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SUSTANABLE ENERGY ENGINEERING

Title: optimization and characterization of biodiesel production from filter mud oil –wonji sugar factories

A thesis submitted to the School of Graduate Studies of Jimma University in partial fulfillment of the requirements for award of Degree of Masters in Sustainable Energy Engineering.

BY: Abowerk Wagank

Advisor :- Pedro Dionisio Remedios Castaneiras (Dr.Ing., PhD)

Co-Advisor :- Professor Dr.Venkata Ramayya

Date of submission: November, 2017

Place: Jimma, Ethiopia

Declaration

I, the under singed declare that the thesis entitled “optimization and characterization of biodiesel production from filter mud oil-Wonji sugar factories’’is my original work and has not been presented by any other person for an award of a degree in this or any other university.

Name: Abowerk Wagank Gebremariam

Signature ___________________________________Date______________________________

Advisor Name: Pedro Dionisio Remedios Castaneiras (Dr.Ing., PhD)

Signature _____________________________________ Date 15-11-2017

Co-Advisor Name: Prof. Dr. A. Venkata Ramayya

Signature______________________________________Date___________________________

External examiner Name:

Signature______________________________________Date___________________________

Internal examiner Name:

Signature______________________________________Date________________________

Chairperson Name:

Signature______________________________________Date___________________________

Date of submission: November, 2017

Place: Jimma, Ethiopia

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Abstract

Significant improvements to Ethiopia's trade balance are needed to stimulate the required economic development. One main issue was that around 65% of Ethiopia export earnings are needed to pay for the import of petroleum products. Biodiesel can be produced from plenty of oil containing feedstock and is an alternative fuel to petroleum diesel with renewable. Production of transportation fuels was part of the effort, it reduce higher level of fossil fuel consumption. This research work was about the production of biodiesel from sugarcane filter mud oil. Sugarcane filter mud was chosen because it was non edible. Therefore; it was not a problem to human food competition. During this work the biodiesel was produced at standard material and at standard condition. The experiments were conducted using filter mud, and n-hexane as extracting solvent with the solvent extraction method by employing Soxhlet apparatus. The time used for extraction of filter mud oil was 2, 4, 6, and 8hours and a filter mud particle size between 1to 2mm. during this experimentation the maximum yield at a filter mud particle size of 1 to 1.25mm, which is 4.001g of filter mud oil was obtained. The maximum yield of filter mud oil was found at the extraction time of 6hour and the reactor temperature of 65^{o}C. After the extraction of filter mud oil the next step was the transesterification of this oil to obtain a good quality of biodiesel. During transesterification, process the influence of methanol to filter mud oil, catalyst to filter mud oil weight ratio, reaction temperature, the rate of mixing and the reaction time was examined. The maximum biodiesel yield was obtained at the mole ratio of methanol to filter mud particle oil, catalyst to filter mud oil weight ratio, reaction temperature, the rate of mixing and the reaction time at 70.875:10.5, 0.3625:0.0906, 60^{o}C, 600rpm and 1hour respectively, at 3.968g constituting a mass percentage of 99.17% the optimization studies and the associated results are presented and discussed along with the potential assessment. The higher heating value and Cetane number of biodiesel obtained from filter mud oil were found to be 44.18MJ/kg and 81.5 respectively.

Table of Contents

List of Figure

List of table

Acronyms and Notations

A =Catalyst weight

AB =Catalyst weight and Temperature

ABC= Catalyst, Temperature, and Alcohol: oil

AC =Catalyst weight and Alcohol: oil

ASTM= American Standards Tests and Materials

AV =Acid Value

B =Temperature

BC= Temperature and Alcohol: oil

BLTV =Blank Level Titration Volume

C= Alcohol: oil

Cm =Concentration of Mass

EN= European Normalization (European Standards)

FFA =Free Fatty Acid

Mm =Molecular Mass

Ms=Mass of Sample

N =Normality

SV= Saponification Value

RF =Reagent factor

TF =Titration Factor

TV =Titration Volume

V/V =Volume per Volume

V/W =Volume per Weight

W/W =Weight per Weight

CCD =Central Composite Design

FAME =Fatty acid methyl esters

Rpm=Revolution per minute

CHAPTER ONE

1. 1. Introduction

Biodiesel is the name for a variety of ester based fuels (fatty ester) generally defined as mono alkyl ester made from renewable biological resources such as vegetable oils (both edible and non-edible), recycled waste vegetable oil and animal fats. This renewable source is as efficient as petroleum diesel in powering unmodified diesel engine. Today diesel engines require a clean burning, stable fuel operating under a variety of conditions. Using biodiesel not only helps maintaining our environment, it also helps in keeping the people around us healthy. Biodiesel is miscible with petro diesel in all ratios. In many countries, this has led to the use of blends of biodiesel with petro diesel instead of neat biodiesel [1]. There are different types of feed stocks that are used for the production of biodiesel. These includes linseed oil, palm seed oil ,waste cooked vegetable oil, sun flower seed oil, cotton seed oil, Jatropha seed oil, vernonia galamensis seed oil and animal fats. Oil seed plants are used for the production of biodiesel through the process called transesterification reaction which is a process by which alcohol reacts with vegetable oil in the presence of catalyst. Triglycerides are major components of vegetable oils and animal fats.

Chemically, triglycerides are esters of fatty acids with glycerol. Fatty acid ethyl esters are mostly involved because ethanol is the cheapest alcohol, but other alcohols, namely methanol, may be employed as well. In this way, highly viscous triglycerides are converted in long chain mono esters presenting much lower viscosity and better combustion properties to enhance the burning. Homogeneous or heterogeneous catalysis are used to enhance the reaction rate. Sugar cane mud (*Saccharumofficinarum*, L.) is a residue of the Sugar Cane Industry obtained by vacuum filtration of the grounds that flocculate when sugar cane juice will be clarified, with the objective of to eliminate non-soluble impurities contained on it. Mud composition is very variable, but in general it has a high content of soil, cane trash, saccharides and sugar cane wax [25]. Sugar cane wax is found near the sugar cane stem nodules, in the cuticle, its main components are high molecular weight esters, polyesters, fatty acids, dicarboxylic acids, aldehydes, ketones, alcohols and hydrocarbons [2]. During the sugar cane grinding process, most of the sugar cane wax is present in the juice; the former will be separated in the vacuum filtration process of the juice, forming part of the mud. The sugarcane industry has several co-products of immense potential. The co products include press mud (filter cake), molasses and spent wash. Press mud is a soft, spongy, amorphous and dark brown material containing sugar, fiber and coagulated colloids including cane wax, albuminoids, inorganic salts and soil particles. It consists of 80% water and 0.9 - 1.5 % sugar, organic matter, nitrogen, phosphorus, potassium, calcium, sulfur, coagulated colloids and other materials in varying amounts. Press mud like other organic materials affects the physical, chemical and biological properties of soil. However, due to its bulky nature and wax content it causes some problems.

1.2 Problem statement

At present, due to industrial revolution and high population growth, the demand of fossil fuel is increasing rapidly. To substitute the fossil fuel demand by renewable fuel, biodiesel production from vegetable oils is one alternative for meeting every going energy demand and Biodiesel has recently attracted much attention all over the world because of its availability, renewability, non-toxicity, better gas emissions and its biodegradability.

Assessing sustainable and renewable energy alternatives is indispensable at present, due not only to combat the fuel supply uncertainty and Price fluctuations, but also to adding global concern and meet each country's responsibility to seek environmentally bring energy sources to reduce greenhouse gases emissions and air pollutions. We also need to address food –fuel debate and the biodiesel production feedstock need to be from non-edible sources. Currently, the sugar industry sector is going through a major expansion and is also contributing to bioethanol production. In addition, one of the waste products i.e sugar cane filter mud can be beneficially used to extract filter mud oil and subsequently converted to biodiesel. This would also alleviate the problem caused by the acidic nature of the filter mud currently used as fertilizer. Hence, this study has been taken up to study and demonstrate the technical feasibility of biodiesel production from sugarcane filter mud.

1.3 Objectives

1.3.1 General Objective

The general objective of this research is to investigate the production of biodiesel from the filter mud oil.

1.3.2 Specifics objectives

1. To determine the experimental parameters associated with the extraction process of sugar cane oil from filter mud using n-hexane as solvent.
2. Characterization of biodiesel obtained from sugar cane filter mud oil

3. To estimate the potential for sugar cane filter mud oil production

4. Optimization of biodiesel yield from filter mud oil

1.4. Significance of the study

This this work has great significance in terms of assuring the production of an alternative form of energy from sugarcane filter mud and in the determination of the potentials in the country in supplying balancing feed stock for biodiesel production. It also would be help full to asses' production of biodiesel from sugarcane filter mud oil using normal hexane, methanol and alkali catalyst. Sugarcane can be abundantly cultivated and grown, and filter mud oil being non-edible is good for production of biodiesel. In addition, the study could be used as a reference material for sugarcane plant cultivation owners who are interested to produce biodiesel from sugarcane filter mud oil using methanol and with alkali catalyst at small scale. Also the result in relation with the production of biodiesel from sugar cane oil prevents an option to increase the productivity and diversification of sugar industry. Therefore the production of biodiesel in Ethiopia from sugar cane filter mud oil has the potential for minimizing the extent of petro diesel imports from abroad.

1.5. Scope

The scope of this thesis work involves extraction of filter mud oil, Estimation of sugar cane filter mud oil produced, Trans esterify the oil into biodiesel and the characterization of biodiesel produced. The other scope of this work comprises optimization of the biodiesel yield by using design expert 7.0 software and to determine the optimum point of maximum biodiesel yield.

1.6 Expected out come

The expected outcome of this thesis work will be the production of biodiesel from sugarcane filter mud oil by using the transesterification processes and solvent extraction method. The other outcome of this work is to pin point the parameters that leads to optimal biodiesel production.

1.7. Limitation of this work

The main limitations during experimental work were the lack of means to characterize refractive index, pour point measuring device and some chemicals. The other limitation during experimental work was lack of glycerol characterizing devices.

CHAPTER TWO

2. RELATED LITRETURE REVIEW

2.1 Introduction

Biodiesel derived from biological resources is a renewable fuel, which has drawn more and more attention recently. A fatty acid methyl ester is the chemical composition of biodiesel. Transesterification is widely used for the transformation of triglyceride into fatty acid methyl ester [10]. The manufacturing process is based on the transesterification of triglycerides by alcohols to fatty esters, with glycerol as a byproduct [11]. In this way, highly viscous triglycerides are converted in to long chain monoesters presenting much lower viscosity and better combustion properties. Homogeneous or heterogeneous catalysis are used to enhance the reaction rate. Raw materials are vegetable oils, preferably non-edible, but also different wastes, such as used frying oils or animal fats [6].

2.2 Raw Materials for Biodiesel Production

The primary raw materials used in the production of biodiesel are vegetable oils, animal fats, and recycled greases. These materials contain triglycerides, free fatty acids, and other contaminants depending on the degree of pre-treatment they have received prior to delivery. Choice of the fats or oils to be used in producing biodiesel is both a process chemistry decision and an economic decision. With respect to process chemistry, the greatest difference among the choices of fats and oils is the amount of free fatty acids that are associated with the triglycerides. The options for the triglyceride choice are many. Among the vegetable oils sources are castor oil, Jatropha oil, soybean, canola, palm, and rapeseed. Animal fats include beef tallow, lard, poultry fat, and fish oils. Yellow greases can be mixtures of vegetable and animal sources [7] .The raw material used for the production of biodiesel is best if the following major criteria are satisfied. The raw materials must not be competitive with food, land used for the oil plantation and oil production, with forest and other agricultural products. Taking into account the competitiveness with food and the planting conditions, Jatropha oil is the best to be a raw material for the production of biodiesel. Jatropha has the ability to be planted even in deserts which makes it more preferable as it avoids deforestation of forests as well as make a good balance for the desert environment [29]

Jatropha oil has great advantages to be used for biodiesel production than other oil bearing plants since the plant can be cultivated in waste lands, its tendency to stabilize soils, erosion control, root part is easier to plant and it costs less due to inedibility of its oil.

Table 2-1 Standard specification of Jatropha oil

Property	Value	Standard	Limit (ASTMD6751)
Specific gravity	0.912	0.9186	ASTMD4052
Cetane value	-	40Min	ASTMD613
Distillation point	-	295^{o}C	ASTMD93
Kinematic viscosity	50 cp	50.73 cs	ASTMD445
Calorific value	-	9470Kca/kg	ASTMD445
Pour point	-	8^{o}C	-
Acid value	38%	1-38.2%	ASTMD664
Iodine value	102	90.8-112.5	EN14111
Saponification value	190	188-198	ISO 3657

Table 2-2 Standard specification of petro diesel

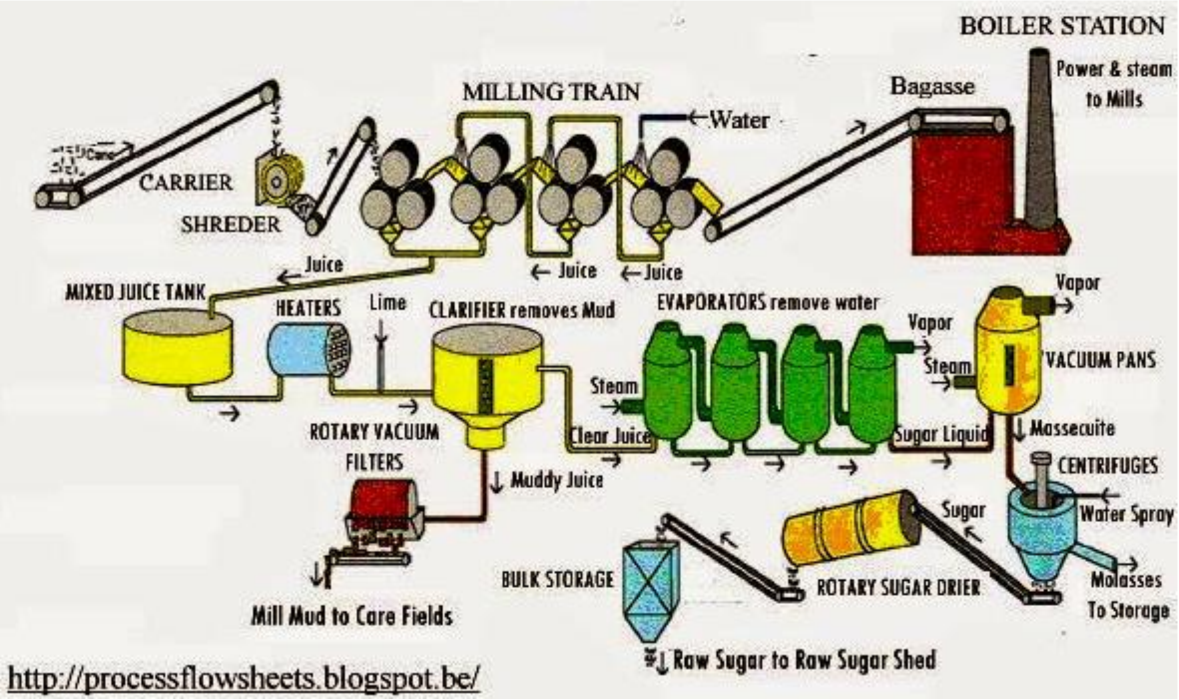
Property	**Value**
Specific gravity	0.82- 0.845
Flash point	50oC
Cetane value	50
Distillation point	350oC
Kinematic viscosity	2.7c.s
Calorific value	10170kcal/kg

Besides the oil, alcohols and catalysts are the major inputs used in the production of biodiesel. Many alcohols have been used to make biodiesel. As long as the product esters meet the specified quality, it does not make any chemical difference which alcohol is used in the process. Other issues such as cost of the alcohol, the amount of alcohol needed for the reaction, the ease of recovering and recycling the alcohol, fuel tax credits, and global warming issues influence the choice of alcohol. Some alcohols also require slight technical modifications to the production process such as higher operating temperatures, longer or slower mixing times, or lower mixing speeds.

The most commonly used primary alcohol in biodiesel production is methanol, although other alcohols, such as ethanol, isopropanol, and butyl, can be used. A key quality factor for the primary alcohol is the water content. Water interferes with transesterification reactions and can result in poor yields and high levels of soap, free fatty acids, and triglycerides in the final fuel.

Methanol is considerably easier to recover than the ethanol. Ethanol forms azoetrope with water so it is expensive to purify the ethanol during recovery. If the water is not removed it will interfere with the reactions [18].Methanol recycles easier because it doesn’t form azoetrope. Because of this reason, even though methanol is more toxic, it is the preferred alcohol for producing biodiesel. The alcohol quality requirements are that it must be un-denatured and anhydrous. Catalysts may either be base, acid, or enzyme materials. The most commonly used catalyst materials for converting triglycerides to biodiesel are sodium hydroxide, potassium hydroxide, and sodium methoxide. Most base catalyst systems use vegetable oils as a feedstock. Although acid catalysts can be used for transesterification they are generally considered to be too slow for industrial processing. Acid catalysts are more commonly used for the esterification of free fatty acids. Acid catalysts include sulfuric acid and phosphoric acid [4]. Currently, there are different methods of biodiesel production such as using heterogeneous catalyst and without catalyst, but they are in developing stage. Heterogeneous catalyzes avoid catalyst removal operations and soap formation, much effort has been spent on the search for solid acid or basic catalysts that could be used in a heterogeneous catalyzed process. The advantage of this method is re-using of the catalyst after reaction (contrary to homogeneous catalyst, which is not possible to use again) [6]. Beside the solid acid or solid base catalyst, the other heterogeneous catalysts are enzymatic catalyst. They have various races of enzymes (rizhomucormiehei, pseudomonas cepacia, caidaantarctica) which are isolated from microorganisms. The reaction takes place at relatively low temperature (25-35°C), but it takes long time (hours).Main problems of usage of lipases in an industrial scale are their price, particular loss of activity in methanol and long duration of the reaction. The second biodiesel production process that is in developing stage is production of biodiesel using alcohol in the supercritical stage (without catalyst). Unfortunately, this process needs high temperature (350 °C) and pressure (45-65 MPa). The advantage is that relatively pure glycerol is gained.

Vernonia galamensis one of the best raw material for producing biodiesel as it is non-edible, thus does not matter on food scarcity; it can be cultivated around poor soil, especially around dry valleys of Ethiopia that the land useful; biodiesel produced from it is less dense [8]. Vernonia galamensis is a plant in the sunflower family, known for its use as an oilseed. This species, often called ironweed, is the largest source of vernonia oil, which is rich in a useful epoxy fatty acid called vernolic acid and is used to make plastics, rubbery coatings, and drying agents. Use of this oil as a replacement for traditional plasticizers and binders in the production of paints and shows promise as a method of reducing pollution [3]. It is grown in many parts of Ethiopia, especially around the city of Harar, with an average seed yield of 2 to 2.5 t/ha. It is reported that the Ethiopian strains of vernonia have the highest oil content, up to 41.9% with up to 80% vernolic acid [2]



http://processflowsheets.blogspot.be/

Figure 2.1 Production process of sugar cane

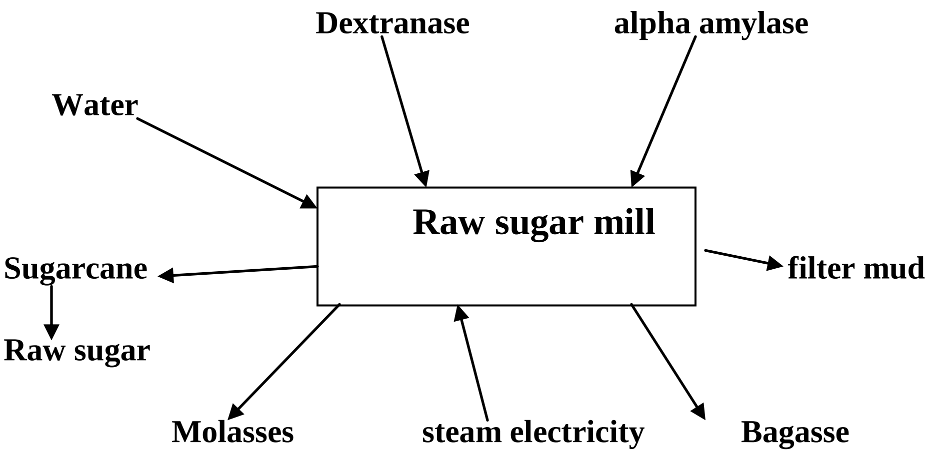


Figure 2.2 Components of sugar cane

Even the filter mud, removed from the raw cane juice before it is concentrated, has value. In addition to soil and plant material, the mud contains a wax that had coated the sugarcane stalks. The mud is usually returned to the cane fields, but Michael Saska of the Audubon Sugar Institute is working on ways to extract the wax [30]. The mud yields up to 1% of a high-value food-grade wax. Cane wax is a potential replacement for a rain forest product, carnauba wax that is widely used in cosmetics, foods, and pharmaceuticals. In addition, with supercritical fluid extraction, the wax is a source of long-chain aliphatic alcohols. Octacosanol (C28) is reported to "increase physical stamina" and "remedy damaged nerve cells" and even to stimulate sex hormones [42] Method for processing sugar cane filter cake mud and extracting component products [31].Like another vegetable oil the sugar cane oil from filter mud (waste cake) of sugar cane process is the vegetable oil and has lots possibilities to use in different field of the human being. Some of research has been identify different possible use of this vegetable oil: generally in cosmetic, medical product, and other, and in the last years there are some preliminary researches in US, Brazil, Cuba to use this oil that indicated its possibilities to use as biodiesel and lubricants [32].

A major residue of the sugar production is filter cake, the residue from cane juice filtration. The filter cake is a dark solid fibrous residue that is extracted from the final process in the manufacture of sugar from sugarcane.

2.3 Characteristics of filter mud oil.

From the filter mud the wax is extracted, a fat fraction also called oil and resin. The fat fraction has not yet been sufficiently exploited despite the value of its components. [33]. It is important that the oil to be used for transesterification is as free as possible free of free fatty acids since these in the transesterification process tend to saponify and form fatty acid soaps which competes with the transesterification process of the esters of Higher alcohols also present in the oil [34]. The presence of water is also inconvenient, although generally it is not in the oils but in the alcohol, especially if ethanol is used. Water tends to dilute the catalyst and to form emulsions with the soaps, difficult to separate[35].On the other hand the presence of moisture, temperature and storage time and the enzymatic action tend to deteriorate the oil increasing the free acidity[36].

2.4 Filter mud oil extraction

The oil can be extracted mechanically (compression or simple grinding) or chemically (solvents). The selection of the solvent for extraction on a commercial scale is based primarily on its availability and cost as well as considering the operations to be performed after extraction; especially if the crude product is to be fractionated later [37]. Several types have been suggested, aromatic hydrocarbons and petroleum solvents acetone, methyl, ether, liquid sulfur dioxide, naphtha's. Etc [38] only commercial use of extractive gasoline, n-heptane and naphtha is reported [39]. The use of n-heptane has provided the best results in terms of consumption and extractive power in the technology used in Cuba [40].This research will focus on the extraction of the oil present in the waste from the sugar industry by using n-heptane or naphtha as solvent. Recent investigations [41] showed that during extraction at low temperatures 28 ° C is higher Soaps during the transesterification reaction.

The composition of the filter cake is estimated to be approximately 10–14% wax, oil, and resin, 12–16% protein, 8–12% ash, 3–5% P2O5, 2.5% CaO, 10–14% saccharose and reductive carbohydrates, 18–25% cane core, and 25–35% other materials. The filter cake usually has a high percentage of water, which is estimated to be in the range 75–77%, meaning that the dry material represents approximately 23–25% [26, 27].

The principal product obtained from the filter cake is the sugarcane crude wax. The industrial process for the extraction of sugarcane crude wax from filter cake is heptanes extraction. Three fractions are usually separated in this process [28]:

(i) wax (55–62%),

(ii) oil (25–31%),

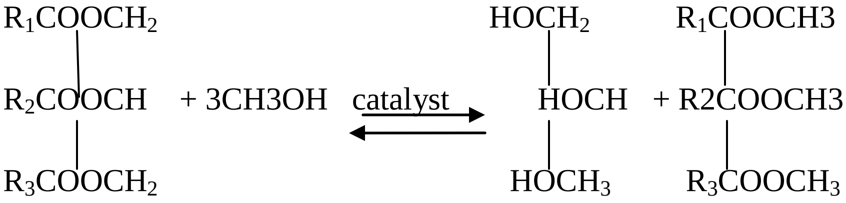
(iii) resin (10–13%), volatiles (0.8–2%), and insoluble (0.7-0.8%).

For the production of biodiesel from filter mud oil, the technique developed in previous works [43] was used for the extraction process of cane oil, which is described below: 1.2 kg of filter mud was weighed, mixing it with 3.6 L of naphtha in a jacketed glass reactor, with a capacity of 10 L. The extraction begins once the filter mud and the solvent are in contact with the equipment and hermetically sealed. The extraction temperature is 65 ° C and the duration time is 1h; this time is taken in case the reaction proceeds with agitation, but in this investigation the time lasted up to 3h because the experiment was not performed with agitation due to insufficient instruments in the laboratory. The procedure is described below: 0.55 g of KOH was dissolved in 38 mL of alcohol, then mixed with 150 mL of sugar cane oil and an excess of 75 mL of alcohol was added. The reaction was carried out at a temperature of 65 ° C, 600 rpm and for 4 h. After the reaction time had elapsed, the product was allowed to cool and 100 mL of naphtha was added and cooled for 1 h at a temperature of -10 ° C in order to precipitate the High Molecular Weight Alcohols. It was filtered under cold vacuum and the naphtha and biodiesel mixture distilled. The distillation conditions were: bath temperature of 80 ° C, for 1 h. In Figure The distillation equipment used in the For both variants approximately 50 mL of Methyl Esters (EM) and Ethyl Esters (EE) were obtained, to which they were later tested to be able to affirm that they actually comply with Cuban standards

2.5 Chemistry of Biodiesel Production

Fatty esters are currently manufactured by the Transesterification of triglycerides with light alcohols. The triglycerides are found in vegetable oils and animal fats, more generally known as lipids. The Transesterification reaction takes place in the presence of a suitable catalyst, acid or base. The fatty ester is released simultaneously with the reformation of the OH group in glycerol. The overall reaction occurs in three stages is controlled by chemical equilibrium, as expressed by the reactions in scheme

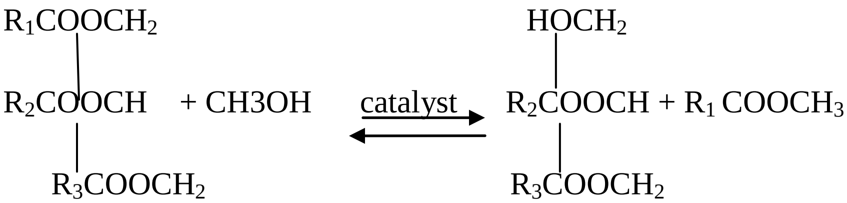
a) Reaction mechanism: Transesterification



$$\begin{array}{l} R_1COOCH_2 \\ \quad | \\ R_2COOCH \\ \quad | \\ R_3COOCH_2 \end{array} + 3CH3OH \overset{catalyst}{\rightleftharpoons} \begin{array}{l} HOCH_2 \\ \quad | \\ HOCH \\ \quad | \\ HOCH_3 \end{array} + \begin{array}{l} R_1COOCH3 \\ \quad | \\ R2COOCH3 \\ \quad | \\ R_3COOCH_3 \end{array}$$

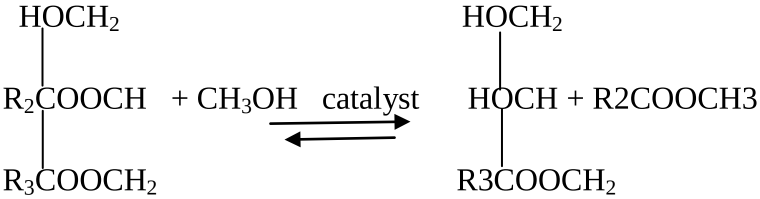
Triglyceride Methanol glycerol Methyl Ester/biodiesel

a) Stepwise consecutive and reversible reaction



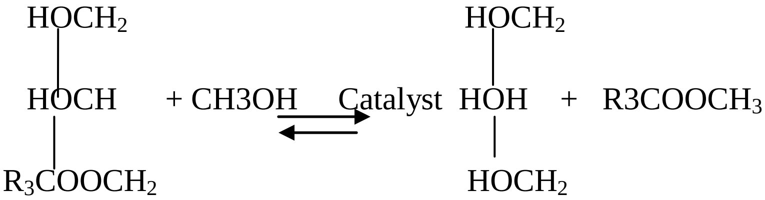
$$\begin{array}{l} R_1COOCH_2 \\ \quad | \\ R_2COOCH \\ \quad | \\ R_3COOCH_2 \end{array} + CH3OH \overset{catalyst}{\rightleftharpoons} \begin{array}{l} HOCH_2 \\ \quad | \\ R_2COOCH \\ \quad | \\ R_3COOCH_2 \end{array} + R_1\,COOCH_3$$

Triglyceride Methanol Diglyceride



$$\begin{array}{l} HOCH_2 \\ \quad | \\ R_2COOCH \\ \quad | \\ R_3COOCH_2 \end{array} + CH_3OH \overset{catalyst}{\rightleftharpoons} \begin{array}{l} HOCH_2 \\ \quad | \\ HOCH \\ \quad | \\ R3COOCH_2 \end{array} + R2COOCH3$$

Diglyceride methanol Monoglyceride



$$\begin{array}{l} HOCH_2 \\ \quad | \\ HOCH \\ \quad | \\ R_3COOCH_2 \end{array} + CH3OH \overset{Catalyst}{\rightleftharpoons} \begin{array}{l} HOCH_2 \\ \quad | \\ HOH \\ \quad | \\ HOCH_2 \end{array} + R3COOCH_3$$

Monoglyceride methanol glycerol

Trans esterification reactions of glycerides with methanol

(a) Overall reaction and

(b) Stepwise consecutive and reversible reactions, where; R1, R2 and R3 represents the hydrocarbon chains of the fatty acid alkyl groups of the triglyceride. Thus, three molecules of fatty esters are produced for each molecule of triglyceride that needs three molecules of alcohol.

Since the reaction rate is not fast enough at low temperature the Trans esterification makes use of catalysts. In fact, they make the difference between technologies. The catalysts can have acid or base character, and be homogeneous or heterogeneous. Base catalysts are preferred since they are faster. Homogeneous catalysts manifest higher activity, but need expensive post processing stages. [1]The lipid feedstock may contain variable proportions of free fatty acids (FFA), which should be converted to esters before trans esterification. Otherwise, the formation of soaps occurs by reaction with the hydroxide catalyst, as it is given in scheme 2.

$\text{R1-COO-CH} + \text{NaOHR1} \longrightarrow \text{COONa} + \text{H2O}$

FFA Base Soap Water

Scheme 2: Reaction between free fatty acid and base

These can be substantially reduced or even suppressed if super active heterogeneous catalysts are employed.

2.6 Biodiesel Production Technologies

There are different technologies which are employed in the production of biodiesel. They have been discussed as follows.

2.6.1 Batch Process

The non-edible vegetable oil is charged to Transesterification in a batch reactor in the presence of an excess amount of methanol, and catalyst.

The Trans esterification reaction may be considered finished when maximum conversion is achieved. However, the mixture composition should respect the quality of biodiesel specifications.

The excess methanol is recovered for the next batch. [1] The remaining mixture is submitted to the separation of esters from glycerol. This can take place either by decantation or by centrifugation. Water may be added to improve the phase split.

The oil phase containing fatty esters is sent to finishing by neutralization with acid, followed by washing and drying. The methanol recovery takes place by flash distillation or film evaporation.

The batch process allows high flexibility with respect to the composition of the feedstock. Intern, the economic indices are on the lower side because of lower equipment productivity and higher operation costs, such as manpower and automation [22].The replacement of a homogeneous catalyst by a heterogeneous one is highly desirable.

An excess of methanol is necessary chiefly to ensure full solubility of triglyceride and keep the viscosity of the reaction mixture low, but also for shifting the chemical equilibrium.

2.6.2 Supercritical Processes

Performing the esterification in supercritical conditions has been studied initially as a method to solve the problem of miscibility of oil and methanol that hinders the kinetics in normal conditions.

The advantage of avoiding a catalyst is obvious. However, the conditions of pressure and temperature are severe and need special equipment. Recent research showed the real yield can be reduced by thermal degradation of biodiesel, namely of unsaturated fatty esters. For this reason, lowering the reaction temperature and pressure is highly desirable. The addition of co-solvent in combination with supercritical conditions seems to be an efficient means to reduce significantly the operating temperature. For example, soybean oil could be converted with methanol into biodiesel with 98% yield by using propane, at least in 0.05 molar ratios to methanol, at 280 ° C and 12.8 MPa. Similar results have been reported with CO2 in a molar ratio of 0.1 with respect to methanol. In both cases the optimal ratio methanol/oil was 24 and residence time of 10 min.

Due to the absence of the catalyst the process flow sheet employing the supercritical technology should be much simpler, but in exchange the manufacture of hardware is much more demanding. Effective energy integration is also necessary. Despite these advantages the industrial implementation of supercritical esterification has not been reported. [6]

2.6.3 Hydrolysis and Esterification

A simpler manufacturing procedure would consist in first performing the hydrolysis of triglycerides and isolating the fatty acids followed by esterification employing the robust technology of a solid heterogeneous catalyst. Significant advantages would be the possibility of extracting high value fatty acids from the lipid material, as well as obtaining high purity glycerol. The hydrolysis reaction can be carried out without a catalyst working in milder conditions compared to full esterification.

A temperature close to 270 °C and pressures from 70 to 200bar has been found applicable.

Another advantage is that the overall yield can be increased by suppressing the back reaction of glycerol with the methyl ester. The reaction exhibits an autocatalytic effect due to the fatty acid produced, from which a small recycle can be provided [6].

The oil and water are brought at high pressure, homogenized in a static mixer and heated. A volumetric ratio water/oil 1:1 is appropriate. The hydrolysis takes place in the reactor in slightly subcritical conditions at 270°C and 100bar. The yield in fatty acids is around 90% for a residence time about 40 to 60 min. Therefore, a simple long coil can be used as the chemical reactor. After cooling and pressure reduction, the reaction mixture is separated into two phase. The oily phase containing a large majority of fatty acids is sent directly to esterification, or optionally to fatty - acid separation unit by vacuum distillation. The heavies from the separator containing glycerides can be recycled to reactor, or disposed of as combustible waste. The second reactor delivers fatty acid methyl esters diluted with methanol in the bottom, from which biodiesel with fuel specifications is obtained after evaporator. The top stream from second reactor is sent to the distillation column, from which water and methanol are recovered and recycled. [6]

Summing up, the process based on the hydrolysis of triglycerides seems very attractive, despite the fact that supercritical operation raises a technical challenge. By making use of recycles the process can be designed to achieve material consumption close to stoichiometric requirements. Pumping liquids at high pressures requires moderate energy. By heat integration the utility consumption could be kept at low level.

2.6.4 Enzymatic Processes

The transesterification reaction can be catalyzed by enzymes, the most common being lipase. The reaction takes place at normal pressure and temperatures 50 to 55°C with low energy Consumption. The yield of methanolysis depends on several factors as temperature, pH, type of microorganism producing the enzyme, the use of co solvents, etc. However, low yields in methyl esters and very long reaction times make the enzymatic processes not competitive enough at this time [6]

2.7 Types of Transesterification Reactions

Biodiesel (Greek, bio, life + diesel from Rudolf Diesel) refers to a diesel-equivalent, processed fuel derived from biological sources. Biodiesel is the name for a variety of ester-based oxygenated fuels from renewable biological sources. It can be made from processed organic oils and fats [10]. The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. Vegetable oil has too high viscosity for use in most existing diesel engines as a straight replacement fuel oil. There are a number of ways to reduce vegetable oil viscosity. One of the most common methods used to reduce oil viscosity in the biodiesel industry is called Transesterification. Chemical conversion of the oil into its corresponding fatty ester is called Transesterification.

Transesterification is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side [10]. There are different types of transesterification and they are discussed as follows.

2.7.1 Homogeneous alkali (base) catalyzed transesterification

Transesterification reaction can be catalyzed by both homogeneous (alkalies and acids) and heterogeneous catalysts. The most commonly used alkali catalysts are NaOH, CH3ONa, CH3OK and KOH. [5] The alkali-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. In the alkali catalytic methanol transesterification method, the catalyst is dissolved into methanol by vigorous stirring in a small reactor. The oil is transferred into a bio-diesel reactor and then the catalyst/alcohol mixture is pumped into the oil. A successful transesterification reaction produces two liquid phases: ester and crude glycerol. [7]

The base-catalyzed reaction is reported to be very sensitive to the purity of the reactant. Free fatty acid (FFA) content should not exceed beyond a certain limit. It has been found that the alkaline-catalyzed transesterification process is not suitable to produce esters from unrefined oils.

In order to prevent saponification during the reaction, FFA and water content of the feed must be below 2 wt. % and 0.05 wt. %, respectively. Because of these limitations, only pure vegetable oil feeds are appropriate for alkali-catalyzed transesterification without extensive pre-treatment.

2.7.2 Heterogeneous acid and base-catalyzed transesterification

Research is now being directed to the application of heterogeneous catalysts for biodiesel forming reactions. Solid catalysts are attractive alternatives for the homogeneous ones because they are easily recovered, facilitate continuous processing, and minimize product separation problems. Homogeneous catalysts showed greater performance toward transesterification to obtain biodiesel. The problems associated with the homogeneous catalysts are the high consumption of energy, form unwanted soap byproduct by reaction of the FFA, expensive separation of the homogeneous catalyst from the reaction mixture and generation of large amount of wastewater during separation and cleaning of the catalyst and the products [23]. The use of heterogeneous catalysts could be an attractive solution. Heterogeneous catalysts can be separated more easily from reaction products. Undesired saponification reactions can be avoided by using heterogeneous catalysts. They enable the transesterification of vegetable oils or animal fats with high contents of FFAs, such as deep-frying oils from restaurants and food processing. The major consequence of using solid or heterogeneous catalyst on the production process are catalyst regeneration (decrease of catalyst cost), utilization of lower quality feed stocks for biodiesel production, simplification of separation process (decrease of production cost) and decrease of wastewater (development of environmental friendly process).

Bio-diesel synthesis using solid catalysts could potentially lead to cheaper production costs Because of reuse of the catalyst and the possibility for carrying out both transesterification and esterification simultaneously [23]. But in case of heterogeneous catalysts, catalysts present in different phases from reactants, providing a surface at which a reaction occurs .Heterogeneous catalysts are utilized for biodiesel preparation comprised mainly of solid-acid and solid-base catalysts. For example, the alkaline earth metal oxides for the catalysts of Transesterification [17]. The possible type of solid catalyst and their uses plus potential yield with concentration done by other researcher is discussed below. They found that MgO had lower activity than that of CaO in transesterification of oil to biodiesel. CaO with 1.5% weight ratio of catalyst using molar ratio of methanol to oil 9:1 in the transesterification of Jatropha curcas oil at 70OC and the yield observed was 93.5% for 2.5hr reaction period [36]. MgO was used in the transesterification of rapeseed oil at a catalyst weight of 1.5wt%, 4:1 molar ratio of methanol to oil and 70OC for 2hr reaction period to obtain 93% yield of fatty acid methyl ester [24].

2.8. Biodiesel production processes

Biodiesel derived from biological resources is a renewable fuel, which has drawn more and more attention recently. A fatty acid methyl ester is the chemical composition of biodiesel. Transesterification is widely used for the transformation of triglyceride into fatty acid methyl ester [11]. The manufacturing process is based on the transesterification of triglycerides by alcohols to fatty acid methyl esters, with glycerol as a byproduct [11]. The base catalyzed production of biodiesel generally has the following process steps [9].

2.8.1. Mixing of alcohol and catalyst

This typical process is mainly done by mixing alkali hydroxide (commonly potassium hydroxide and sodium hydroxide) with common alcohols (methanol and ethanol) in the mixer with standard agitator to facilitate the mixing. Alkali hydroxide is dissolved in the alcohol to produce alkoxide solution.

2.8.2. Chemical reaction

The alcohol and catalyst mixture is then charged into a closed reaction vessel and the oil is added. The reaction system is totally closed to the atmosphere to prevent the loss of alcohol, since it easily vaporizable. The reaction mixture is kept just near the boiling point of the alcohol to speed up the reaction. Excess alcohol is normally used to ensure total conversion of the oil to its esters as there is no problem of recovering of the alcohol for later use after recycling.

2.8.3. Separation

After the reaction is completed, there exists glycerol and biodiesel formation. Both have a significant amount of the excess alcohol that was used in the reaction which is in need of being recovered. The reacted mixture is sometimes neutralized at this step if the basic media that is caused by alkali hydroxide is occurred. The glycerol phase is much denser than biodiesel phase, making biodiesel to be floated [12]. The two products can be separated by gravity using settling vessel. The glycerol is drawn off at the bottom of the settling vessel and biodiesel is drawn off at the top. In some cases, a centrifuge is used to separate the two materials faster by screening both phases.

2.8.4. Alcohol removal

After the glycerol and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation commonly. But currently extractive distillation can instead be used to fasten the process and to be more economical. On the other hand, the alcohol is removed and the mixture neutralized before the glycerol and esters have been separated to prevent the effect of basic media inside the reactor. After the alcohol is being recovered it is used as main raw material.

2.8.5. Biodiesel washing

After the Biodiesel is separated from the glycerol, It is sometimes purified by washing gently with cold water to remove residual catalyst, alcohol or soaps to make more pure. The washed biodiesel needs drying in order to remove trace impurities. In some processes washing step is not necessary depending on the quality of biodiesel produced.

2.9. Transesterification reaction

Plant oils usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Because of these, the oil cannot be used as fuel directly. To overcome these problems the oil requires slight chemical modification through transesterification, pyrolysis, dilution and emulsification [9]. Among these, the transesterification is the key step to produce the cleaner and environmentally safe biodiesel fuel from vegetable oils. Transesterification is the reaction of triglycerides with alcohols to generate methyl or ethyl esters and glycerol as by product. Transesterification of vegetable oil is commonly carried out with methanol or ethanol, using alkali catalyst, acid catalyst, without catalyst by supercritical alcohol or enzyme catalyst [13, 20].

2.9.1. Supercritical transesterification

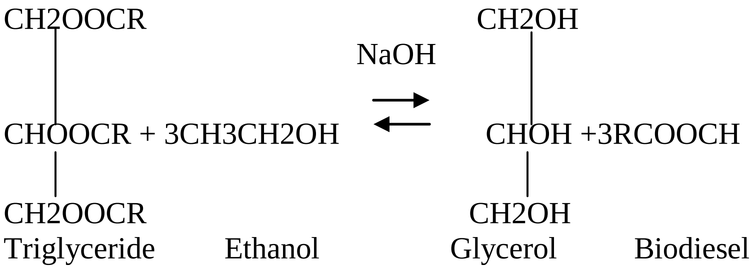
An alternative, catalyst free method for transesterification uses supercritical alcohol at high temperatures and pressures in a continuous process. In the supercritical state, the oil and ethanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock and free fatty acids are converted to esters instead of soap, so a wide variety of feedstock can be used. Also the catalyst removal step is eliminated. As high temperature and pressure are required, cost energy production is higher [21].

2.9.2. Lipase catalyzed transesterification

Using enzymes as a catalyst for the transesterification is verified by many researchers as good yield could be obtained from crude and used oils using lipases. The use of lipases makes the reaction less sensitive to high FFA content which is a problem with the standard biodiesel process. One problem with the lipase reaction is that ethanol cannot be used because it inactivates the lipase catalyst after one batch [20].

2.9.3. Transesterification reaction using alkali catalyst

Transesterification is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side [10]. Commercial biodiesel from plant oils are produced mostly by using very effective homogeneous catalysts such as alkali or acid. Sodium hydroxide and potassium hydroxide are more effective alkali catalysts. Alkali catalyzed transesterification is much faster than the acid catalyzed reaction; However, the acid catalyzed transesterification reaction is more suitable if a vegetable oil has a high free fatty acid and water content as it prevents the formation of soap stock [11]. Conversely, the addition of an excessive amount of catalyst gives rise to the formation of an emulsion, which increases the viscosity and leads to the formation of gels. These hinder the glycerol separation process and, reduce the apparent ester yield.



$$\begin{array}{l} CH_2OOCR \\ | \\ CHOOCR \\ | \\ CH_2OOCR \end{array} + 3CH_3CH_2OH \xrightleftharpoons{NaOH} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} +3RCOOCH$$

2.10. Variables Affecting Alkali Catalyzed Transesterification Reaction

Transesterification reaction process is influenced by a variety of working factors. These are molar ratio of alcohol to oil, amount and catalyst type, reaction time, reaction temperature, stirring rate, presence of free fatty acids and moisture [12].

2.10.1. Molar ratio of alcohol to oil

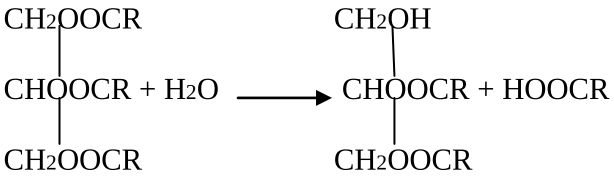
One of the most important parameters affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride. Stoichiometrically 3 moles of alcohol and 1 mole of triglyceride are required for trans esterification to yield 3 moles of fatty acid methyl/ethyl esters and 1 mole of glycerol is used. Transesterification is an equilibrium controlled reaction in which excess of alcohol can be used to get complete conversion and alcohol is easily recoverable. Further, the conversion efficiency is remains the same, but to decrease the energy increment required for the recovery of alcohol, we should avoid increasing molar ratio of alcohol to oil. Additionally, excessive amount of alcohol makes the recovery of the glycerol difficult, since more excess alcohol hinders the decantation by gravity so that the apparent yield of esters decreases since part of the glycerol remains in the biodiesel phase. The molar ratio is associated with the type of catalyst used such as; alkali catalyzed transesterification reaction the alcohol to oil molar ratio is about 6:1 to 12:1 which are the most acceptable for maximum conversion to esters. When using acid catalyst instead of alkali catalyst, the desirable maximum conversion is obtained with sulfuric acid with alcohol to oil molar ratio of 30:1 [13, 14, and 15]. The molar ratio of alcohol to oil has no effect on acid value, saponification values and iodine values of esters.

2.10.2 Strring rate

Oils and alcohols are not totally miscible, thus reaction can only occur in the interfacial region between the liquids and transesterification reaction is a moderately slow process; for this reason dynamic mixing is required to increase the area of contact between the two immiscible phases. Alcoholic's process can be enhanced by the agitation intensity of the reactor. Mass transfer of biodiesel from the oil phase towards the alcohol-oil interface might be a vital step that limits rate of alcoholic's reaction because the reaction is heterogeneous mixture. Reduced mass transfer between two phases in the initial phase of the reaction results in a sluggish reaction rate, the reaction being mass transfer controlled. Fast stirring accelerates transesterification reaction; therefore, variations in mixing strength are expected to change the kinetics of the transesterification reaction [12, 13].

2.10.3. Free fatty acid and moisture content

The free fatty acid and moisture content are the key parameters for determining the viability of vegetable oils to be used in transesterification process. Presence of moisture content in the oil increases the amount of free fatty acids. To carry out this reaction to completion, less than 3% free fatty acid content in oils is needed [16]. Higher the acidity of the oil, smaller is the conversion efficiency. Free fatty acids react with the basic catalyst added for the reaction and give rise to soap, as a result of which, one part of the catalyst is neutralized and is therefore no longer available for transesterification. High free fatty acid content oils are processed with an immiscible basic glycerol phase so as to neutralize the free fatty acids and cause them to pass over the glycerol phase. The starting materials used for base catalyzed alcoholysis should meet certain specifications. The triglycerides should have lower acid value and all material should be substantially anhydrous. The addition of more sodium hydroxide catalyst compensates for higher acidity, but the resulting soap causes formation of gels that interferes in the reaction as well as with separation of glycerol [11, 12, and 16]. The presence of water at high temperature resulted hydrolysis of triglycerides to diglyceride and form a free fatty acid as shown below.



$$\begin{array}{lcl} CH_2OOCR & & CH_2OH \\ | & & | \\ CHOOCR + H_2O & \longrightarrow & CHOOCR + HOOCR \\ | & & | \\ CH_2OOCR & & CH_2OOCR \end{array}$$

Triglyceride Water Diglyceride Free fatty acid

2.10.4. Alkali catalyst amount

A catalyst is needed to improve the transesterification reaction and amount of yield production. The alkaline catalysts such as sodium hydroxide and potassium hydroxide are most widely used. These catalysts increase the reaction rate several times faster than acid catalysts. Alkaline catalyst concentration in the range of 0.5 to 1.125% by weight yields 94 to 99% conversion efficiency. Further increase in catalyst concentration does not increase the yield, but it adds to the cost and makes the separation process more complicated [10].

2.10.5. Reaction time and temperature

The rate of the transesterification reaction is strongly influenced by the reaction temperature. Generally, the reaction is carried out close to the boiling point of ethanol (70-75°C) at atmospheric pressure. With further increase in temperature there is more chance of loss of ethanol. When the reaction temperature exceeds the boiling point of alcohol, the alcohol will vaporize and form a large number of bubbles which may inhibit the reaction. The completion of the basic catalyzed transesterification process depends on reaction time. The transesterification reaction is commonly conducted close to the boiling point of the alcohol at atmospheric pressure for one hour [17]. Excess reaction time does not increase the conversion but favors the backward reaction (hydrolysis of esters) which results in a reduction of product yield.

2.10.5. Biodiesel specification standards

The fuel specification defines and sets the quality standards for biodiesel which is based on the standard ASTM D6751. The kinematic viscosity is equal to the dynamic viscosity divided to the density and is a basic design specification for the fuel injectors used in diesel engines which is the resistance to flow of a fluid under gravity. If the viscosity is too high, the injectors do not perform properly. The viscosity of biodiesel can be predicted ± 15 % using the esters composition determined. The viscosity has to be in a range of 1.9-6.0mm2/s. The acid number is "the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point''. The acid number is a direct measure of free fatty acids. The free fatty acids can lead to corrosion and may be a symptom of water in the fuel. Usually, for a base catalyzed process, the acid value after production will be low since the base catalyst will strip the available free fatty acids. [19]

Table 2-3 Standard properties of biodiesel

Property	Units	USA	EU	
		ASTMD6751	EN14214	Recommended test method
Density at 15^{o}C	Kg/m^{3}	-	860-900	ASTM4052
Kinematic viscosity at 40^{o}C	mm^{2}/s	1.9 - 6	3.5 – 5	ASTM445
Flash point	^{o}C	≥120	≥130	ASTM D 93
Cloud point	^{o}C	-	-	ASTM D 2500
Cetane number	-	-	≥ 51Min	EU Standard
Sulfur content ,100%	Wt%	≤0.05%	≤0.01%	ASTM D5453
Sulphated ash	Wt%	≤0.02%	≤0.02%	ASTM D 874
Water content	mg/kg	-	≤ 500	EN ISO12937
Total contamination	mg/kg	-	≤ 24	EN 12662
Water and sediment content	Vol%	≤0.05		ASTM D2709
Acid number	mgKOH/kg	≤0.8	≤0.5	ASTM D 664
Easter content	Wt%		≤96.5	EN 14103
Free glycerol	Wt%	≤0.02	≤0.02	ASTM D 6584
Iodine value	gI2/100g	-	≤120	EN14111

CHAPTER THREE

3. MATERIALS AND METHODS

Materials

Materials and apparatus used in the production of the biodiesel are as follows: thermometer, retort stand, pipette, measuring cylinder, separating funnel, oven, water bath, hydrometer, conical flask, digital weighing balance, stop watch, hot plate, distilled water, methanol, n-hexane and sugar cane filter mud.

3.1 Raw material preparation

Filter mud was obtained from wonji sugar factories. Impurities like dusts and metals were removed by hand. Filter mud were crushed by hands with 1.0 mm to 2.0 mm sieve size in chemistry laboratory; then the sample was ready for oil extraction.

Figure 3.1(a). Filter mud collections from wonji sugar factory

Figure 3.2(b). Filter mud collections from wonji sugar factory

3.2 Samples analysis

3.2.1 Determination of the moisture content of the filter mud

The cleaned sample was weighed 50g,100g,150g,and 200g dried in an oven dryer and the weight was measured every 2hrs. The procedure was repeated until a constant weight was obtained. The percentage moisture in the filter mud was calculated using the following:

Moisture in % = (W1 – W2)/W1)*100………………………………….eq(3.1)

Where

W1 = original weight of the sample before drying

W2 = final weight of the sample after drying

3.2.2 Sieve analysis of the filter mud and size reduction

The moisture was removed by placing the sample in an oven at 65°C for 4 hours. The dried filter mud was crushed in manually by hands with sieve size 1 to 2mm. The sample was sieved using hand shake with set of sieves sizes arranged in descending order 2mm, 1.75mm, 1.50mm, 1.25mm, and 1mm.

Figure 3.3 Size separations by sieving process and measuring mass for extraction per batch

Methods

Extraction using solvent had several advantages. It gives higher yield and less turbid oil than mechanical extraction, and relative low operating cost compared with supercritical fluid extraction.

3.3 Solvent Extraction

Experimental work was conducted using soxhlet extraction setups. In solvent extraction process, this used soxhlet extraction apparatus. The result from soxhlet extraction like extraction time was used as the starting parameter for the extraction of filter mud oil.

3.3.1 Soxhlet Extraction

250ml of normal hexane was poured into round bottom flask. 40g of the sample was placed in the thimble and was inserted in the center of the extractor. The Soxhlet was heated to 65^{o}C.This was allowed to continue for two, four, six and eight hours. The experiment was repeated by placing the same amount of the sample into the thimble again by varying particle sizes (1-1.25mm, 1.25-1.5mm and 1.5-1.75mm and 1.75-2mm). The weight of oil extracted was determined for each run hours. At the end of the extraction, the resulting mixture containing the oil was heated to recover solvent from the oil.

Figure 3.4 Oil extractions by Soxhlet apparatus

3.3.2 Determination of the yield of sugar cane filter mud oil extracted

100g (W1) of the sample was placed in the thimble and about 400ml of normal hexane was poured into the round bottom flask. The apparatus was heated at 65°C and allowed for 2hrs, 4hrs, and 6hrs and 8hrs continuous extraction using Soxhlet apparatus. The experiment was repeated for four different particle sizes with one replica. At the end, the filter mud was weighed and dried in the oven at 100C until the constant weight (W2) is attained and the percentage of oil extracted was determined as:

%yield oil = (mass of filter mud oil/mass of sample)*100 …………………………..eq (3.2)

3.3.3 Determination of Specific Gravity

The density of the filter mud oil was determined by using density bottle. A clean and dry bottle of 25ml capacity was weighed (W0) and then the bottle was filled with the oil, stopper inserted and reweighed to give (W1). The filter mud oil was substituted with water after washing and drying the bottle and weighed to give (W2). The expression for specific gravity (Sp.gr) was:

$$\text{Sp.gr} = \frac{(W1-W0)}{(W2-W0)} = \frac{Mass\ of\ substance}{Mass\ of\ an\ equal\ volume\ of\ water} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{eq (3.3)}$$

3.3.4 Determination of viscosity of the filter mud oil

45m1 of filter mud oil was poured into a test tube and a viscometer was used to measure the viscosity at a temperature of 35^{o}C [52]. This experiment was done on Jimma university chemistry department postgraduate laboratory.

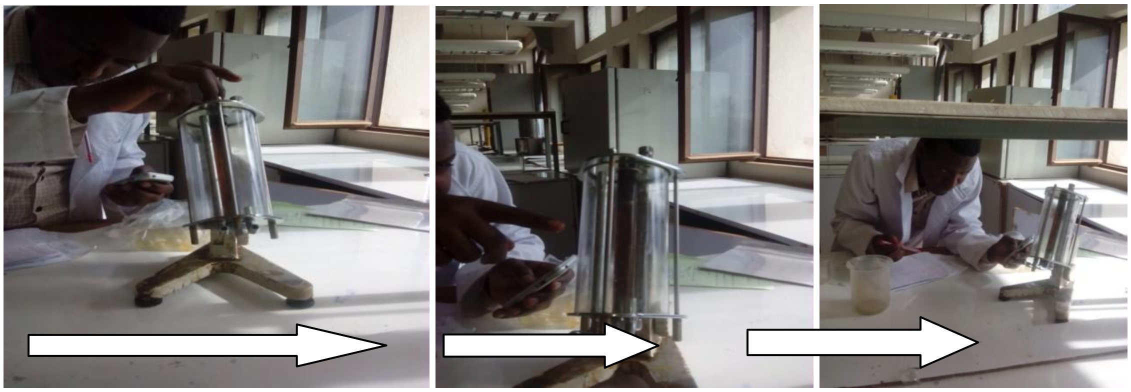


Figure3.5 laboratory setup of viscosity measurement by using viscometer

Table 3.1 Data during dynamic viscosity measurement

Time taken of the ball reached to the bottom end	Time(s)
T1	X(second)

T2	Y(second)
T3	Z(second)
Average time	W(second)

The data are; the density of the ball = ρ_b = 5g/3.42ml = 1.4619g/mL, the multiplication factor the working angle 70^0,F ==0.952,the volume of filter mud oil displeased by the ball was 3.42ml,the density of the filter mud oil was determined before 890.4kg/m^3

Therefore the kinematic viscosity of the filter mud oil was the ratio of the dynamic viscosity that measured by viscometer to the density of the filter mud oil;

The dynamic viscosity (η) = $t_{av*}(d_b - d_{fo})*k_b*F$……………………….eq (3.4)

$$V = \frac{\eta}{\rho o}$$

η = dynamic viscosity

Po = density of the filter mud oil

V= kinematic viscosity

3.3.5 Determination of pH Value

2g of the sample was poured into a clean dry 25ml beaker and 13ml of hot distilled water was added to the sample in the beaker and stirred slowly. It was then cooled in a cold-water bath to 25°C. The pH electrode was standardized with buffer solution and the electrode immersed into the sample and the pH value was read and recorded.

3.3.6 Ash content of the oil

Ash content of oil was determined using a furnace. A 20 g of oil was added in a burning cup. Then, the sample was placed in a furnace. A furnace was located at a temperature of 500^{o}C for 1 hour and after burning the residue sample was weighted and ash content was calculated.

3.4 Quality evaluation of the product

The quality of filter mud oil can be expressed based on the average molecular weight of triglycerol present in the oil and the amount of free fatty acid present in the oil, which was determined through determination of Saponification value, acid value, Iodine value and pH-value.

3.4.1Determination of Saponification Value

Indicator method was use as specified by [45]. 2g of the sample was weighed into a conical flask; 25ml of 0.5N methanolic Sodium hydroxide was then added. The content which was constantly stirred was allowed to boil gently for 30min. A reflux condenser was placed on the flask containing the mixture. Few drops of phenolphthalein indicator was added to the warm solution and then titrated with 0.5M HCl to the end point until the pink color of the indicator just disappeared. The same procedure was used for other samples and blank. The expression for saponification value (S.V.) was given by

Saponification Value (S.V) = $\frac{40*N*(V0-V1)}{M}$ ………………………………………Eq (3.5)

Where V0 = the volume of the solution used for blank test; V1 = the volume of the solution used for determination S.V; N = Actual normality of the HCl used; M = Mass of the sample.

3.4.2 Determination of Acid Value

25ml of n-hexane and 25ml of methanol was mixed in a 250ml beaker. The resulting mixture was added to 2g of filter mud oil in a 250ml conical flask and few drops of phenolphthalein were added to the mixture. The mixture was titrated with 0.1M NaOH to the end point with consistent shaking for which a dark pink color was observed and the volume of 0.1M NaOH was noted. The Acid value was calculated as:

Acid Value (A.V) =.$\frac{V*C*40}{M}$ ………………………………………………………eq(3.6)

Where V =Volume of sodium hydroxide (ml), C=Concentration of sodium hydroxide

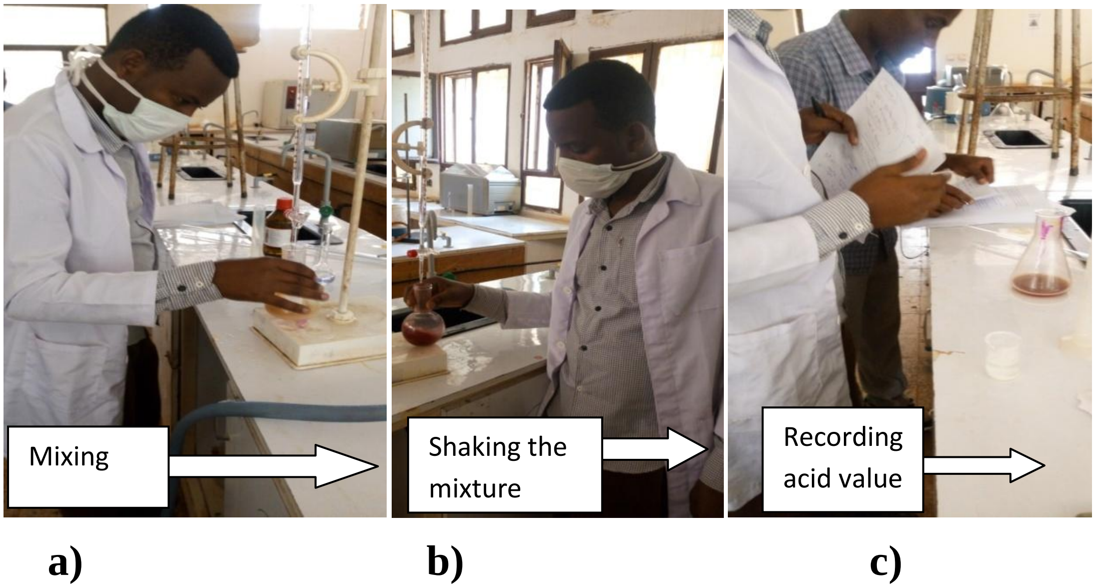


Figure 3.6 Acid value checking a) mixing b) shaking mixture c) recording values

3.4.3 Determination of Iodine value

The method specified by [46] was used. 2gm of filter mud oil sample was weighed into a conical flask and 20ml of carbon tetra chloride was added to dissolve this oil. Then 25ml of Dam's reagent was added to the flask using a safety pipette in fume chamber. Stopper was then inserted and the content of the flask was vigorously swirled. The flask was then placed in the dark for 2 hours and 30 minutes. At the end of this period, 20ml of 10% aqueous potassium iodide and 125ml of water were added using a measuring cylinder. The content was titrated with 0.1M sodium-thiosulphate solutions until the yellow color almost disappeared. Few drops of 1% starch indicator was added and the titration continued by adding thiosulphate drop wise until blue coloration disappeared after vigorous shaking. The same procedure was used for blank test and other samples. The iodine value (I.V) is given by the expression:

Iodine Value (I.V) = $\frac{12.69*C*(V1-V2)}{M}$ ……………………………………Eq (3.7)

Where: C = Concentration of sodium thiosulphate used; V1 = Volume of sodium thiosulphate used for blank; V2 = Volume of sodium thiosulphate used for determination, M = Mass of the sample.

3.4.4 Determination of higher heating value

Higher heating value (the energy content per unit quantity) of acid treated oil and fatty acid methyl ester was estimated from their saponification value and iodine value using the following correlation:

$\mathrm{HHV} = 49.43 - [0.041(\mathrm{S.V}) + 0.015(\mathrm{I.V})]$ ………………………………Eq (3.8)

3.4.5 Determination of Cetane number

Cetane number, which is the ignition delay after injection of the fuel of filter mud oil and Fatty acid methyl ester, was estimated based on saponification value and Iodine value using the following correlation.

$\mathrm{C.N} = 46.3 + \frac{5458}{\mathrm{S.V}} - 0.225(\mathrm{I.V})$ ………………………………………eq (3.9)

3.4.6 Flash point of filter mud oil and biodiesel, ASTMD 93

The flash point of biodiesel and filter mud oil was determined using empirical formula by [47]. The equation between FP and HHV for biodiesel is:

$\mathrm{HHV} = 0.021\mathrm{FP}+32.12$ ………………………eq(3.10)

3.5 Purification of filter mud Oil

The extracted crude filter mud oil contains waxes, gums and other complex compounds which can promote hydrolysis (increase in free fatty acid) of filter mud oil during storage. During transesterification process, these compounds can also interfere. There for this extracted crud filter mud oil was purified by using a filter paper. During a purification process the wax remains in the filter paper and the pure oil was passing in the filter paper and collecting in a conical flask.

Figure 3.7 Purification of filter mud oil in by using filter paper

3.6 Transesterification and Experimental Design for Biodiesel Production

In these work the biodiesel was prepared using purified filter mud oil and methanol with alkalies catalyst. Experimental design was analyzed and done by the Design-Expert 7.0.0 program. The experimental design selected for this study was Central Composite Design (CCD) and the response measured was the yield of fatty acid methyl esters (FAME). Furthermore, the physicochemical analysis of the biodiesel was carried out. The three transesterification process variables studied are reaction temperature, molar ratio of methanol to filter mud oil ratio and catalyst to filter mud oil ratio. The reaction period and rotation speed was set at optimum point where the maximum conversion could be achieved based on literature data. Atmospheric pressure is used for all the runs. Table 3.2 lists the range and levels of the four independent variables studied. The levels of the variables investigated are chosen by considering the operating limits of the biodiesel production process condition.

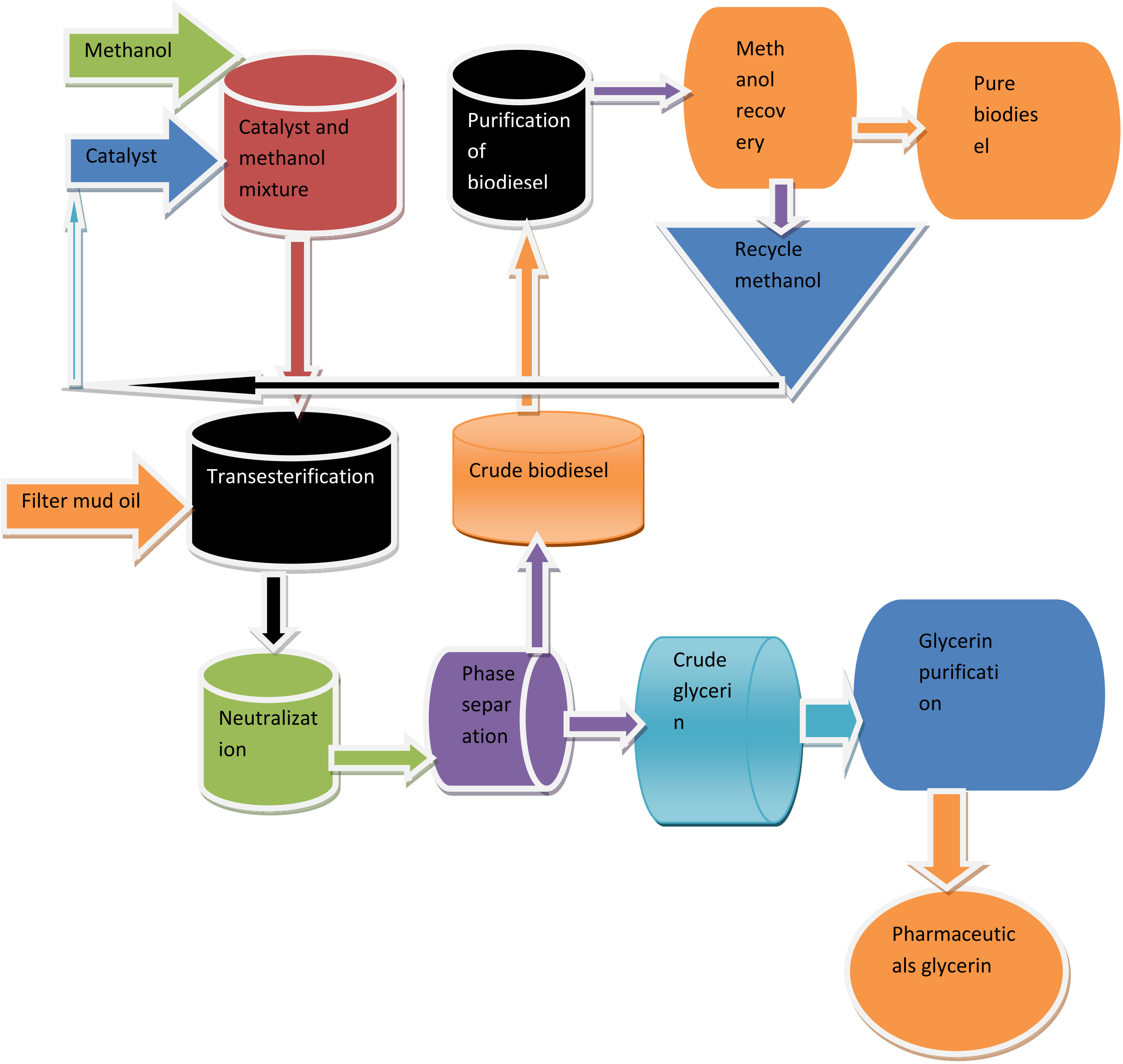


Figure 3.8 process flow diagram of biodiesel production

A three-level-four-factor CCD was employed in the optimization study, requiring 30 experiments. The methanol to filter mud oil molar ratio, catalyst to filter mud oil ratio and reaction temperature were the independent variables selected to optimize the conditions for FAME production of alkali-catalyzed transesterification. The 30 experiments were carried out and data was statistically analyzed by the Design-Expert program to find the suitable model for the % fatty acid methyl ester (% FAME) as a function of the above four variables.

Table3.2 Independent variables and levels used in central composite design for the alkali catalyzed transesterification process chosen for this study

Factors	Factor coding	Unit	Levels		
			-1	0	1
Reaction temperature	X1	^{O}C	55	60	65
Methanol to filter mud ratio	X2	-	63:9.333	70.875:10.5	78.75:11.66
Catalyst to oil weight ratio	X3	g/g	0.25:0.0625	0.3625:0.0906	0.475:0.119
RPM	X4	Rad	500	600	700
Yield of biodiesel (g)		gram	3.42	3.968	3.958

Table 3.3 Factor of Biodiesel in design expert 7.0 soft ware

Std order	Run order	Reaction temperature(oC)	Methanol to filter mud ratio(ml/ml)	Catalyst to filter mud oil weight(g/g)	Revolution per minute(rad)	Response biodiesel yield (g)
20	1	60	7.5	5.8	600	
23	2	60	6.75	5.8	500	
3	3	55	7.5	4	500	
19	4	60	6	5.8	600	
12	5	65	7.5	4	700	
7	6	55	7.5	7.6	500	
17	7	55	6.75	5.8	600	
29	8	60	6.75	5.8	600	
9	9	55	6	4	700	

8	10	65	7.5	7.6	500	
4	11	65	7.5	4	500	
14	12	65	6	7.6	700	
30	13	60	6.75	5.8	600	
26	14	60	6.75	5.8	600	
22	15	60	6.75	7.6	600	
6	16	65	6	7.6	500	
15	17	55	7.5	7.6	700	
27	18	60	6.75	5.8	600	
11	19	55	7.5	4	700	
28	20	60	6.75	5.8	600	
21	21	60	6.75	4	600	
13	22	55	6	7.6	700	
5	23	55	6	7.6	500	
2	24	65	6	4	500	
10	25	65	6	10	700	
24	26	60	6.75	5.8	700	
1	27	55	6	4	500	
16	28	65	7.5	7.6	700	
18	29	65	6.75	5.8	600	
25	30	60	6.75	5.8	600	

CHAPTER FOUR

RESULT AND DISCUSTION

4. Filter mud Preparation

13kg of sugarcane filter mud were taken from wonji sugar factories and draying using by oven at a temperature of 102^{O}C. Then, the dried filter mud is purifying from dust and the filter mud was powdering by manually by hand. The filter mud powders obtained were used for oil preparation.

4.1Moisture Content Determination

The amount of sample was weighted using a balance for each experiment. Then; it was dried in an oven at 102OC for 12hours. Again, the weight of the sample after dying was measured. Six experiments was conducted and the moisture content was determined for each of them and averaged to give the filter mud moisture content of 74.76%.

Table4.1The moisture content determination of the filter mud conducted laboratory result

	Draying time (hour)							% of moisture content
	0	2	4	6	8	10	12	
Sample weight (gram)	100	40	34	28	27.71	27.21	27.21	72.79
	125	52	36	30	28.62	27.98	27.98	77.6
	130	60	40	38	36.2	34.42	34.41	73.53
Average weight(gram)	118.33	50.6666	36.66	32	30.63	29.87	29.8666	74.64
% Average moisture content	-	57.18	27.63	12.73	4.28	2.48	0.01	-

The moisture content of the filter mud of sample with 100,125 and 130 gms was 72.79, 77.6 and 73.53%, respectively. Thus, the average moisture content of the three samples would be 74.76%.

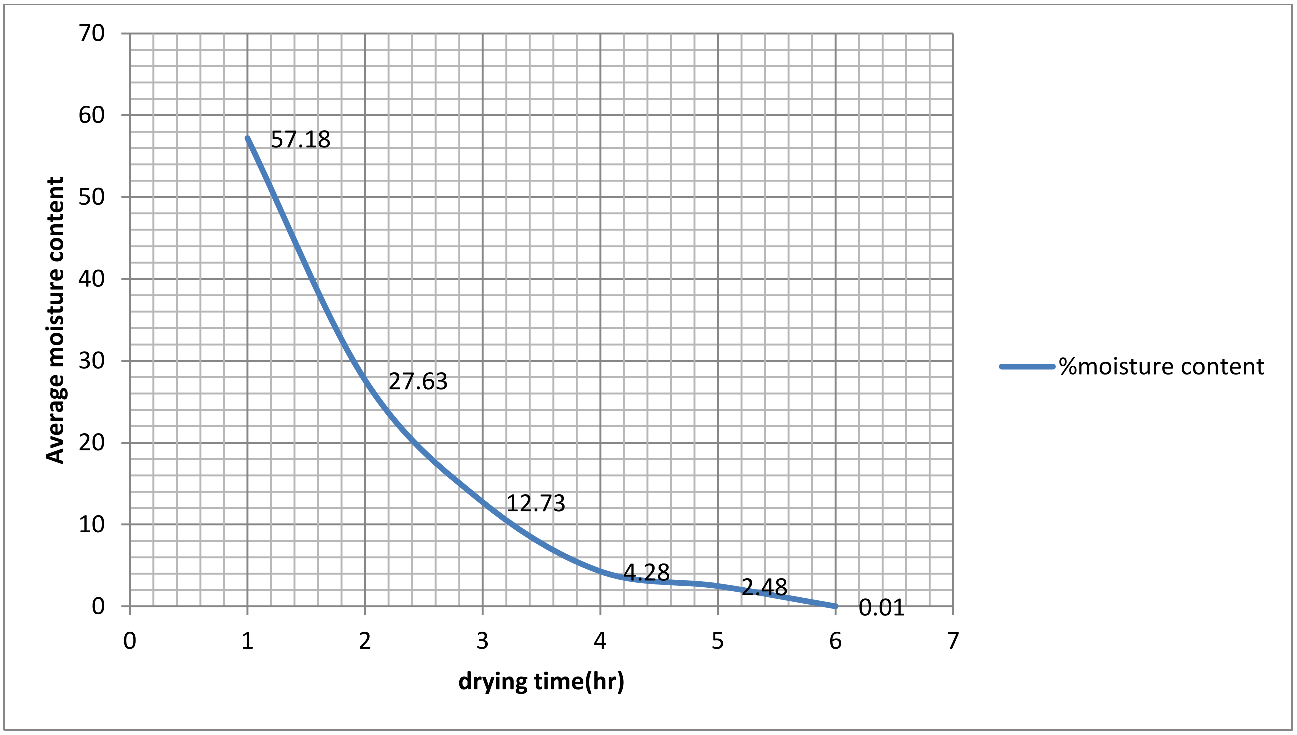


Figure 4.1 Average moisture content verses drying time

4.2. Extraction of oil from sugarcane filter mud and percentage yield of filter mud oil at different sample size

4.2.1 Extraction of oil from sugarcane filter mud

In this study, crude oil was extracted from sugarcane filter mud using n-hexane solvent in Soxhlet unit. After completion of extraction and removal of n-hexane, the total yield of crude oil obtained was found to be 4% as shown below.

Mass of sample =100gram = M1

Mass of sample after extraction = 96gram =M2

The difference mass of M1and M2 is mass of oil

M1-M2 = 100 gram - 96 gram =4 gram or

% of oil from filter mud = $\left(\frac{M1-M2}{M1}\right)*100$ ……………………………..Eq (4.1)

$= \left(\frac{100-96}{100}\right)*100$

$= 4\%$

4.2.3Estimation of oil yield from sugarcane filter mud

In general, the filter mud residue produced in sugar factory a large volume (30 – 40kg/ton of crushed cane) [53].

The maximum filter mud Estimation of produced annually

Kg of filter mud produced annually = 40kg/ton*3000ton/day*300day/year

= 36000000kg/year

The minimum filter mud estimation produced annually

= 30kg/ton*3000ton/day*300day/year

= 27000000kg/year

Total filter mud = $\frac{36000T/y + 27000T/y}{2}$

= 31500 filter mud per annum

From the above moisture content determination point, the moisture content of the filter mud was 74%

Therefore, the dry filter mud would be,

Filter mud = 31500*(1-0.74 = 8190 filter mud per annum

The oil yield = 8190 *0.04 = 327.6T/annum

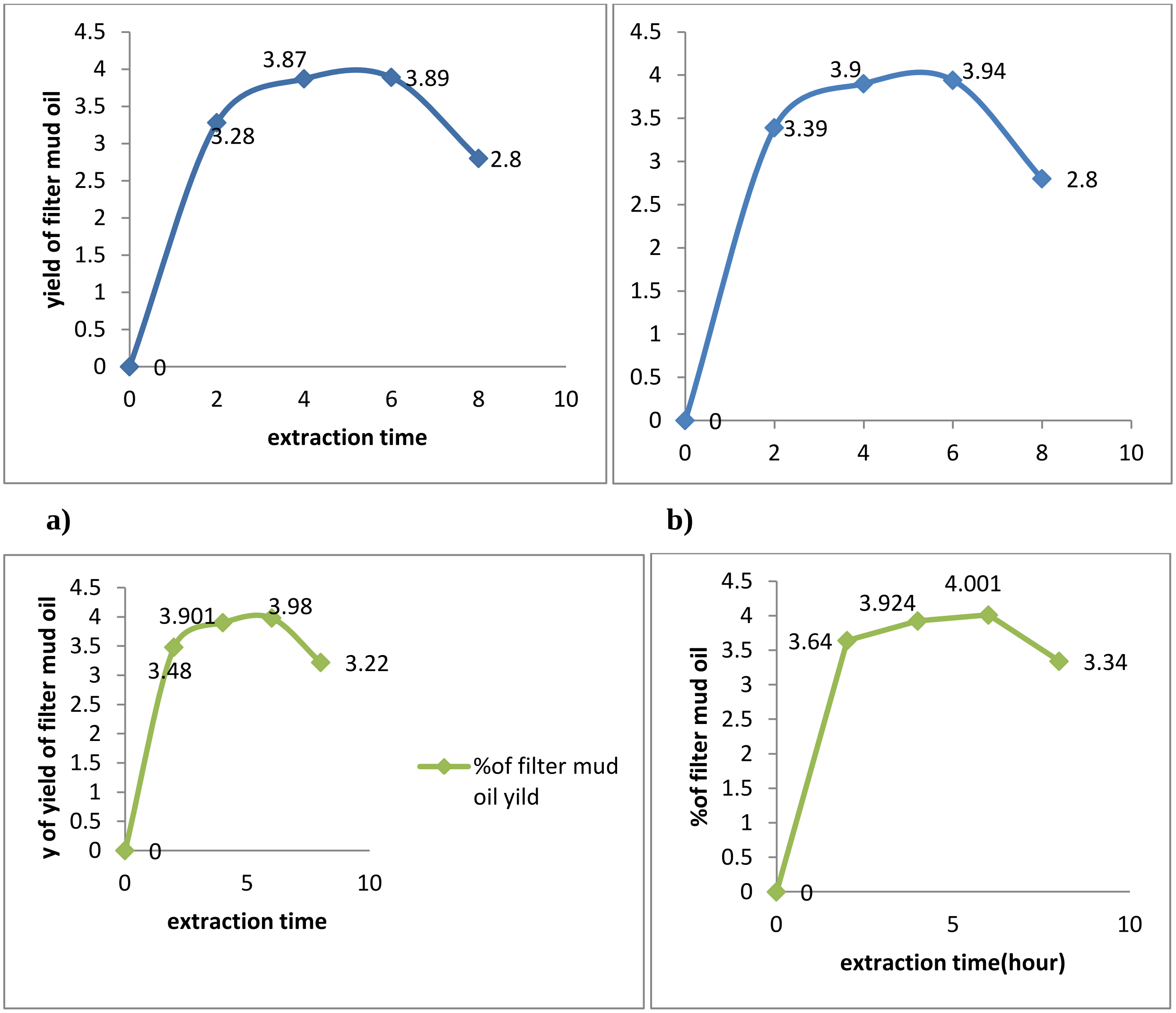
4.2.4 Percentage yield of sugarcane filter mud oil at different samples size

The percentage yield of filter mud oil was determined from the above equations (4.1). The size of the sample increases the oil yield would be decreases. At the smallest size we would get more oil yield.

Table 4.2Percentage yield of filter mud oil at different size, extraction time and n-hexane as a solvent

Sample size(mm)	Dry filter mud weight and yield of oil	Extraction time(hr)	2	4	6	8
		Temperature(^{o}C)	55	60	**65**	68
		n-hexane solvent(ml)	400	400	**400**	400
1.75 – 2	Dry filter mud weight (gram)	100	96.82	93.5	**90.26**	88.28
	Yield of filter mud oil(g)	0	3.28	3.54	**3.58**	2.24
1.5 - 1.75	Dry filter mud weight (gram)	100	96.72	93.45	**90.2**	88.17
	Yield of filter mud oil(g)	0	3.39	3.50	**3.61**	2.30
1.25 -1.5	Dry filter mud weight(gram)	100	96.7	93.28	**89.96**	87.93
	Yield of filter mud oil(g)	0	3.40	3.68	**3.88**	2.32
1 – 1.25	Dry filter mud weight (gram)	100	96.69	92.81	**89.23**	87.15
	Yield of filter mud oil(g)	0	3.42	3.924	**4.001**	2.4

The minimum yield of filter mud oil was 2.24 a filter mud size of 1.75 to2 at a minimum extraction time of 8 hours and the maximum extraction of this filter mud oil was 4.001 at a filter mud size of 1 to 1.25 sieve size with the maximum extraction time of 6 hours.



a)

b)

c)

d)

Figure 4.2 Yield of filter mud oil with respect to extraction time at different size

a)1.75- 2mm b) 1.50-1.75mm c) 1.25-1.50mm d)1.0-1.25mm size of sample

4.2.5 Effect of extraction time on percentage yield of filter mud oil

The percentage yield of filter mud oil can be affected by the extraction time, temperature, solvent type, filter mud size and other component in the filter mud. The extraction time plays a great role on the percentage yield of filter mud oil using n- hexane as a solvent. In the figure 4.2 a, b, c and d above figure shows that as the contact time increases the oil yield increases this was continue until transfer of oil from the filter mud powder to the solvent attains zero. In the other means, when the maximum amount of extractable oil was obtained the oil yield level remains invariable even by extending the reaction time. So that in the soxhlet extraction apparatus the maximum oil yield could be finding at the extraction time of 6 hours and above. As shown the graph of figure 4.2, extracting the oil beyond 6 hours was wasting time because using n- hexane as a solvent can be find maximum yield at this time. The extraction time fasting at the beginning of the extraction but slow gradually. The reason was that when the filter mud powders were exposed to the fresh solvent, the free oil on the surface of mud was solibilized and oil gets extracted quickly inducing a fast increase in the extraction rate. Furthermore, since the oil concentration was low in the solvent at the beginning of extraction process, the oil diffuses quickly from the filter mud to the liquid phase due to the difference in concentration of the oil. As the time passing by, the concentration of oil increases in the solvent resulting in a decreasing in the diffusion rate.

Table 4.3 Percentage yield of filter mud oil at different temperature and filter mud sizes by using n-hexane as a solvent

Sample size(mm)	Dry filter mud weight and yield of oil	Extraction time(hr)	2	4	6	8
		Temperature(^{o}C)	55	60	**65**	68
		n-hexane solvent(ml)	400	400	**400**	400
1.75 – 2	Dry filter mud weight (gram)	100	96.82	93.5	**90.26**	88.28
	Yield of filter mud oil	0	3.28	3.54	**3.58**	2.24
1.5 - 1.75	Dry filter mud weight (gram)	100	96.72	93.45	**90.2**	88.17
	Yield of filter mud oil	0	3.39	3.50	**3.61**	2.30
1.25 -1.5	Dry filter mud	100	96.7	93.28	**89.96**	87.93

	weight(gram)					
	Yield % of filter mud oil	0	3.40	3.68	**3.88**	2.32
1 – 1.25	Dry filter mud weight (gram)	100	96.69	92.81	**89.23**	87.15
	Yield of filter mud oil	0	3.42	3.924	**4.001**	2.4

4.2.6 Effect of sugarcane filter mud size on the percentage yield of oil

Particle size plays a great role on the yield of filter mud oil. Smaller particle size gives high yield while samples with large particle size delivers low yield. That means less oil was extracted from the larger particles (2mm) compared to the small size of the particle (1mm). The main reason was that larger particle size with smaller contact area, have more resistant to solvent entrance and oil diffusion towards the solvent. Therefore, fewer amounts would be transferred from inside the larger particles to the surrounding solution in comparison with the smaller ones. Thus, an increase in particle size would decrease the oil yield. Nevertheless, we know that when the particle was too small (very fine particle size) i.e., below <1mm, the extracted oil become small in its amount, even though the contact surface area for small particle was supposed to be significantly higher than that for the larger particles. These were due to the agglomeration of the particles which reduces the effective surface area available for the free flow of solvent towards inside the solid particles.

4.2.7 Effect of temperature on the filter mud oil yield

The amount of oil can be affected by temperature. From this experimental result of the work, for instance, let's look at figure 4.2 above for particle size ranges from 1.75 – 2mm,the percent yield of filter mud oil using n- hexane as a solvent at a temperature of 55,60 ,65 and 68^{o}C are 3.28,3.54,3.58 and 2.24 respectively. This result would be shown us increasing temperature with raising oil yield. Based on the findings, for solvent, the yield was found to enhance with increasing temperature. This was because of raising the temperature, both the diffusion coefficient and the solubility of the oil in solvent was enhanced, thus heat treatment improves the extraction filter mud oil. The higher extraction temperature the easier to break the molecules inside the oil; as a result, the yield also gets high.

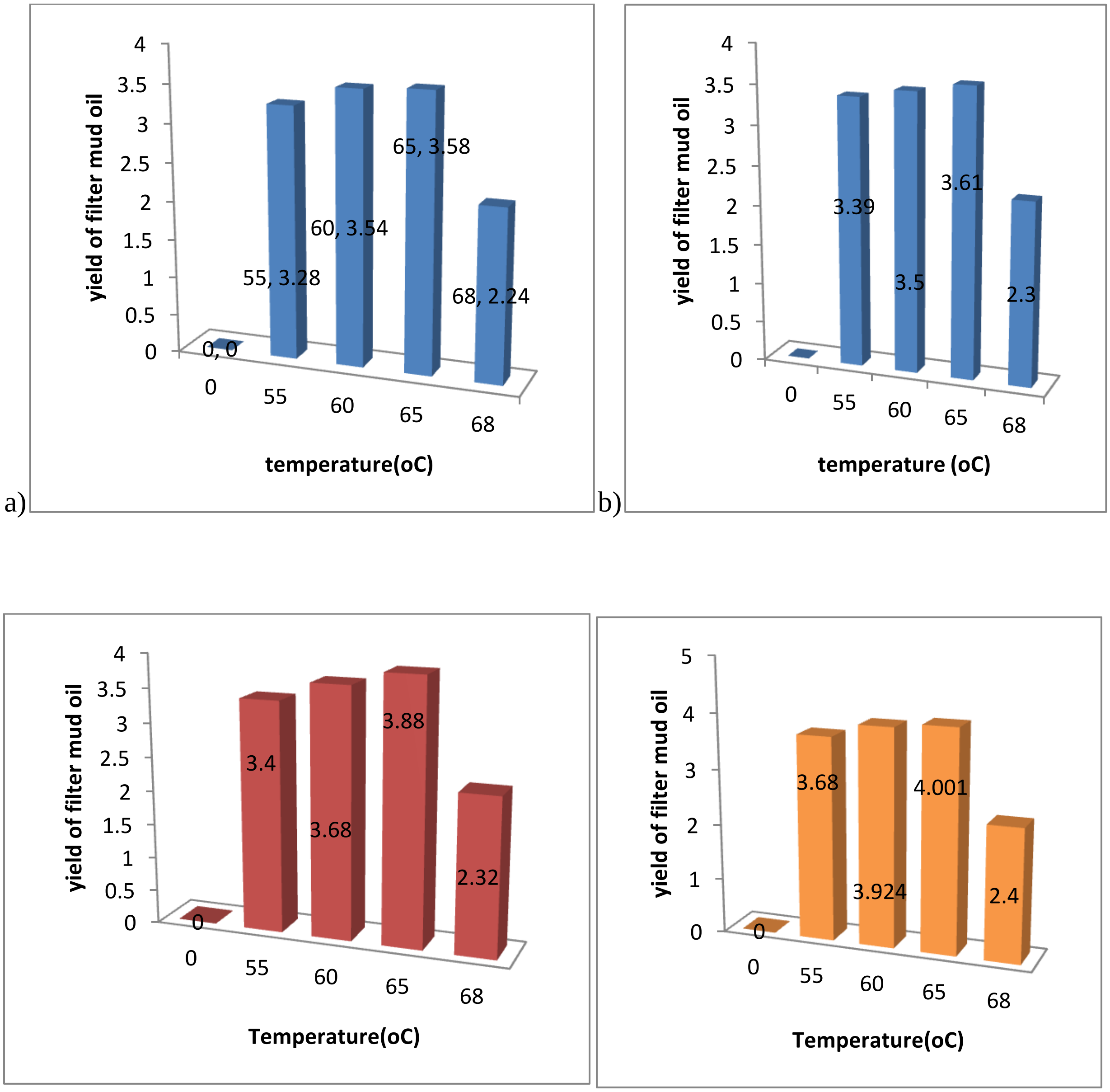


Figure 4.3 Effect of temperature on the yield of filter mud oil at different sample size

a) 1.75-2mm b) 1.5-1.75mm   c) 1.25-1.50mm d) 1.0-1.25mm sample size

4.2.8 Effects of the solvent type in the filter mud oil yield

By considering the table below and let's take particle size ranges from 1.75 – 2mm, then the percentage yield of the filter mud oil was differ in the n- hexane solvents, at this particular case, the maximum oil yield using n – hexane was found 3.58g at a temperature of 65^{o}Cand a minimum yield of 2.24g at a temperature of 68^{o}C and for that of ethanol as a solvent at the same size that is 1.75- 2mm the maximum yield of oil was 3.51g and the minimum yield of oil was 2.20g at a temperature of 65 and 68oC respectively. By using the solvent n-hexane and at the same temperature by varying the size that is 1 to 1.25mm the maximum and minimum oil yield were 4.001 and 3.68g respectively. For that of ethanol as a solvent at the same size the minimum and the maximum of oil yield was 3.29 and 3.94 respectively. From this result n– hexane were the best extractive purposes of producing filter mud oil.

Table 4.4(a) extraction of filter mud oil n-hexane as a solvent

Sample size(mm)	Dry filter mud weight and yield of oil	Extraction time(hr)	2	4	6	8
		Temperature(^{o}C)	55	60	**65**	68
		n-hexane solvent(ml)	400	400	**400**	400
1.75 – 2	Dry filter mud weight (gram)	100	96.82	93.5	**90.26**	88.28
	Yield of filter mud oil(g)	0	3.28	3.54	**3.58**	2.24
1.5 - 1.75	Dry filter mud weight (gram)	100	96.72	93.45	**90.2**	88.17
	Yield of filter mud oil(g)	0	3.39	3.50	**3.61**	2.30
1.25 -1.5	Dry filter mud weight(gram)	100	96.7	93.28	**89.96**	87.93
	Yield of filter mud oil(g)	0	3.40	3.68	**3.88**	2.32

1 – 1.25	Dry filter mud weight (gram)	100	96.69	92.81	**89.23**	87.15
	Yield of filter mud oil(g)	0	3.42	3.924	**4.001**	2.4

Table 4.4(b) Extraction of filter mud oil by using ethanol as a solvent

Sample size(mm)	Dry filter mud weight and yield of oil	Extraction time(hr)	2	4	6	8
		Temperature(^{o}C)	55	60	**65**	68
		Ethanol solvent(ml)	400	400	**400**	400
1.75 – 2	Dry filter mud weight (gram)	100	97.19	93.97	**90.78**	88.3
	Yield (g)	0	2.89	3.42	**3.51**	2.20
1.5 - 1.75	Dry filter mud weight (gram)	100	96.79	92.2	**88.98**	85.36
	Yield (g)	0	3.31	3.50	**3.60**	2.4
1.25 -1.5	Dry filter mud weight(gram)	100	85.36	82.32	**79.33**	76.89
	Yield (g)	0	3.21	3.69	**3.76**	3.18
1 – 1.25	Dry filter mud weight (gram)	100	96.67	93.17	**89.64**	86.78
	Yield(g)	0	3.44	3.75	**3.94**	3.29

4.3 characterization of the filter mud oil

4.3.1 Saponification value of the oil

The indicator method was use as specified by [45].2g of the sample was weighted in to a conical flask; 25ml of 0.5N methanolic sodium hydroxide was then added. The contents were constantly stirred and boil gently for 30 minutes. A reflux condenser was placed on the flask containing the mixture. Few drop of phenolphthalein indicator was added to the warm solution and then stirred with 0.5HCL to the end point until the pink color of the indicator just disappeared. The sample procedure was used for samples and blanks. The expression for saponification value (S.V) was given by the following equation

$$\mathrm{Saponificationvalue(S.V)} = \frac{40 * \mathrm{N} *}{\mathrm{M}}(\mathrm{BLTV} - \mathrm{V})$$

Where

V_0 = the black level titration volume = 35ml

V_1 = the titration volume = 20ml

N = actual normality of the Hcl used = 0.5mol/l

M = mass of the sample = 2gram

Therefore, S.V $= \dfrac{40\,\frac{gram*}{mol}L**\frac{0.5}{l}mol}{2gram}(35 - 20)ml$

$$= 0.15\frac{gram\ NaoH}{gram\ of\ oil}$$

$$= \frac{150\ mg\ NaOH}{gram\ of\ oil}$$

4.3.2 Determination of Acid Value

25ml of n-hexane and 25ml of methanol was mixed in a 250ml beaker. The resulting mixture was added to 2g of filter mud oil in a 250ml conical flask and few drops of phenolphthalein were added to the mixture. The mixture was titrated with 0.1M NaOH to the end point with consistent shaking for which a dark pink color was observed and the volume of 0.1M NaOH was noted.

Table4.5 Determination of acid number

Run	Titration volume(ml)	Color change
1	7.1	Pink to red
2	6.8	Pink to red
3	7.2	Pink to red
4	7.0	Pink to red
Average of thus component	7.025	

The Acid value was calculated as:

Acid Value (A.V) =.$\frac{V*C*40}{M}$

Where

V = Titration volume of sodium hydroxide (ml) = 7.025ml

C=Concentration of sodium hydroxide = 0.1M

Molecular weight of sodium hydroxide = 40gram/ mol.L

M= sample weight = 2gram

$$A.V = \frac{0.007025\,L*0.1\frac{mol}{l}*\frac{40gram}{mol}.}{2gram}$$

= 0.01405

= 1.41%

4.3.3 Free fatty acid (FFA)

Percentage free fatty acid (FFA) content of the oil was calculated empirically using the acid value perversely determined as follow:

%FFA = $\frac{A.V}{2}$

Where

%FFA – percentage free fatty acid content
A.V = Acid value of the oil
%FFA = $\frac{A.V}{0.503}$
= $\frac{0.01405}{2}$
= 0.00702

4.3.4 Determination of specific gravity

After the sample was filled into graduate cylinder at 50ml and its temperature was recorded; hydrometer was used to measure the specific gravity of the oil at 20 ^{o}C specified. Hence, the density of the oil was determined using the specific gravity. In this measurement the specific gravity of the filter mud oil was 0.8904.

4.3.5 The density of the filter mud oil

The specific gravity of the oil was measured by hydrometer to be 0.8904 and after multiplying the specific gravity of the oil with the water density, and then gained the density of the filter mud oil.

Density of oil = specific gravity of the oil $*$ Density of water ……………………..4.3

Where

The density of the water = 1000kg/m^3

The specific gravity of the oil = 0.8904

By substituting all this value we would gain density of the oil

Therefore,

Density of oil = 0.8904*1000kg/m^3

= 890.4kg/m^3

4.3.6Kinematic Viscosity

45m1 of filter mud oil was poured into a test tube and a viscometer was used to measure the viscosity at a temperature of 35^{o}C,the kinematic viscosity was determined after determined the dynamic viscosity of the filter mud oil. The dynamic viscosity of the filter mud oil was determined below;

Table 4.6 kinematic viscosity measuring data

Time that taken the ball reached the bottom of viscometer	Time(s)
T1	10
T2	9
T3	8
Average time(s)	9

Other data

V_d = volume displaced during measuring =3.42ml

M_b = mass of the ball = 5gram

K = ball constant = 6.799mpa/(cm^3/gm)

F = multiplication factor at viscosity measurement at viscometer at 70^0 inclination 0.952

The density of the ball was = $d_b = \frac{mb}{vd}$ = 5g/3.42ml = 1.4619g/ml

V= $t_{av*}(d_b - d_{fo})$*K*F

= 9*(1.4619 – 0.8904)*6.799*0.952 m pas

= 33.297m pas = 33.297*10^{-3}kg/m s

Kinematic viscosity =33.297*10^{-3}kg/m s/(890.4kg/m^3)

= 37.39mm^2/s

4.3.7 Determination of Iodine value (I.V) of filter mud oil

The iodine value of the filter mud oil determined experimentally by titration described in equation (3.7) above. Where

12.69 = factor proceeding from the reason between the number of transferred electrons and the molar mass of iodine values.

V1 = volume of sodium thiosulfate used for blank

V2 = volume of sodium thiosulfate used for determination

Ms = mass of filter mud oil sample = 2gram

C = concentration of sodium thiosulfate used = 0.1mol/liter

Iodine value (I.V) = $\frac{12.69*C*(V1-V2)}{Ms}$

Table 4.7 Titration result of iodine value of filter mud oil

Factor proceeding	Mass of sample of filter mud oil	Concentration of sodium thiosulfate (c)	Volume of sodium thiosulfate used for blank(V1)ml	Volume of sodium thiosulfate used for determination	I.V(gI2/100g) of the filter mud oil during experimental titration
12.69	2	0.1	160	13	93.2717
12.69	2	0.1	163	14	94.5405
12.69	2	0.1	158	12.5	92.32
12.69	2	0.1	162	12	95.175
12.69	2	0.1	156	13.5	90.42
12.69	2	0.1	159	14.3	91.8
12.69	2	0.1	157	14	90.733

This experiment was done on Jimma University, school of natural science, and department of chemistry post graduate laboratories. The I.V was a measure of the total unsaturated (double bond) within the FAME product of the filter mud oil. There for iodine absorption occurs at the double bond position thus a higher quantity of the double bonds in the filter mud oil sample and greater potential to polymerize in engine and hence less stability. The process of transesterification reduces the iodine value to a small extent. The iodine value of this filter mud oil shown in the above table 4.8, that was fitted the ASTM requirement (i.e, the iodine value of the filter mud oil is less than 115). From the above table the maximum amount of I.V of the filter mud oil was 95.175 and the minimum amount of (I.v)gI2/100g of filter mud oil. There for which used the maximum amount of I.v for other experimental analysis.

4.3.8 Determination of HHV

The determination of the heating value(calorific value) of the filter mud oil was by using the empirical formula suggested by above in equation(3.8) [48]. Higher heating value (the energy content per unit quantity) of acid treated oil and fatty acid methyl ester was estimated from their saponification value and iodine value using the following correlation:

HHV (energy content per unit quantity) = 49.43-[0.041(S.V)+0.015(I.V)]

= 49.43-[0.041(150) +0.015(95.175)]

= 41.85MJ/Kg

Therefore the energy content of the filter mud oil was 41.85MJ/Kg

4.3.9 Determination of Cetane number (C.N)

The determination of Cetane number was used for knowing the ignition delay after injection of the fuel, of filter mud oil. From the equation (3.9) above determine the Cetane number of the filter mud oil by correlation of the S.V and I.V suggested by [49] as shown below.

C.N = 46.3+ (5458/S.V)-0.225(I.V)

= 46.3+ (5458/150)-0.225(95.175)

= 104.1

4.3.10 Determination of the flash point of the filter mud oil

The flash point of filter mud oil was determined using empirical formula by [47]. The equations between FP and HHV of oil shown Eq(3.10) above. The flash point of the filter mud oil calculated from the equation below.

HHV = 0.021FP+32.12

41.85 = 0.021FP+32.12

FP = [(41.85-32.12)/0.021]

= 463.33oC

The flash point of the filter mud oil was 463.33oC, that were fitted to the ASTMD93

4.4Ash content of the oil

Ash content of the oil was determined using a furnace. A 28 gram of oil was added in a burning cup. Then, the sample was placed in a furnace. A furnace located at a temperature of 500Oc for 1 hour and after burning the residence sample was weighted and ash content was calculated.

Ash content% (w/w) =final mass of oil after burning∗100%Initial mass of sample

Ash content of the oil%(w/w) = $\frac{\text{final weight of the filter mud oil after burning}*100}{\text{inial weight of the filter mud oil}}$

Initial weight of filter mud oil was 28 gram and after burning a furnace the weight of the filter mud oil was 0.0078gram.Therefore

Ash content of the filter mud oil% =$\frac{0.0078}{28} * 100$

= 0.0278%

From this result the ash content of the filter mud oil was refined and suitable for the production of biodiesel.

4.4.1Moisture content of filter mud oil

The empty measuring cylinder was weighted with and without the amount of filter mud oil and dried in an oven at 105 ^{o}C for 6hr, weighting each 2hr till constant weight of was obtained and finally the weight 28gram was taken and compared with the initially recorded weight. Then, the percentage of the moisture content of the filter mud oil was determined by the equation below,

Moisture content of the oil (%) = $\frac{m1-m2*100}{m1}$

= $\frac{28-27.963*100}{28}$

= 0.132%

This lower value of oil moisture content helps to prevent the formation of soap during transesterification reaction which causes difficulty of glycerol separation and reduction of biodiesel yield.

4.5. Transesterification and Production of biodiesel from filter mud oil

The filtered filter mud oil was heated up to a temperature of 60oC in a heater to melt coagulated oil. The heated oil of 10ml was poured in to the conical flask containing catalyst – alcohol solution, and this moment was taken as the starting time of the reaction. The reaction mixture was then shaken by using shaker at a speed of 500 to 600rpm.

The yield and characteristics of biodiesel was depending on the type of oil used due to variation in the fatty acid composition and other characteristics of oil. Taking in to this consideration aspect, the filter mud oils from inedible sources have been taken as a raw material for the preparation of biodiesel using NaOH catalyst and methanol alcohol.

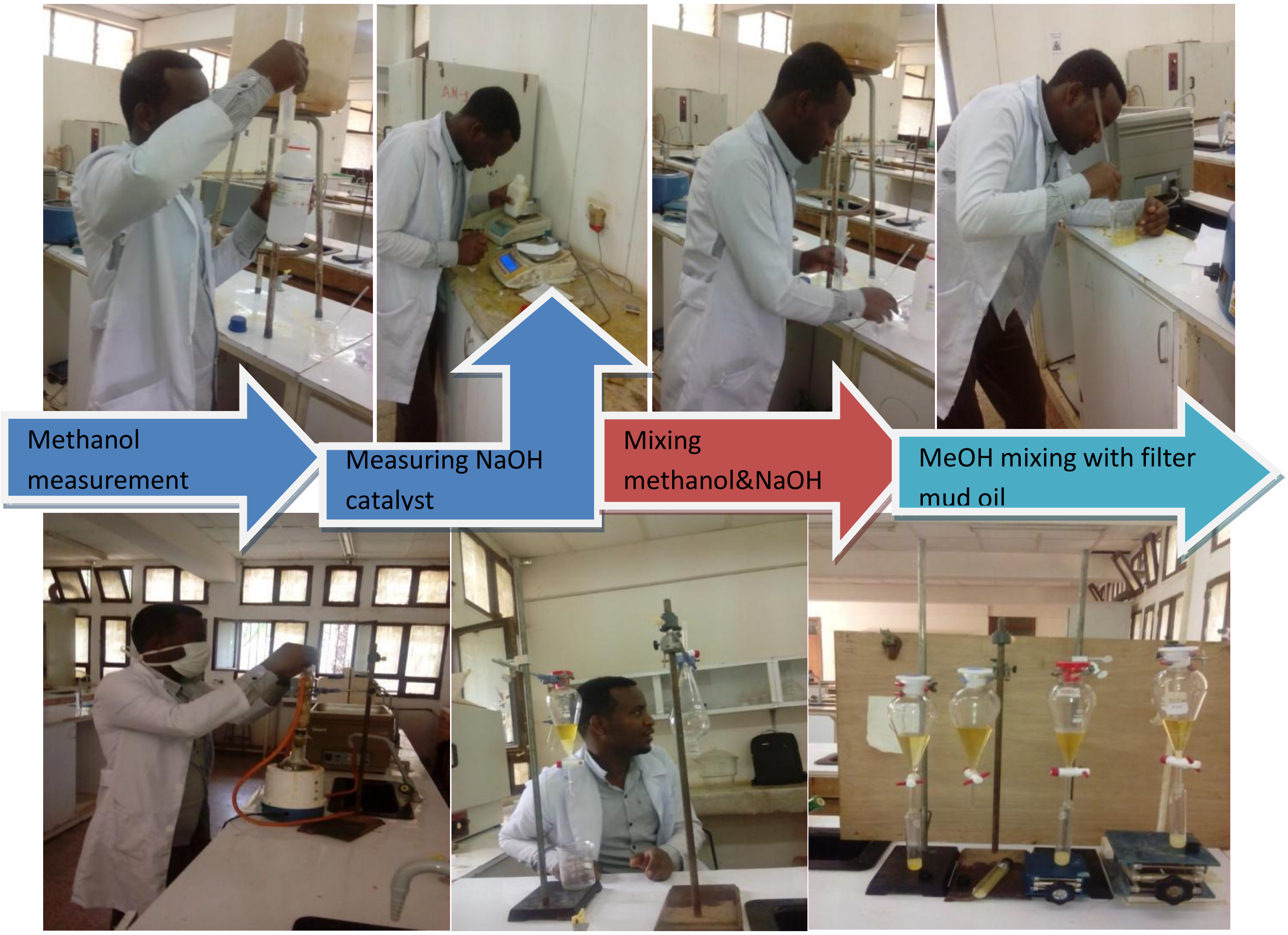


Figure 4.4 Biodiesel production procedure and glycerol separation

The transesterification was carried out at a reflux of methanol, a stirrer, condenser, a 250ml capacity glass reactor, and thermostat. The effect of process variables (reaction temperature, methanol to filter mud oil ratio, and catalyst weight and rpm) was investigated by response surface methodology. Both main and interaction effects of the variables towards FAME yield was thoroughly studied as shown on the table (4.8) below.

4.5.1 Biodiesel separation from glycerol

During separation, the layers were formed in such manner that the crude biodiesel phase present at the top and the glycerol phase at the bottom after settling the product to 24hour. The lower layer consists of glycerol, excess methanol, catalyst and other impurities whereas the upper layer consists of methanol, biodiesel and residual catalyst. The glycerin and other impurities were removed from biodiesel by opening the tap at the bottom. After separating the glycerin from the biodiesel, the biodiesel were washed by warm distilled water to remove the residual soap from the biodiesel. The main purpose of biodiesel washing step was to remove any soap formed during transesterification reaction. Warm water with acetic acid provides neutralization of the remaining catalyst and removes the formed salts. In this process the use of warm water was prevent the formation of precipitated saturated fatty acid ester.

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Figure 4.5 separation of biodiesel from glycerol

4.5.2. Transesterification reaction process variable optimization

Optimization of FAME was carried out by varying the input variables to predict the model and it was analyzed with surface and contour plot. The adequacy of fitted equation was also checked.

Table 4.8, Experimental data

Std order	Run order	Reaction temperature (oC)	Methanol to filter mud ratio	Catalyst to filter mud oil weight(gram)	Revolution per minute(rad)	Actual biodiesel yield	Predicted biodiesel yield	Residuals
20	1	60	7.5	5.8	600	3.95	3.99	-0.045
23	2	60	6.75	5.8	500	3.95	3.96	3.801E-003
3	3	55	7.5	4	500	3.68	3.68	-1.775E-003
19	4	60	6	5.8	600	3.92	3.86	0.060
12	5	65	7.5	4	700	3.52	3.51	5.892E-003
7	6	55	7.5	7.6	500	3.88	3.89	-9.719E-003
17	7	55	6.75	5.8	600	3.91	3.84	0.070
29	8	60	6.75	5.8	600	3.96	3.97	-8.088E-003
9	9	55	6	4	700	3.61	3.62	-0.013
8	10	65	7.5	7.6	500	3.78	3.76	0.018
4	11	65	7.5	4	500	3.58	3.56	0.021
14	12	65	6	7.6	700	3.46	3.45	7.336E-003
30	13	60	6.75	5.8	600	3.97	3.97	-6.088E-003
26	14	60	6.75	5.8	600	3.96	3.97	-9.088E-003
22	15	60	6.75	7.6	600	3.96	3.99	-0.030
6	16	65	6	7.6	500	3.47	3.46	0.013
15	17	55	7.5	7.6	700	3.86	3.84	0.025
27	18	60	6.75	5.8	600	3.96	3.97	-7.088E-003
11	19	55	7.5	4	700	3.57	3.59	-0.022
28	20	60	6.75	5.8	600	3.96	3.97	-0.012
21	21	60	6.75	4	600	3.92	3.87	-0.046
13	22	55	6	7.6	700	3.63	3.66	-0.031
5	23	55	6	7.6	500	3.71	3.71	-3.304E-004
2	24	65	6	4	500	3.44	3.46	-0.019
10	25	65	6	4	700	3.42	3.42	2.807E-004
24	26	60	6.75	5.8	700	3.93	3.91	0.019

1	27	55	6	4	500	3.69	3.71	-0.017
16	28	65	7.5	7.6	700	3.76	3.75	7.947E-003
18	29	65	6.75	5.8	600	3.62	3.67	-0.054
25	30	60	6.75	5.8	600	3.97	3.97	-4.088E-003

4.5.3. Effect of process variables on transesterification reaction

Temperature, methanol to filter mud oil ratio, and catalyst weight was considered as input process variables. Analysis of variance on table shown below that was mains and interaction effect was significant in this model and variation of those process variables affects the product greatly.

Table 4.9 ANOVA for response surface Quadratic model

Source	Sum square	Df	Mean square	F value	P value Prob> F	
Model	1.06	14	0.075	52.89	<0.0001	Significant
A-reaction temperature	0.12	1	0.12	86.43	<0.0001	Significant
B-methanol to filter mud oil ratio	0.084	1	0.084	59.09	<0.0001	Significant
C-catalyst to filter mud oil ratio	0.065	1	0.065	45.74	<0.0001	Significant
D-RPM	9.988E-003	1	9.988E-003	7	0.0184	Significant
AB	0.016	1	0.016	10.95	0.0048	Significant
AC	2.500E-005	1	2.500E-005	0.018	0.8965	N.S
AD	2.025E-003	1	2.025-003	1.42	0.2521	N.S
BC	0.042	1	0.042	29.45	<0.0001	Significant
BD	2.500E-005	1	2.500-005	0.018	0.8965	N.S
CD	1.225E-003	1	1.225E-003	0.86	0.3689	N.S
A^2	0.12	1	0.12	83.80	<0.0001	Significant
B^2	5.930E-003	1	5.930E-003	4.16	0.0595	Significant

C^2	4.113E-003	1	4.113E-003	2.88	0.1102	N.S
D^2	4.113E-003	1	4.113-003	2.88	0.1102	N.S
Residual	0.021	15	0.021			
Lack of fit	0.021	10	0.021	286.19	<0.0001	Significant

4.5.4Development of regression model equation

The model equation that correlates the response yield of filter mud oil to biodiesel to the transesterification process variables in terms of actual value after excluding the insignificant terms was given below in equation. Final equation in terms of coded factors:

Biodiesel yield = $+3.97-0.083*A+0.068*B+0.060*C-0.024*D+0.031*A*B+0.051*B*C-0.21*A^2$

Where

A = Reaction temperature

B = Methanol to filter mud oil ratio

C = Catalyst to filter mud oil ratio

D = RPM

As shown the table 4.9 above, the model F-value of 52.89 implies the model is significant. Value of “Prob> F” less than 0.0500 indicate model terms are significant. In this case A, B, C, D, AB, BC, A^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

4.6. Effect of Interaction between Process Variables

4.6.1Temperature effects on biodiesel yield

The rate of reaction and bases catalyzed biodiesel production was highly influenced by temperature. Increasing temperature leads to decrease in the viscosity of biodiesel, increase in mass transfer between the solid catalyst and liquid reaction mixture, and increases rate of penetration of the filter mud oil into the pore of the catalyst. Thus, temperature was important parameter for higher reaction rate and higher yield biodiesel.

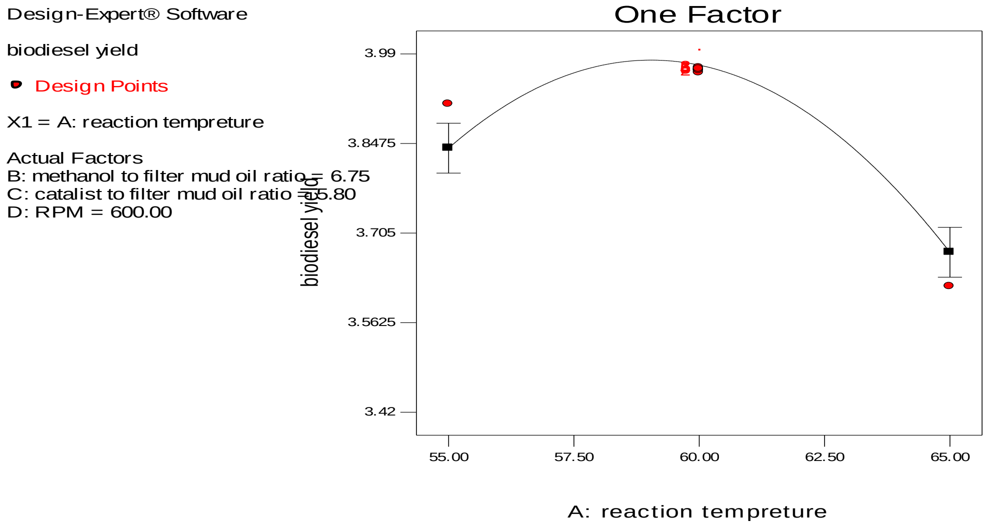


Figure 4.6 Effect of temperature on biodiesel yield at constant methanol to filter mud oil ratio and catalyst to filter mud oil ratio

The effect of temperature at constant methanol to filter mud oil ratio (6.75%) and the catalyst to filter mud oil weight ratio (5.8%) was studied. The figure shown above as the temperature increases from 55 to 60 ^{o}C, very small amount of increase in biodiesel yield seen. However, the yield has started to decline after 60oC. The reduction was significant after 60oC. The reason behind was as the temperature approaches the boiling point of methanol ,methanol start to appear in the vapor phase at the expense of available methanol for the reaction. As the temperature gets beyond the boiling point, significant methanol bubble formation was appeared, which inhibits the mass transfer process.

4.6.2 The effect of methanol to oil ratio on the biodiesel yield

The transesterification process consists of three consecutive reversible reactions. The triglyceride was successively transformed in to diglyceride, Monoglyceride and finally into fatty acid methyl ester (FAME) and glycerin. The ratio of methanol to filter mud oil ratio was one of the important factors that affect the conversion of triglyceride to biodiesel. Stoichiometrically, four mole of methanol are required for each mole of triglyceride, but in practice, a higher molar ratio was required in order to drive the reaction towards completion and produce more biodiesel as products. The results obtained in this study are in agreement with this, as shown the figure (4.7) below, where at higher methanol to filter mud oil ratio, the biodiesel yield was increased. Higher ratio of methanol used could also minimize the contact of accesses triglyceride molecules on the catalyst active sites which could decrease the catalyst activity. Besides that, an increase in ratio of methanol could also lead to increase in the purity of the biodiesel layer which would also be responsible for the observed increase the in biodiesel yield.

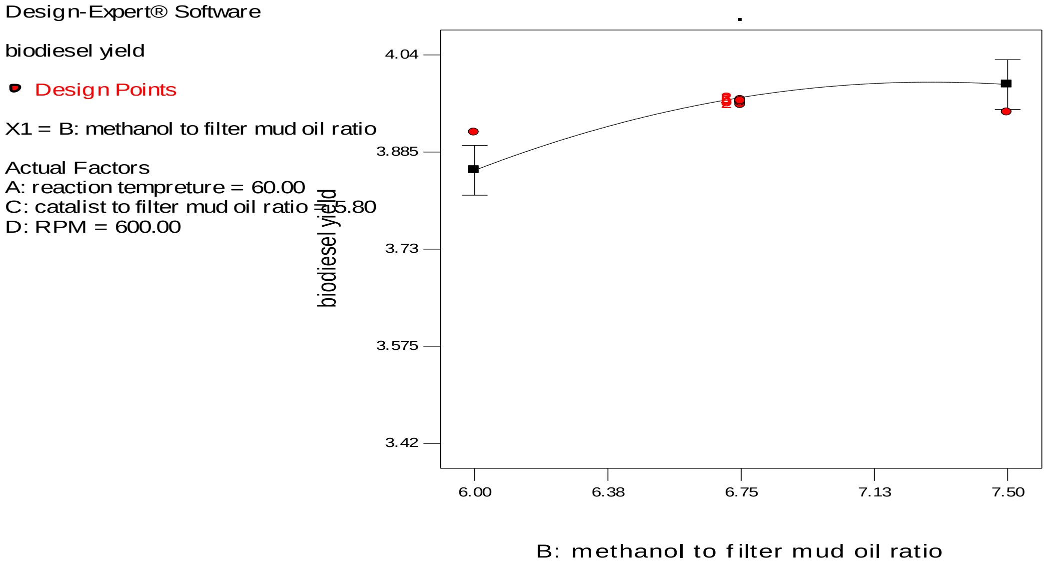


Figure 4.7 Effect of methanol to filter mud oil ratio on the biodiesel yield at constant temperature and catalyst to filter mud oil ratio

From the above figure, effects of methanol on the FAME yield was studied at constant temperature and catalyst to filter mud oil weight ratio 60oC and 5.8, respectively as shown the figure above. This was indicating that increasing of methanol to filter mud oil ratio from 6 to 7.5, increasing FAME yield from 3.36 to 3.97g. However, further increase doesn’t have significant impact on the yield. Methanol to filter mud oil of 6.75 results 3.97g FAME yield. In addition, most probably at higher amount of methanol, the reverse reaction which was recombination of glycerol and Ester may had started to takes place, this in turn can leads to formation of di and Monoglyceride, which ends up with incomplete conversion.

4.6.3 Effects of catalyst to filter mud oil weight on the biodiesel yield

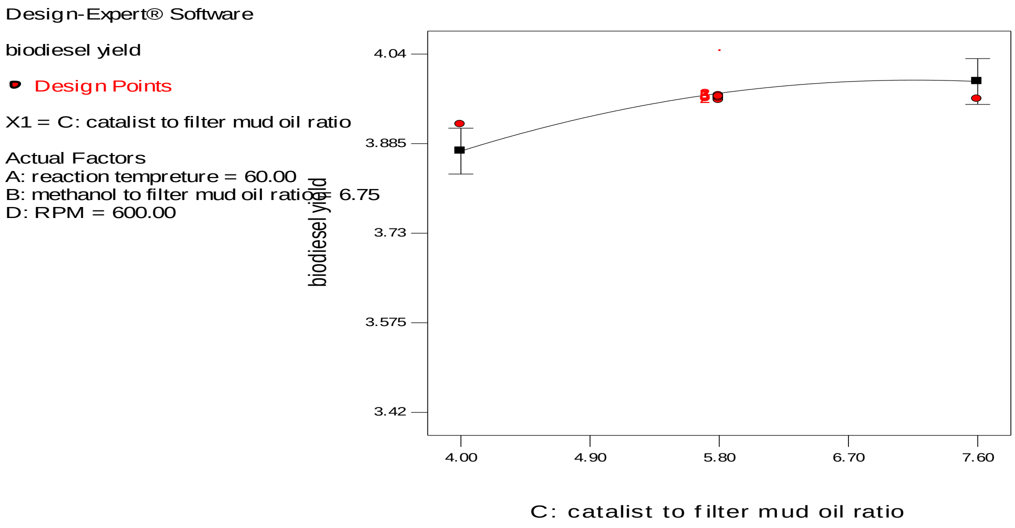


Figure 4.8 Biodiesel yield verses catalyst to filter mud oil weight

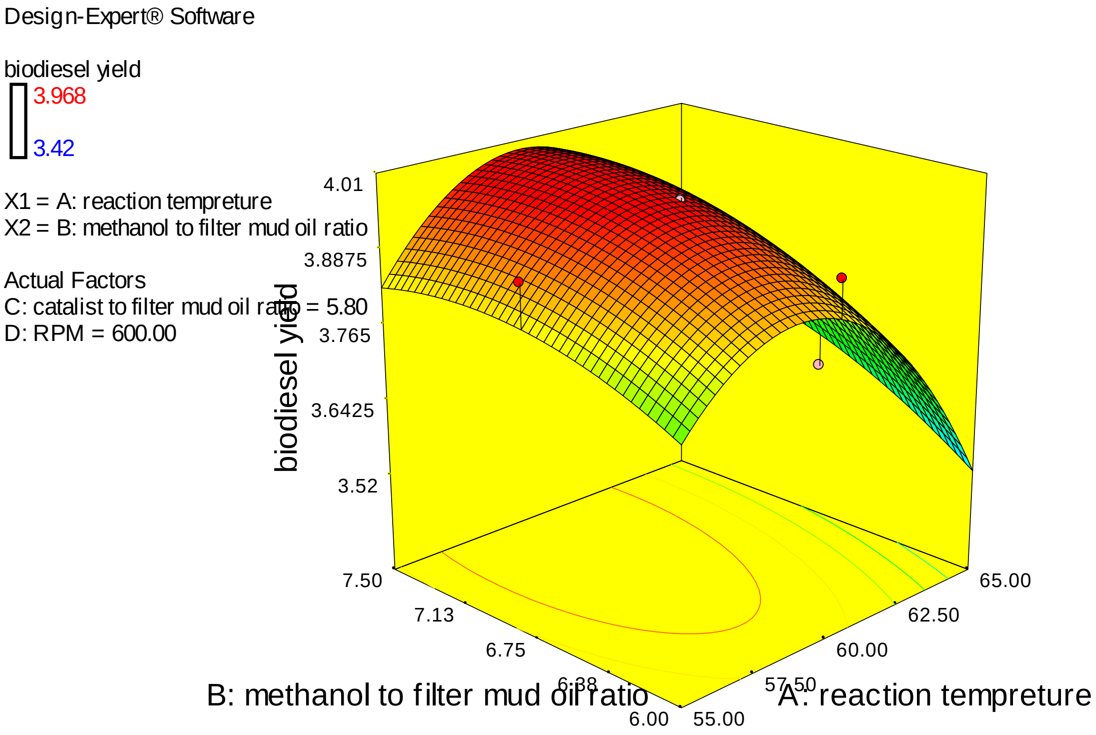
The amount of catalyst was important process variables for the production of biodiesel. In this experiment, catalyst to filter mud oil weight ratio was varied from 4 to 7.6 at constant temperature and methanol to filter mud oil ratio. The addition of more sodium hydroxide catalyst compensated for higher acidity, but the resulting soaps caused an increase in viscosity or formation of gels and interfered with separation of glycerol and contribute to emulsion formation during the water wash. When the active site of the solid catalyst was increased; accelerating transesterification reaction and increasing biodiesel yield. The Figure shows that increasing of the catalyst amount has significant positive effect on biodiesel yield. It was observed that when the catalyst does is low, incomplete transesterification was occurred. However, as the amount increases, more triglyceride was changed to ester. The reason behind was increasing of catalyst provides more active sites for the reaction of available triglyceride and methanol. In addition, the amount of available catalytic active surface was one important parameter to shift the reaction equilibrium forward in addition to the amount of methanol in the reaction mixture.

4.7 Interaction effect of process variables on biodiesel yield

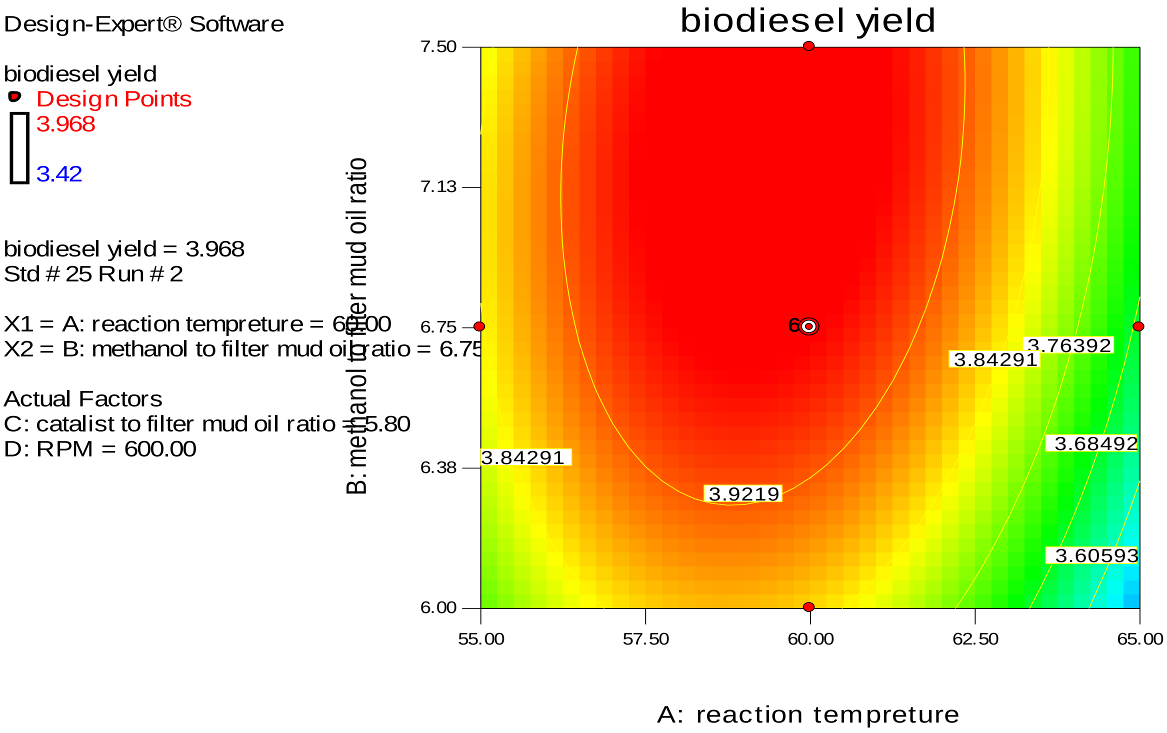
The process variables were found to have significant interaction effects. The interaction effect of reaction temperature, methanol to filter mud oil ratio, and the catalyst to filter mud oil ratio on the biodiesel yield was studied. From the design expert 7 generated data, 3-D surface, response surface and their contour are plotted.

4.7.1The interaction effect of temperature and methanol to filter mud oil ratio on the biodiesel yield

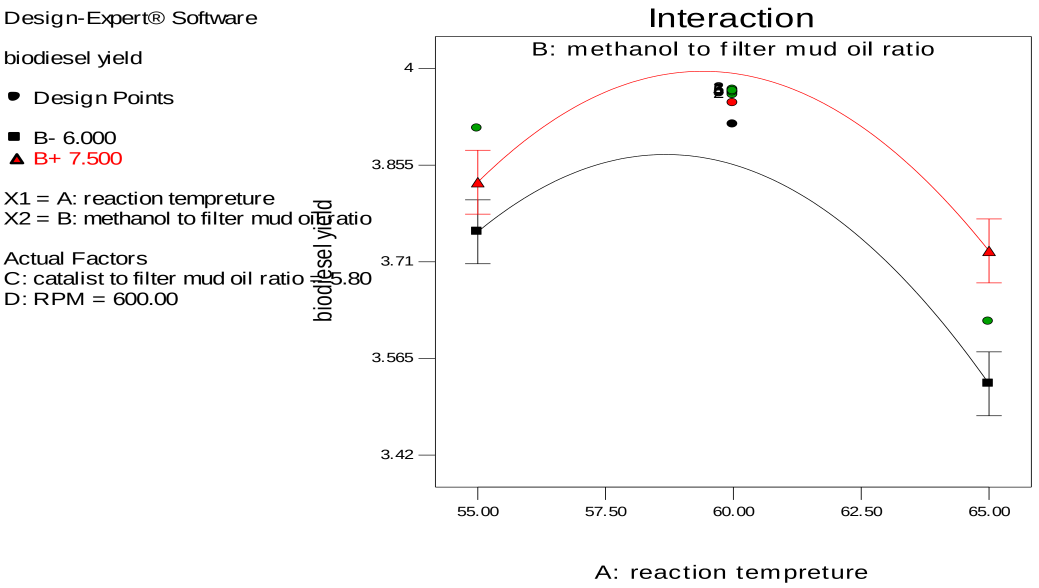
Interaction effect of temperature and methanol to filter mud oil ratio was studied by making catalyst to filter mud oil weight (5.8%) and RPM (600rad) constant respectively. From the figure below, it was observed that the increase of temperature and methanol to filter mud oil ratio together has increase the yield of biodiesel; and by keeping one at the higher and increasing the other, provide smaller improvement on the biodiesel yield.



a) 3D-response surface



b) Contour



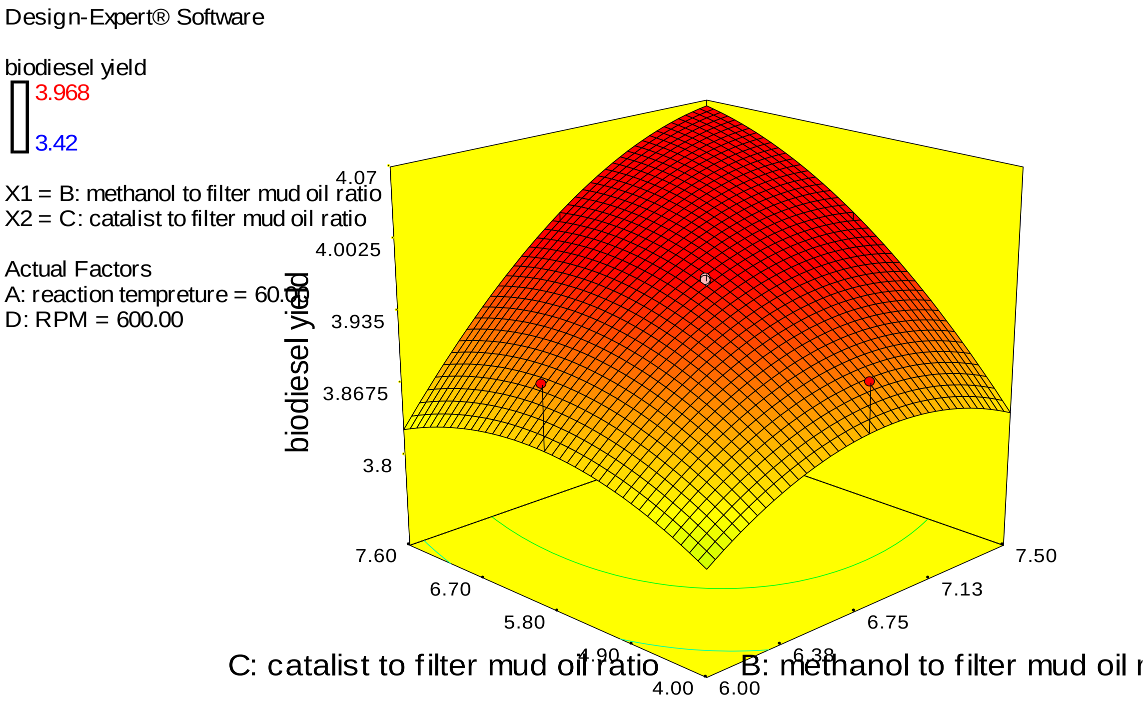
C) Interaction plotting

Figure 4.9: Interaction effect of temperature and methanol to filter mud oil ratio on the biodiesel yield (a) In 3-Dsurface (b) Contour surface (c) Interaction surface

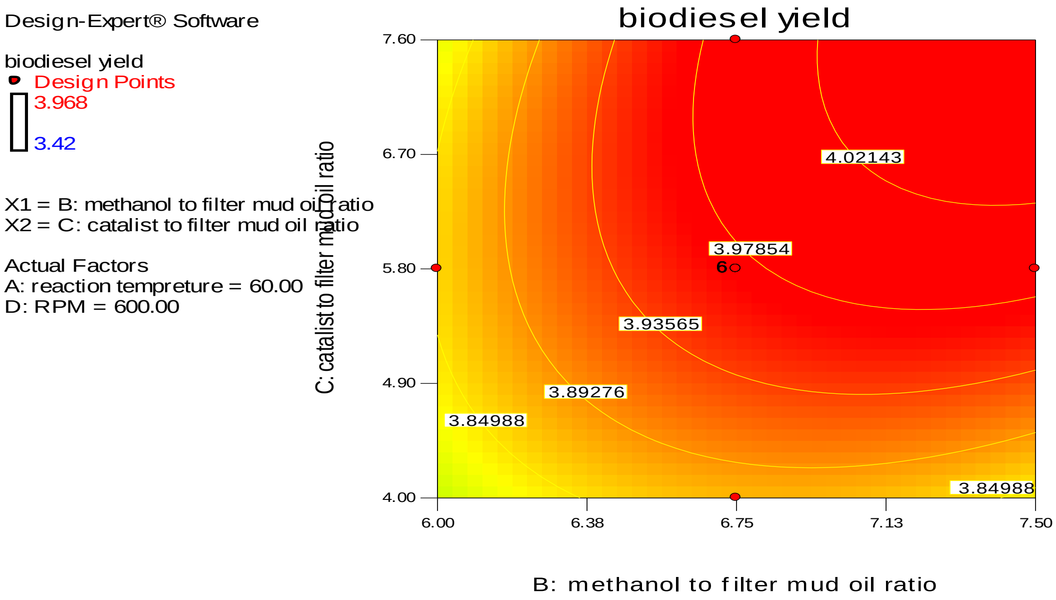
The main effect study shows that the reaction temperature and methanol to filter mud oil had positive effect on the biodiesel yield. This observation was clearly shown on interaction effect plot of the figure (4.9) above, which was proportional addition of reaction temperature and methanol to filter mud oil ratio resulted higher biodiesel yield. As it was shown on figure 4.9 above, increasing of methanol to filter mud oil ratio at any temperature level provide relatively better yield except above methanol to filter mud oil molar ratio of 6.75, which starts to lie down slightly. In the other way round, increasing temperature up to 60^{o}C, at any level of methanol to filter mud oil ratio has resulted insignificant increment in biodiesel yield. Thereafter, temperature has shown negative effect on the yield. This negative effect of temperature was exaggerated at lower methanol amount. Temperature has two opposing effect on the reaction. As the temperature increase, it would increase rate of reaction and reduce mass transfer resistance, which affects the yield positively which showed on the figure 4.9 above up to 60^{o}C. But, at higher temperature (near and beyond boiling point of methanol to filter mud oil ratio), it reduces the availability of methanol to filter mud oil ratio in the reaction mixture and mass transfer process, which has negative effect on the yield.

4.7.2 Interaction effect of methanol to filter mud oil ratio and catalyst to filter mud oil weight ratio on biodiesel yield

The interaction effect of methanol to filter mud oil ratio and catalyst to filter mud oil ratio was studied by holding temperature constant (60^{o}C). From the figure below it was observed that increasing of catalyst to filter mud oil ratio and methanol to filter mud oil ratio together, has increased the yield of biodiesel; and keeping one at higher and increasing the other has also generated and identical effect on the biodiesel yield. When performing one at the lower and increasing the other, provide smaller improvement in the biodiesel yield. The catalyst to filter mud oil ratio and methanol to filter mud oil ratio has the positive effect on the biodiesel yield that shown the figure below. This observation was clearly shown on the interaction effect plot of figure below, which is proportional. The addition of catalyst to filter mud oil and methanol to filter mud oil resulted higher yield. However, the FAME yield was reduced when the addition was disproportional. Because the excess methanol leads to dilution of the catalyst and excess catalyst leads the formation of soap.



a) 3D-response surface

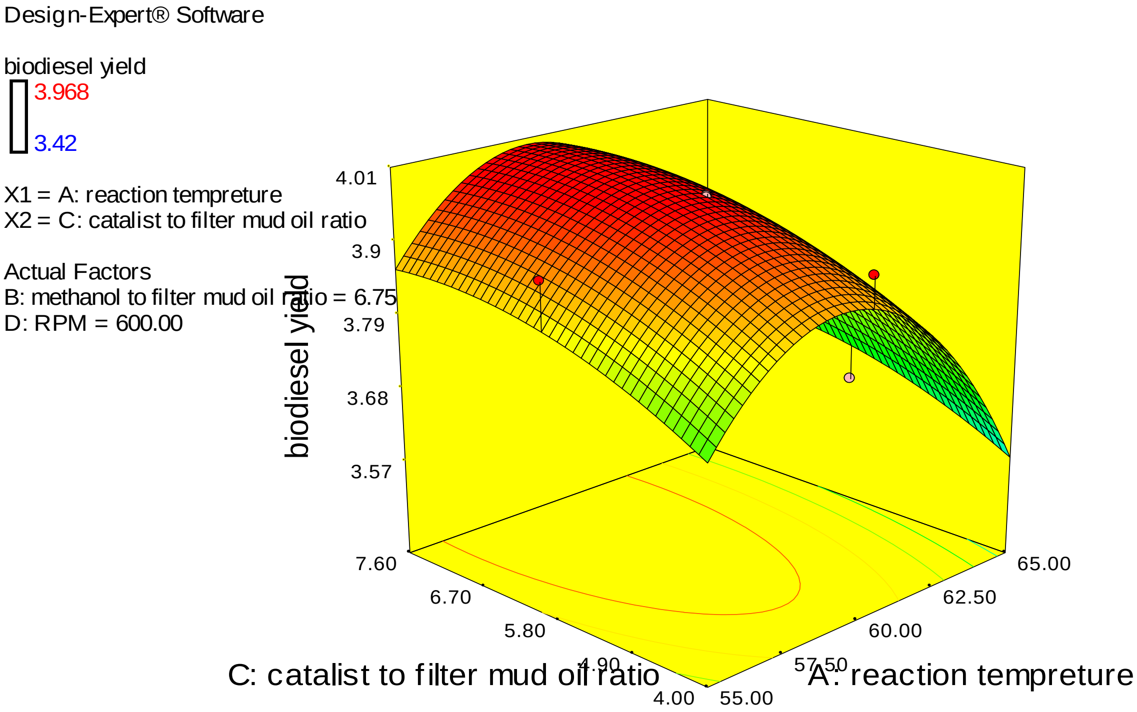


(b)Contour

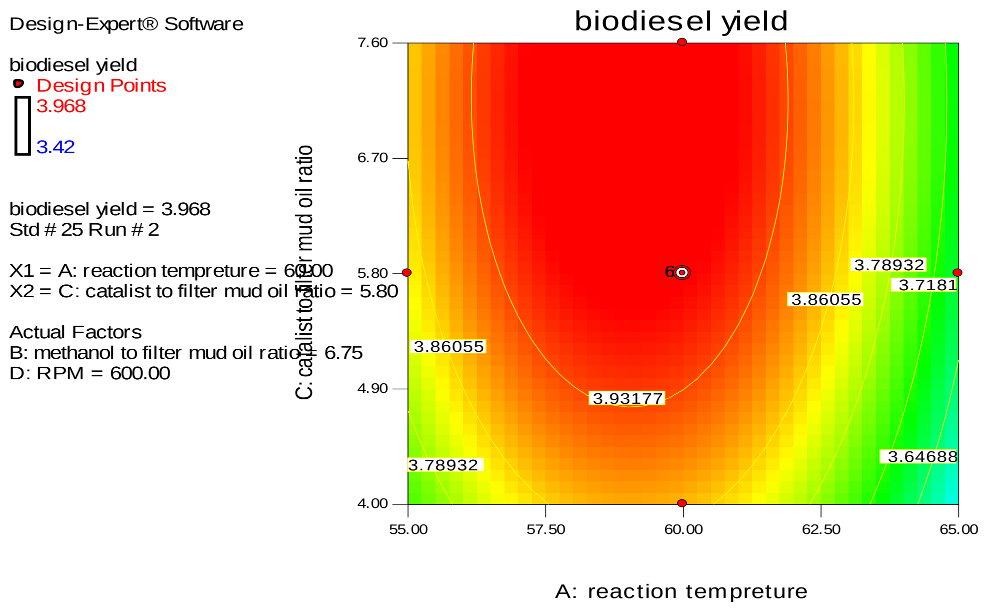
Figure 4.10 Interaction effect of catalyst to filter mud oil ratio and methanol to filter mud oil ratio at 60oC (a) 3-D surface (b) Contour surface

4.7.3 Interaction effect of temperature and catalyst to filter mud weight ratio on the biodiesel yield

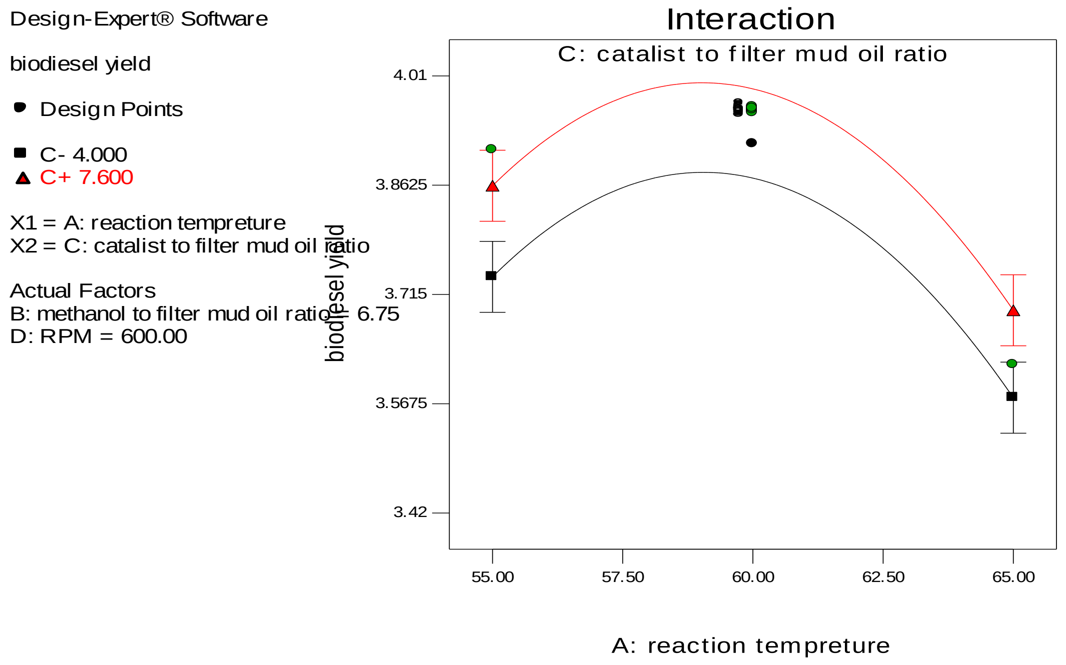
The interaction effect of reaction temperature and catalyst to filter mud oil ratio was studied by making methanol to filter mud oil ratio constant at 6.75%. From the figure shown below, increasing temperature at higher catalyst loading that was beyond 5.8% has negative effect on the yield, this effect was negligible at lower catalyst to oil weight ratio. The maximum biodiesel yield was observed at higher catalyst to filter mud oil ratio. The increasing of reaction temperature and catalyst to filter mud oil ratio the similar time leads to lower amount of methanol in the reaction mixture.



a) In 3-D surface response method



b) In contour surface



c) In interaction surface

Figure 4.11 Interaction effects of reaction temperature and catalyst to filter mud oil weight ratio (a) In 3- D surface (b) In contour surface (c) In interaction surface

4.7.4 Model adequacy checking

The effectiveness of the model in approximating to the true value was measured using regression coefficient (R2). Always its value was [0 1], however, a value close to 1 indicates well fitted model, otherwise indicates failure of approximation. In this case, R2 0.9077 was obtained, which is close to 1 and the value of Adj-R2 was0.9616 that is in good agreement with R2.

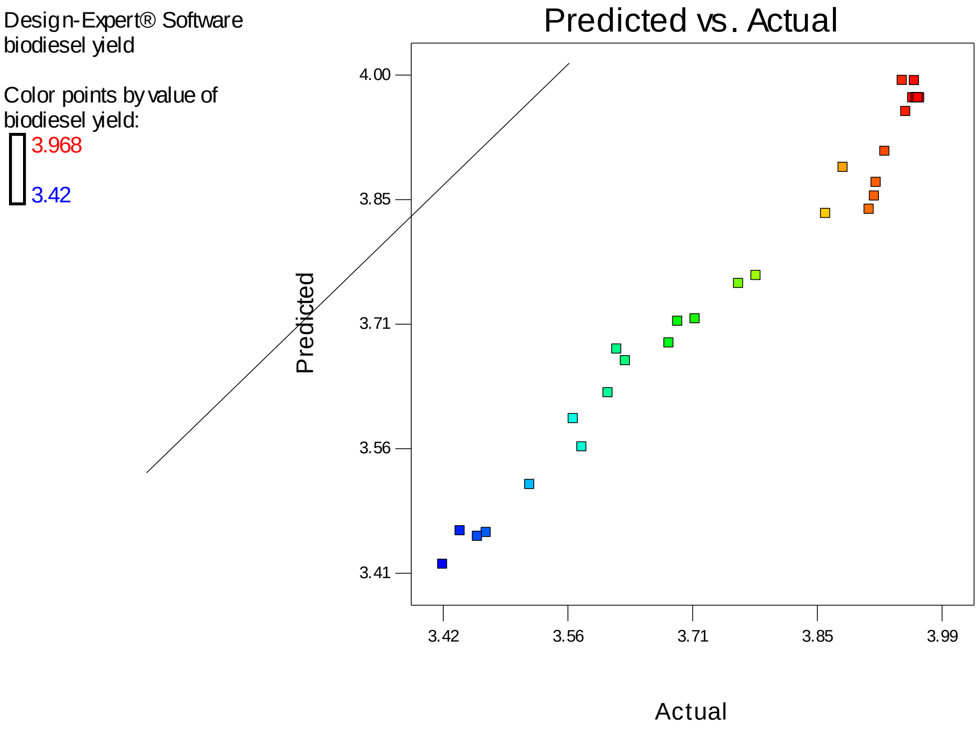
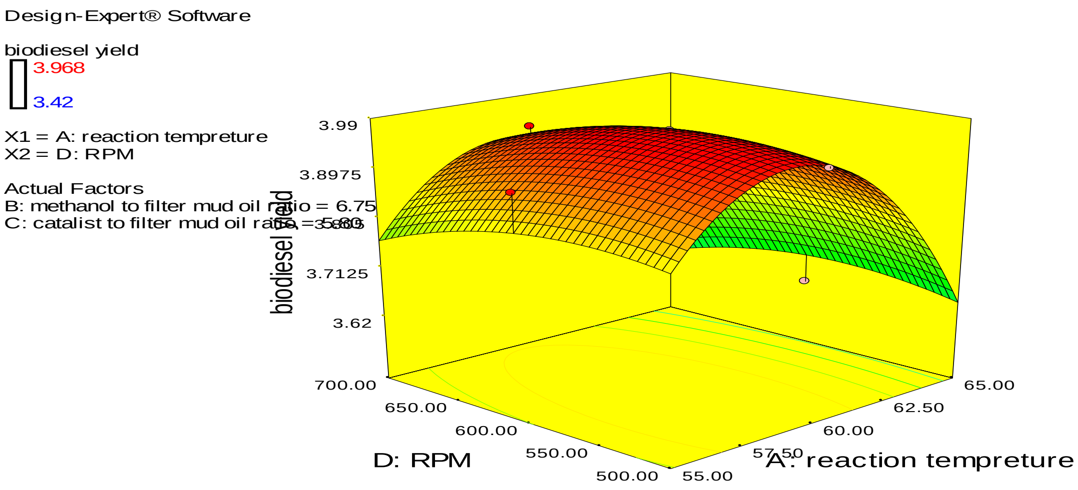


Figure 4.12 Predicted verses actual value of biodiesel yield

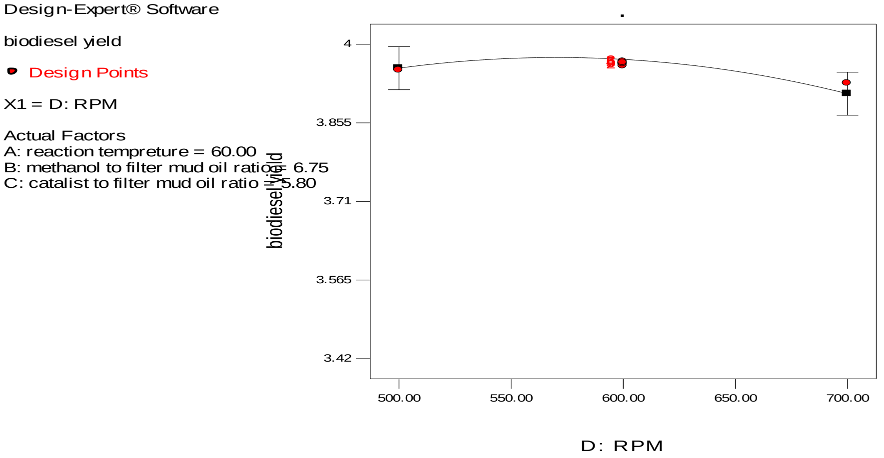
From the figure above 4.12 indicate that the plot of predicted verses actual value of biodiesel yield shown as a slope line. The graph of predicted verses actual value of biodiesel show that all the points are close to the line; it show that the validity of the reliability of the model. As shown the table 4.9 above the central composite design has generated the model F- value of 52.89 and “Prob> less than 0.0500 which indicates that the model term are significant. In this case, main effect of Tr(Reaction temperature),M(methanol to filter mud oil ratio),C(catalyst to filter mud oil weight ratio) ,interaction effect of temperature with methanol to filter mud oil ratio, temperature with catalyst to filter mud oil weight ratio, methanol to filter mud oil ratio with catalyst to filter mud oil ratio and the quadratic effect of T2(temperature),M2(methanol to filter mud oil ratio) are significant model terms. Value greater than 0.1000 are indicating the model terms are not significant.

4.7.5 Interaction effect of mixing rate in transesterification process

The effect of rate of mixing was studied in conducting experiments as shown above table 4.8, varying the rate of mixing between 500 and 700rpm. In this time the catalyst used varying between 0.25 and 0.375 g of NaOH with a reaction time was 1hr. the minimum and the maximum of biodiesel yield was 3.68 and 3.968% respectively.



a) In 3-Dsurface



b) One factor

Figure 4.13 Effect of rpm in the biodiesel yield a) 3- D response surface b) one factor

Mixing was very important in the transesterification reaction; filter mud oil is immiscible with sodium hydroxide – methanol solution. When the filter mud oil and sodium hydroxide- methanol solution are well mixed and the reaction is started, stirring is very important. As shown the above figure, when the stirring rate was 600rpm we would got the highest biodiesel yield that is 3.968 and at a temperature of 60Oc with the methanol to filter mud oil ratio of 6.75 and a catalyst to filter mud oil ratio of 5.8%. So no reaction was observed without mixing, when NaOH-MeOH was added to the melted filter mud oil in the reactor, in this time the reaction time was the controlling system in the determination of the yield of biodiesel.

4.8 Characterization of biodiesel

The biodiesel obtained through transesterification process was characterized to know the fuel properties. The characterization of the biodiesel that produced from the filter mud oil were conducted from experimental analysis. The quality of biodiesel was very important for the performance and emission characteristics of a diesel engine. The characterization was performed for the five properties namely saponification value, acid value, flash point and kinematic viscosity. These properties were chosen for these main reasons. One because they are the defining properties of biodiesel and the other is because of the limitation of resource to perform other tests.

4.8.1 Acid value of biodiesel

The titration method was used to determine the acid value of biodiesel. The experimental procedures were the same to those used in the filter mud oil acid value in the equation (3.6). Therefore, the acid value of biodiesel for each experiment is given the table below.

The Acid value was calculated as:

Acid Value (A.V) =.$\frac{V*C*40}{M}$

Where

V = Titration volume of sodium hydroxide (ml) = 2.675ml

C=Concentration of sodium hydroxide = 0.1M

Molecular weight of sodium hydroxide = 40gram/ mol*L

M= sample weight of biodiesel = 2gram

Table 4.10Experimental titration volume of Acid value

Run no.	Titration volume(ml)	Color change
1	3.0	Gray to pink
2	2.8	Gray to pink
3	2.5	Gray to pink
4	2.4	Gray to pink
Average titration volume(ml)	2.675	Gray to pink

From this result, the acid value of the biodiesel determined below:

$$\text{A.V} = \frac{VT*Mw*C}{Ms}$$

$$= \frac{2.675*40*0.1}{2}$$

$$= 0.00535\text{mgNaOH/g}$$

By taking the average titration volume, the acid value of biodiesel is 0.00535(mgNaOH/g). The acid is used to determine the amount of free fatty acid content in the biodiesel. The lower acid value indicates that the quantity of free fatty acid in the biodiesel is lower[50].During this result the color of change to gray to pink as shown the figure 3.5 above.

4.8.2 Saponification value of biodiesel

The saponification value of biodiesel was determined by a titration procedure. The method of titration was the same as for filter mud oil saponification determination in equation (3.5).The expression for saponification value (S.V) is given by the following equation

$$\text{Saponificationvalue(S.V)} = \frac{40*\text{N}*}{\text{Ms}}(\text{Vo} - \text{V1})$$

Where

V_0 = the black level titration volume = 28ml

N = Actual normality of the HCl used

Ms = mass of biodiesel sample constant = 2g

Table4.11Experimental titration of biodiesel saponification value

Molecular mass of NaOH	Actual normality of the HCl(mol/l)	(V1)Tv(ml)	(Vo)BLTV(ml)	Saponification value (mgNaOH/g)
40	0.5	16	28	120
40	0.5	16.5	28	115
40	0.5	17	28	110
40	0.5	15.6	28	124
40	0.5	16.2	28	118
40	0.5	18.3	28	97
40	0.5	18	28	100

The saponification value shows the amount of biodiesel that change to soap by applying NaOH catalyst in the high temperature in the presence of water. The lower saponification value of the result is higher in quality of the product. So from the above table the saponification value of the biodiesel was between 97mgNaOH/g to 124mgNaOH/g.

4.7.3 Specific gravity of the biodiesel

For the determination of the specific gravity of the biodiesel we follow the same procedure to that of the filter mud oil specific gravity measuring technique. After the sample was filled into graduate cylinder at 50ml and its temperature was measured and recorded; hydrometer was used to measure the specific gravity of the oil at 20 ^{o}C specified. From this hydrometer measurement the specific gravity of the biodiesel reads 0.8802. Therefore we compare to ASTMD6751 for biodiesel is acceptable.

4.8.4 Determination of the density of biodiesel

The specific gravity of the biodiesel produced from the filter mud oil was measured by hydrometer to be 0.8802 and after multiplying the specific gravity of the oil with the water density, and then gained the density of the filter biodiesel. Therefore the density of the biodiesel was determined by the correlation of the specific gravity of the biodiesel and the water density as follow:

Specific gravity of biodiesel = density of biodiesel/water density

Density of biodiesel (kg/m^3) = $0.8802*1000kg/m^3$

$= 880.2kg/m^3$

From this result the density of the biodiesel was $880.2kg/m^3$, which are between the literature density (ASTM D6751 for biodiesel 870–890 kg/m3). Therefore the density of the biodiesel was acceptable.

4.8.5 Dynamic viscosity measurement

As shown the figure 3.4 above the dynamic viscosity of biodiesel was measured by taking the average time taken to reach the ball to the end point of biodiesel filled viscometer. 45m1 of filter mud biodiesel was poured into a test tube and preparing stop watch to measure the time to reach the ball from the top of the a viscometer to end of the viscometer ,this was used to measure the viscosity at a temperature of 35°C,

Table 4.12Experimental data during dynamic viscosity measurement

Time taken the ball reach to the bottom end	Time(s)
T_1	6
T_2	5
T_3	4
Average time taken(s)	5second

Parameters of dynamic viscosity measurement

d_b = density of biodiesel = 880.2kg/m^3 = 0.8802g/ml

V_d = volume displaced during measuring =3.42ml

M_b = mass of the ball = 5gram

K = ball constant = 6.799mpa/(cm^3/gm)

V= kinematic viscosity

η = dynamic viscosity

F = multiplication factor at viscosity measurement at viscometer at 70^0 inclination 0.952

The density of the ball was = $d_b = \frac{mb}{vd}$ = 5g/3.42ml = 1.4619g/ml

The dynamic viscosity (η) = $t_{av*}(d_b – d_b)*k_b*F$

= 5*(1.4619-0.8802)*6.799mpa/(cm^3/gm)*0.952

= 18.825mpa

18.825mpa = 18.825*10^{-3}kg/m s

Justifications: From this result the dynamic viscosity of biodiesel was less than that of filter mud oil, because the density of biodiesel was lower than that of filter mud oil.

4.8.6 Kinematic viscosity of biodiesel

The kinematic viscosity of biodiesel was determined after the determination of the dynamic viscosity of the filter mud oil. The viscosity was a very important property related to the biodiesel utilization in direct injection diesel engines. The high value of viscosity gives rise to poor fuel atomization, incomplete combustion, and deposition in the injectors. Therefore, the biodiesel viscosity must be low. The kinematic viscosity of the biodiesel was determined by the following correlation,

V = kinematic viscosity

$\eta =$ dynamic viscosity of biodiesel

$V = \frac{\eta}{\rho o}$

V = 18.825*10^{-3}kg/m s/(density of biodiesel)

=18.825*10^{-}3(kg/m s)/ (880.2kg/m^3)

= $2.1387*10^{-5}m^2/s$

= $21.38718mm^2/s$

Justification: The kinematic viscosity of the biodiesel was less than the kinematic viscosity of the filter mud oil because the biodiesel was less viscose than the filter mud oil. The kinematic viscosity was decrease when the transesterification temperature was increase. Therefore, the best temperature for the production of biodiesel was 60oC.

4.8.7 Iodine value (I.V) of biodiesel

Iodine value indicates degree of unsaturation of the biodiesel components. So the iodine value is a measure of the total unsaturated bond within the FAME product of the filter mud oil. Therefore iodine absorption occurs at the double bonds in the filter mud biodiesel sample and the greater potential to polymerize in engine and less stability. The values of iodine number minimize a small extent in the Trans esterification process. The experimental results of iodine number of biodiesel shown in the table4.14 below. The iodine values of the biodiesel determined experimentally by titration described in equation (3.7) above.

Where

12.69 = factor proceeding from the reason between the number of transferred electrons and the molar mass of iodine values.

Ms = mass of biodiesel sample = 2gram

C = concentration of sodium thiosulfate used = 0.1mol/liter

Iodine value (I.V) = $\frac{12.69*C*(V1-V2)}{Ms}$

Table 4.13 Experimental titration of biodiesel iodine number

Factor proceeding	Mass of sample of biodiesel	Concentration of sodium thiosulfate (c)	Volume of sodium thiosulfate used for blank(V1)ml	Volume of sodium thiosulfate used for determination	I.V(gI2/100g) of the filter mud oil during experimental titration
12.69	2	0.1	144	11	84.388

12.69	2	0.1	145	11.5	84.71
12.69	2	0.1	139	12.5	80.26
12.69	2	0.1	141	12	81.85
12.69	2	0.1	142.5	13.5	81.86
12.69	2	0.1	140.5	12.5	81.216
12.69	2	0.1	140	14	79.96

The iodine number it specifies the amount of iodine in g that are consumed by 100g of the biodiesel sample under the given conditions. The determination of the iodine number by titration with a solution of sodium thiosulfate was described by the [51]. From this experimental analysis the iodine number of the biodiesel was the range between “79.96 to 84.388(gI2/100g)”, so the maximum amount of iodine number was used to determine the higher heating value of the biodiesel.

4.8.8 Higher heating value of the biodiesel (HHV)

The heating value of biodiesel determined by using the same procedure of the filter mud oil in the above eq(3.8). The determination of the heating value (calorific value) of biodiesel was by using the empirical formula suggested by [48].Higher heating value (the energy content per unit quantity) of fatty acid methyl ester was estimated from their saponification value and iodine value using the following correlation:

HHV (energy content per unit quantity) = 49.43-[0.041(S.V) +0.015(I.V)]

= 49.43-[0.041(97) +0.015(84.71)]

=44.182MJ/kg

Therefore the biodiesel that produced from the filter mud oil was the higher heating value.

4.8.9 Biodiesel Cetane number

The Cetane number was another important property of fuel; this was a measure of the combustion quality of a diesel during compression ignition. The determination of Cetane number was used for knowing the ignition delay after injection of the fuel, of biodiesel. The Cetane number was determined with the same procedure to that of the Cetane number of filter mud oil. From the equation (3.9) above determine the Cetane number of the biodiesel by correlation of the saponification value and iodine value suggested by [49] below.

C.N = 46.3+ (5458/S.V)-0.225(I.V)

= 46.3+ (5458/97)-0.225(95.175)

= 81.15

From this result, the Cetane number of biodiesel was high; high Cetane numbers also lead to incomplete combustion and smoke if the fuel ignites too soon by not allowing enough time for the fuel to mix with air for complete combustion.

4.8.10 Measurement of flash point of biodiesel

The flash point of the biodiesel was determined using the empirical formula by [47] and the flash points of biodiesels were determined according to the standard procedure of the flash point measurement of flash point of biodiesel, i.e.ASTMD93. The equations between FP and HHV of biodiesel had shown Eq (3.10) above the same procedure to filter mud oil. The flash point of the biodiesel calculated from the equation below.

HHV = 0.021FP+32.12

44.182MJ/kg = 0.021FP+32.12

FP = [(44.182-32.12)/0.021]

= 574.38oC

The flash point of the biodiesel was 574.8oC, which was fitted to the ASTMD93. The high value of the flash point because do to the maximum amount of the heating value. Therefore, do to this result of higher plash point of biodiesel; it was too safe to storage of biodiesel compare to petro diesel.

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Filter mud was shown to be a potential and promising feedstock for biodiesel production based on its filter mud oil content and biodiesel yield. Biodiesel was produced using methanol as a solvent and sodium hydroxide pellet as catalyst with a reaction time of 2, 4, 6, and 8 hours and the rate of mixing of 500, 600, and 700rpm at atmospheric pressure. It is concluded that the extraction time and the solvent type are the basic thing to get the appropriate amount of the filter mud oil, therefor in this thesis work the best extraction time and the best solvent were 6 hours and n-hexane solvents respectively. In this work, the effect of molar ratio of methyl alcohol to filter mud oil, catalyst to filter mud oil weight ratio, reaction temperature and the rate of mixing were assessed. In order to know the optimum point of experimental analysis we would use design expert 7.0soft ware. By using this design expert 7.0 software three levels; three factors central composite design with full type was used. The biodiesel yield increase when the catalyst to filter mud oil, reaction temperature, the mixing rate, and the methanol to filter mud oil increased until the optimum point reach. The optimum point that produced biodiesel was a methanol to filter mud oil ratio, catalyst to filter mud oil weight ratio, the mixing rate and a reaction temperature are 6.75, 5.8,600 and 60^{o}C respectively. From this optimum point, the biodiesel yield was 3.968%. From the variables studied, the interaction between Methanol to filter mud oil and catalyst to filter mud oil ratio had more influence on the biodiesel yield, which conclude that further addition of these parameters during transesterification reaction results in reduction of biodiesel yield due to the formation of emulsion which brings in difficulty in the separation of biodiesel from glycerol layers. Further mole characterization of both the Physico-chemical properties of the filter mud oil and biodiesel was necessary to ensure the quality of the product produced.

5.2 Recommendation to future work

- Ethiopia has the potential of harvesting about 30 tons of filter mud from sugarcane plant per hector of land, due to this, it is highly recommended to use these resources in producing a biodiesel, this fuel environmentally friendly fuel, to partly replace petro diesel.
- The laboratory equipment must be free of water contact, because water from any direction introduced can reduce biodiesel yield due to the formation of soap.
- For future work it is recommended that to recovery excess methanol by vacuum distillation from Trans esterifies mixture using a lower temperature, and to carry out the economics feasibility analysis of the production cost.
- This biodiesel production studied was in batch system; for future work production should be conducted in continuous process route.
- It is also recommended for future work to measure the refractive index of both the filter mud oil and that of biodiesel.
- The Physico chemical property of glycerol was not determined, glycerol has relevance in cosmetics and soap industries, and the property of glycerol should be analyzed and purified for further applications.
- The other future work for students or researchers is use of ethanol from wonji sugar factories molasses as a solvent for the production of biodiesel in those factories.

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APENDEX

Table (A) ANOVA for response surface Quadratic model

Source	Sum square	Df	Mean square	F value	P value Prob> F	
Model	1.06	14	0.075	52.89	<0.0001	Significant
A-reaction temperature	0.12	1	0.12	86.43	<0.0001	significant
B-methanol to filter mud oil ratio	0.084	1	0.084	59.09	<0.0001	significant
C-catalyst to filter mud oil ratio	0.065	1	0.065	45.74	<0.0001	Significant
D-RPM	9.988E-003	1	9.988E-003	7	0.0184	significant
AB	0.016	1	0.016	10.95	0.0048	significant
AC	2.500E-005	1	2.500E-005	0.018	0.8965	N.S
AD	2.025E-003	1	2.025-003	1.42	0.2521	N.S
BC	0.042	1	0.042	29.45	<0.0001	significant
BD	2.500E-005	1	2.500-005	0.018	0.8965	N.S
CD	1.225E-003	1	1.225E-003	0.86	0.3689	N.S
A^2	0.12	1	0.12	83.80	<0.0001	significant
B^2	5.930E-003	1	5.930E-003	4.16	0.0595	significant
C^2	4.113E-003	1	4.113E-003	2.88	0.1102	N.S
D^2	4.113E-003	1	4.113-003	2.88	0.1102	N.S
Residual	0.021	15	0.021			
Lack of fit	0.021	10	0.021	286.19	<0.0001	Significant

Appendix B

Figure: During biodiesel production

Appendix C

Figure: During purification of filter mud oil

Appendix D

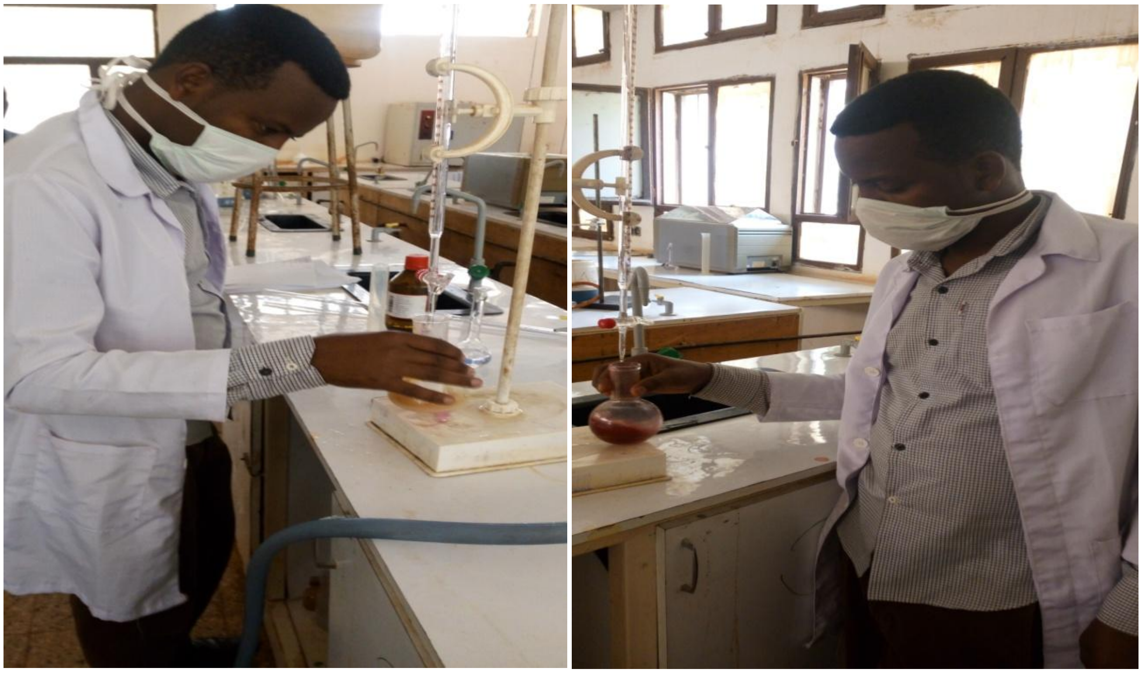

Figure: During acid value determination

Appendix E

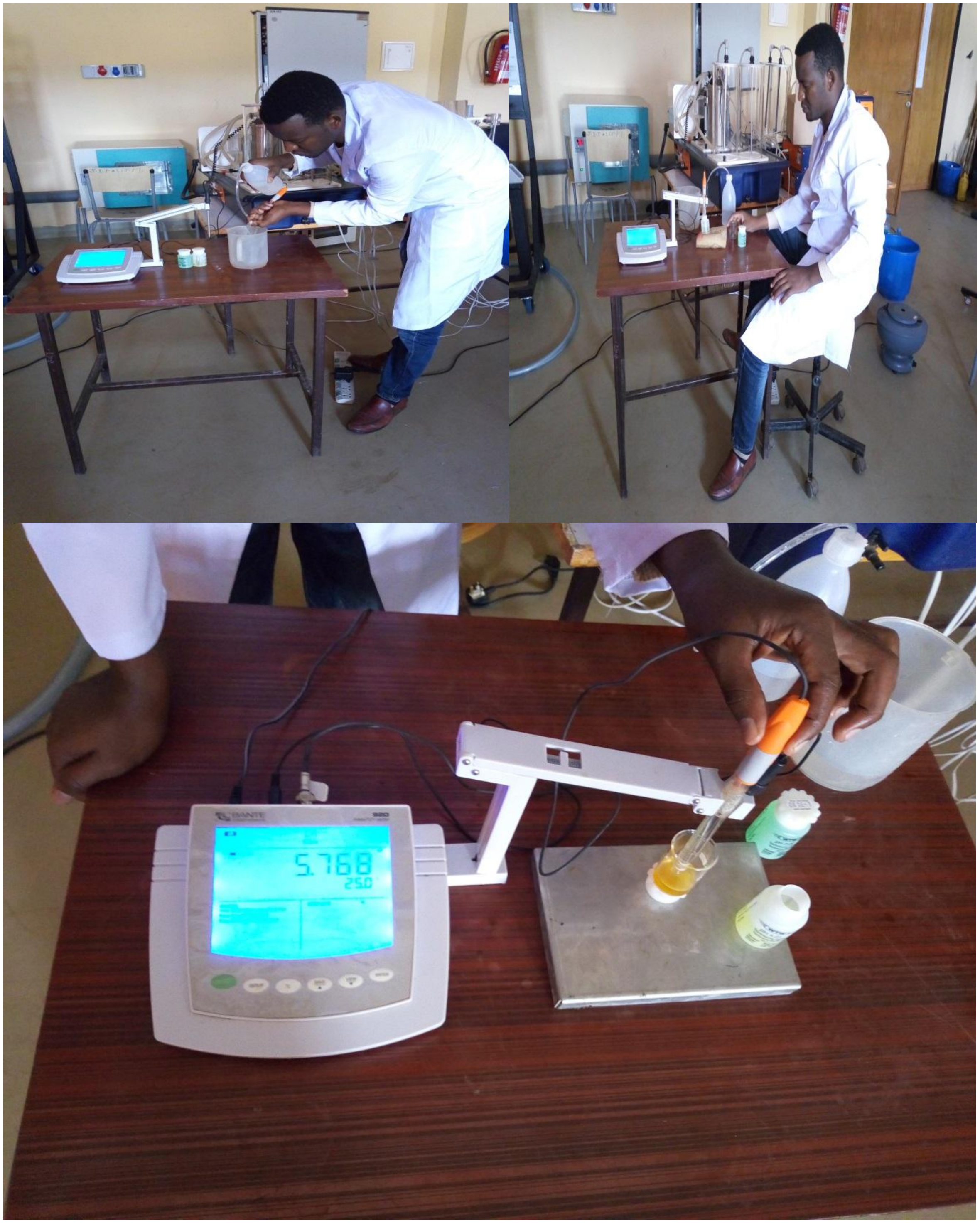

Figure E. PH Measurements of filter mud oil.

Appendix F

Figure F. PH Measurements of Biodiesel measurement.

Appendix G

Figure G. Further separation of Biodiesel, residual and glycerin by using centrifugal separation