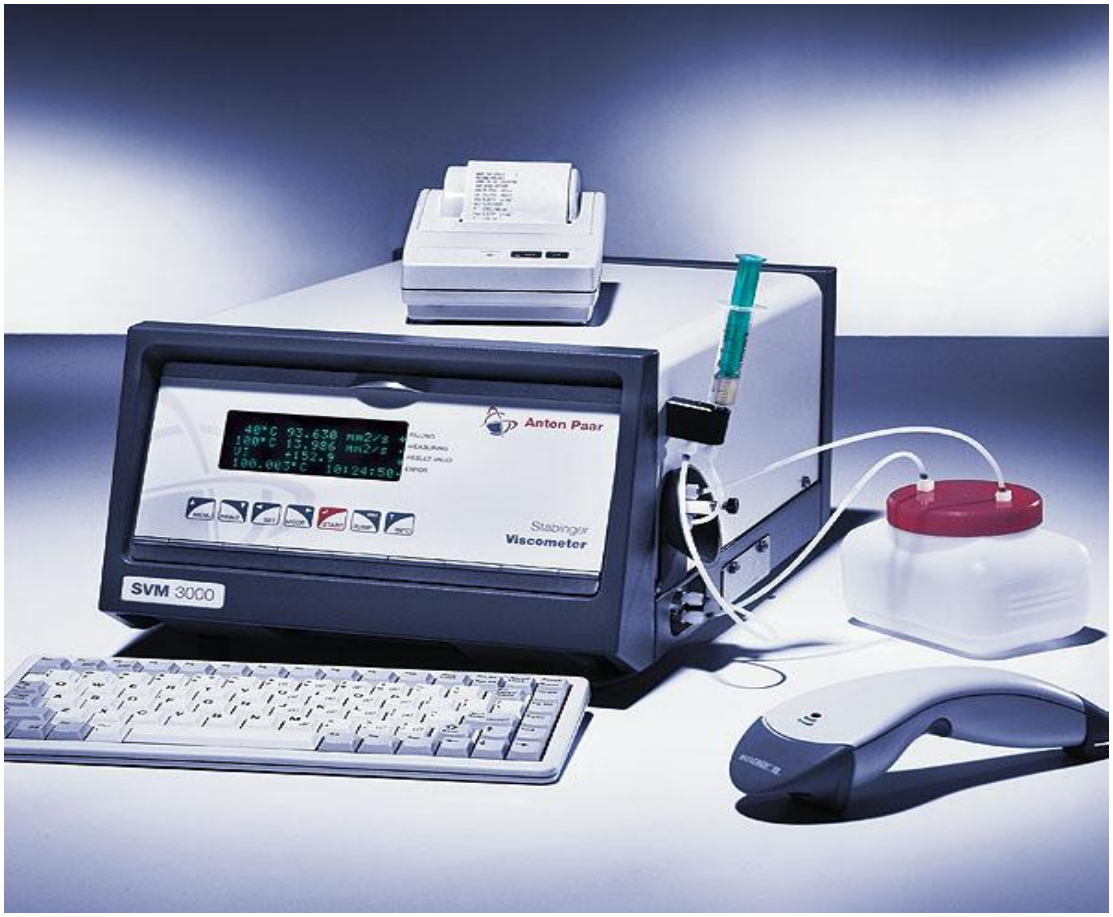

Fig. B Anton Paar viscometer[ii]

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Figure C is of thebiodiesel test kits developed and how the kits would be packaged. Appendix 1.1 – 1.5 consists of the instruction manuals of the biodiesel test kits.

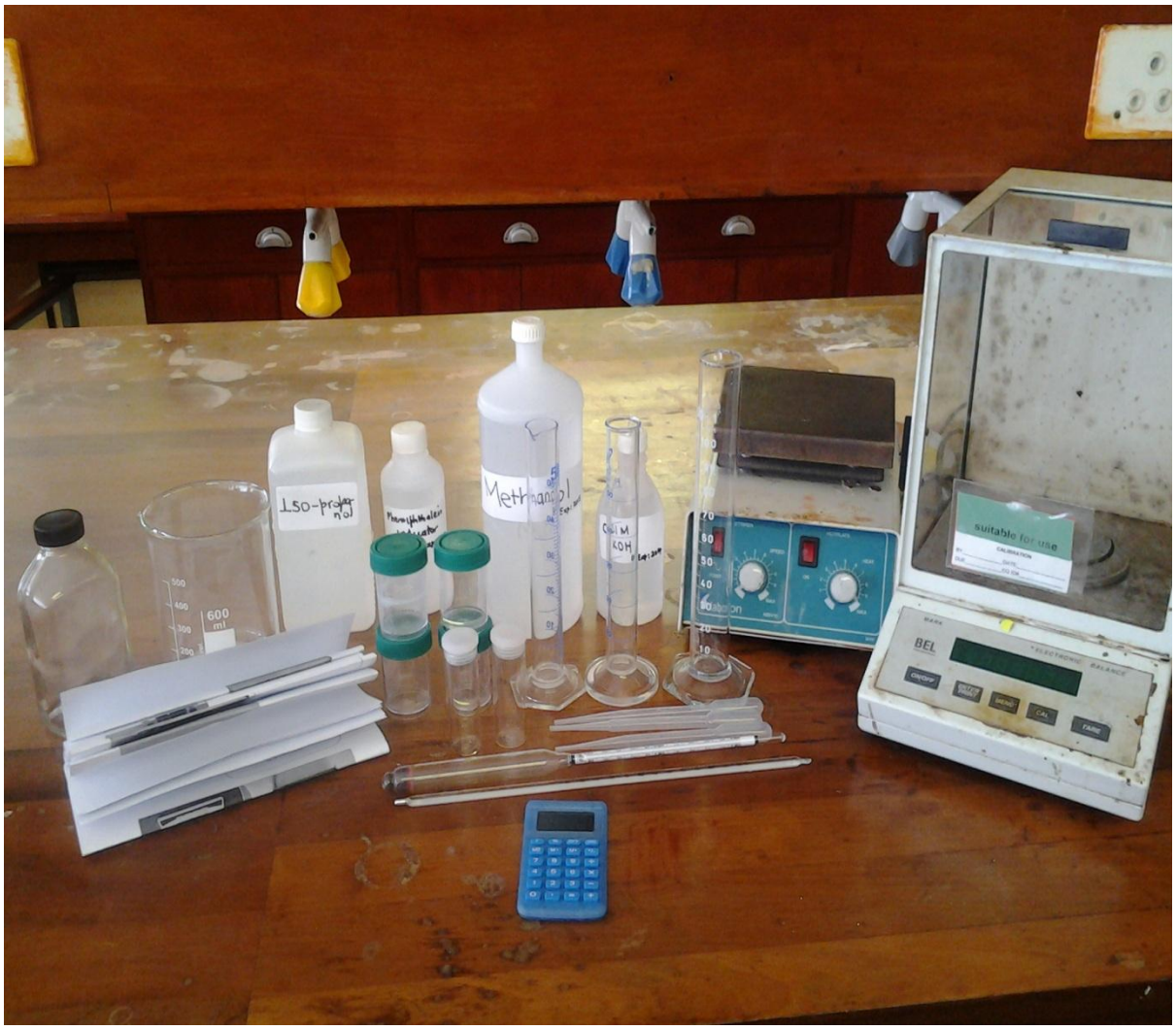

Fig. C: Biodiesel test kits

A.4 Unique selling proposition

The unique selling proposition (USP) is the force that drives the business and success. It is about what makes the product exclusive, valuable and visible in the market. Having a unique selling proposition will dramatically improve the positioning and marketability of the biodiesel test kits. Building a unique selling proposition takes some effort, however, it is absolutely worth it because of the added advantage the product will have on the market. Making use of a powerful unique selling proposition

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will make the job of marketing the test kits much easier, resulting in an increase in sales and profits.

The greatest advantage of the biodiesel test kits is the ease of use and the fact that anyone can use them without any chemistry knowledge or background. They are affordable. Any company that is starting out and has not yet established itself financially can make use of the test kits.

The unique selling proposition for the biodiesel test kits would be: the operational technical ease of use and low financial cost of all the test kits combined.

B. Conclusion

Based on the financial analysis, making use of the test kits proved to be beneficial and made economic sense.The cost of purchasing the test kits was far less compared to the cost of a produced defect biodiesel and therefore lost sales. Biodiesel testing is a major obstruction financially for growing companies; as they rely on sending their samples for outsources testing to determine the quality of their biodiesel and whether it complies with the specification requirements. Usually the reports came back reporting that the samples are defect. With the development and validation of simple and easy to use biodiesel test kits, these companies will be able to determine the quality of their biodiesel before sending samples for outsource testing if necessary.

These test kits are used before, during and after biodiesel testing and the growing biodiesel producing companies will save thousands of rands worth of raw materials as they will be able to detect, making use of the test kits, whether a particular step needs to be redone. These test kits are relatively inexpensive compared to the price of producing a defect. The test kits are simple to use, easy to put together and they can be understood easily by even layman. For highly advanced companies and laboratories there are options of purchasing expensive equipment like the gas chromatography instrument for fatty acid methyl esters (FAMEs) determination which will allow the companies to cut more costs as they will test their samples themselves.

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The blending of biodiesel and diesel will in a few years become be mandatory, it is therefore important that the synthesis and testing of biodiesel is done right the first time as this alternative and green way of producing fuel has major contributions on our economy and on the environment.

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C. References

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(ii) Labsource [image on the internet]; cited 2013. Available from: http://www.labsource.co.uk/1977.jpg

(iii) Fontelera J., Distribution Channels and Marketing Analysis [homepage on the internet]; cited 2013. Available from: http://smallbusiness.chron.com/distribution-channels-marketing-analysis-60985.html

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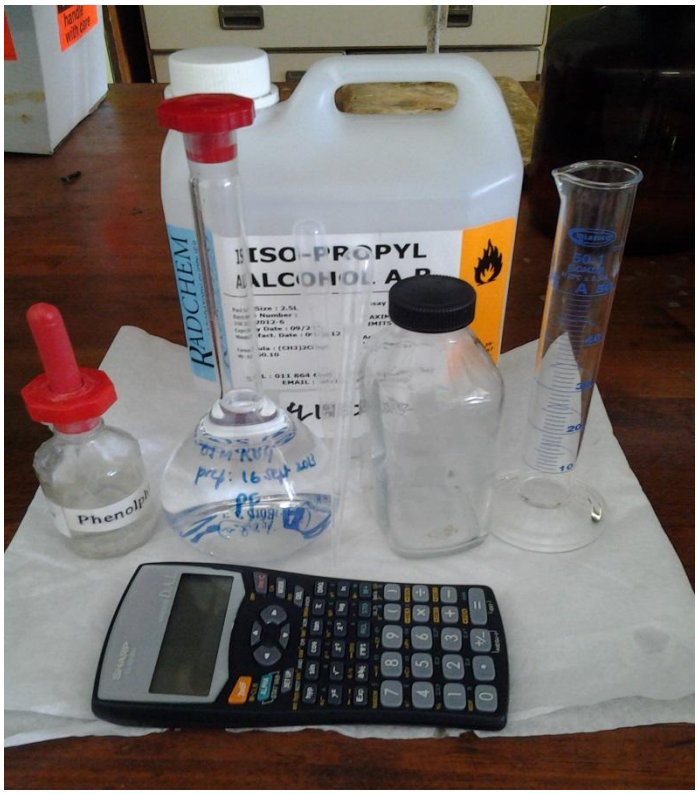
D. Appendix

Appendix 1.1 – 1.5 consists of the biodiesel test kits instruction manuals.

Appendix 1.1: % free fatty acid test kit instruction

The purpose of this test kit is to determine the quality of the oil.



Requirements:

a) Isopropyl alcohol
b) Phenolphthalein indicator
c) 0.1 M Potassium hydroxide
d) Glass bottle
e) 2 medicine droppers
f) Measuring cylinder
g) Calculator

- With a medicine dropper, add 1 mL of oil into a glass bottle
- Add 10 mL of Isopropanol alcohol, 2-3 drops of phenolphthalein indicator and shake or swirl.
- Drop-wise, titrate with or add 0.1 M potassium hydroxide until a permanent pink colour is reached which lasts for about 30 seconds. (Note: 1 drop = 0.61 mL).
- Record how many drops were used and convert them to millilitres.
- Use the following formula to calculate the % free fatty acid content:

% free fatty acid = titre (mL) x 0.75

-

Appendix 1.2: 3/27 test kit instruction

The purpose of this test kit is to determine how well the oil has been converted to form biodiesel.

Requirements:

a) Vial with cap
b) Medicine dropper
c) Measuring cylinder
d) Methanol

- Add 3 mL of biodiesel to be tested in a vial
- Add 27 mL of methanol
- Close the vial and shake for about 15 minutes
- Allow the vial with contents to sit for about 5 min
- Hold the vial at a 45 degree angle and look out for unreacted oil
- Test complies when there is no oil residue settling at the bottom of the vial

-

Appendix 1.3: Soap test kit instruction

The purpose of this test kit is to detect the presence of soap in biodiesel water wash. Biodiesel needs to be washed several times to get rid of excess catalyst.

Requirements:

a) Phenolphthalein Indicator
b) 20 mL Plastic/ glass containers with lids

- Add 2-3 drops of the phenolphthalein indicator to every water wash. The presence of soap will be indicated by the change of the water wash from colourless to pink.
- Test complies if the water washes remains clear and colourless after the addition of the indicator.

-

Appendix 1.4: Density test kit instruction

The purpose of this test kit is to test the density of biodiesel. According to SANS 35, biodiesel should have a density that is within the range 0.800-0.900 g/cm^3.

Requirements:

a) Heating mantle
b) Beaker 600 mL
c) 100 ml measuring cylinder
d) Hydrometer
e) Thermometer

- Heat biodiesel to 40 ^{o}C and measure the temperature
- Pour enough oil in a measuring cylinder for the hydrometer to float in it.
- Insert the hydrometer and allow it to stabilize
- Record the reading where the hydrometer intersects with the top meniscus of the biodiesel.

-

Appendix 1.5: Water test kit instruction

Requirements:

a) Heating mantle
b) Beaker
c) Stirrer bar
d) Weighing balance
e) Calculator

- The water test kit method is referred to as the water heat weight method (WHW)
- Heat the oil or biodiesel for about an hour to get rid of excess water.
- Weigh the mass of the oil before and after and determine the percentage or ppm water using the following formula:
  % water = ((wet weight – dry weight)/ wet weight x 100)
  ppm water = multiply the % water by 10000