ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
ADDIS ABABA INSITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMICAL ENGINEERING

INVESTIGATION OF BIODIESEL PRODUCTION USING HETEROGENEOUS CATALYST

By

Temesgen Mathewos Fitamo

JUNE 2011
ADDIS ABABA, ETHIOPIA

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A thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, Department of Chemical Engineering in partial fulfillment of the requirements for the attainment of the Degree of Masters of Science in Chemical Engineering under Process Engineering Stream.

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Advisor: Dr. Ing Nurelegn Tefera

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ACRONYMS

ASTM	American Society for Testing and Material
AV	Acid Value
CCD	Central Composite Design
CN	Cetane Number
CP	Cloud Point
DG	Diglycerides
EN	European committee for standardization
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FP	Flash Point
GC	Gas Chromatography
GHG	greenhouse gas
HHV	Higher Heating Value
HPLC	High performance liquid chromatograph
IV	Iodine Value
QC	Quality Control
SNNP	Southern nations, nationalities and people of Ethiopia
SV	Saponification Value
SG	Specific Gravity
TG	Triglycerides

ABSTRACT

Biodiesel production is a very hot issue within research, politics and investments worldwide. The problem of finding economically viable and environmentally friendly renewable energy sources is an urgent matter. Not only is the world faced with a finite supply of fossil-fuels, but concern is growing over the possibility of climate change caused by greenhouse gas emissions. Biodiesel, a liquid fuel derived from plant oils or animal fats, represents a renewable energy source that could contribute to the solution of both problems; it can be continually produced as long as we are able to grow plants and it can be made in such a way as to release no net addition of greenhouse gases to the environment. However, technical challenges must be overcome before biodiesel can contribute significantly to the world's energy supply; with current technology biodiesel production is profitable only under special circumstances.

This thesis research seeks to address this problem by studying the production of biodiesel using heterogeneous catalysts. Heterogeneous catalysts can make biodiesel more energy efficient, and therefore less expensive, by eliminating the need for expensive purification processes that separate the catalyst from reaction products typical in the use of homogeneous catalysts. The experimental design and statistical analysis was done by Design-Expert 7.0.0 program. Fatty acid methyl ester was produced via transesterification process using sodium phosphate as a heterogeneous catalyst and purified jatropha curcas oil which is extracted from the jatropha seed bought from dessie. To obtain a high quality biodiesel fuel that comply the specification of standard methods, some important variables such as reaction temperature, molar ratio of methanol to oil and mass weight of catalyst were selected and studied. At the following conditions; 333K of reaction temperature, methanol to jatropha oil ratio of 4 and 5 mass wt% of catalyst, an optimum fatty acid methyl ester yield of 94.98% was obtained, indicating that sodium phosphate has the potential as a heterogeneous catalyst for the production of fatty acid methyl ester from jatropha oil. Moreover, physico-chemical characterization of the fatty acid methyl ester was performed and compared with the standard biodiesel properties.

1. INTRODUCTION

1.1 Background

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats.

Recently, because of increases in crude oil prices, limited resources of fossil oil and environmental concerns, there has been a renewed focus on vegetable oils and animal fats to make biodiesel fuels. Continued and increasing use of petroleum will intensify local air pollution and magnify the global warming problems caused by carbon dioxide emission.

Due to the depletion of the world’s petroleum reserves and the increasing environmental concerns, there is a great demand for alternative sources of petroleum-based fuel, including diesel and gasoline fuels. Biodiesel, a clean renewable fuel, has recently been considered as the best candidate for a diesel fuel substitution because it can be used in any compression ignition engine without the need for modification. [1]

Ethiopia is among the poorest of the world’s least developed countries, with over 45% of the population living below the poverty line. Significant improvements to Ethiopia’s trade balance are needed to stimulate the required economic development. One main issue is that around 65% of Ethiopian export earnings are needed to pay for the import of petroleum products. Ethiopia does not have any petroleum resources and all its petroleum products need to be imported, either through the port of Djibouti or from Sudan. Besides the cost of fuel, long transportation distances add to the costs of getting the fuels to Addis Ababa, this is a large burden on Ethiopia’s trade balance.

The use of petroleum based fuels as sources of energy are increasingly coming under inspection. Petroleum based fuels are non-renewable and as such are unsustainable long run sources of energy. In addition to this, consumption of petroleum based fuels is a major source of air pollution and significant contributor to green house gas emissions. These apparent costs have caused many to look towards as an alternative source of transport fuel energy worldwide.

Coming to our country, so far there is no observable market use of biodiesel product in Ethiopia. But currently there are more than 50 projects in progress from which 14 has started operation in five different regions (Benshangl Gumuz, Amhara, Oromia, SNNP and Gambella).

Biodiesel has a major project underway in a region to the north west of Addis Ababa (Benshangul Gumuz), which will produce biodiesel, form a large scale jatropha plantation of more than 80,000 hectares. This project will produce more than 100 million liters of biodiesel per year, and if total production was converted to biodiesel, it would be equivalent to almost 15% of Ethiopia‘s current diesel consumption. Obviously, this will have a significant positive impact on Ethiopia’s trade balance. Additionally, the inward investment that this project brings will create a large number of jobs in the sectors, the plantation and in the production of oil and biodiesel, all helping to alleviate rural poverty. Global biodiesel industry is projected to grow and touch around 3,900 million gallon by 2014.

Liquid biofuels made from biomass are attracting interest worldwide. Industrial countries see biofuels as a way of reducing GHG emissions from the transport sector and diversifying energy sources. Developing countries see biofuels as a way to stimulate rural development, create jobs, and save foreign exchange. However, both groups view biofuels as a means of increasing energy security. These concerns taken together and highlighted by recent surges in the world oil price have prompted.

Biodiesel is a renewable substitute fuel for petroleum diesel fuel which is made from nontoxic, biodegradable, renewable sources such as refined and used vegetable oils and animal fats. Biodiesel is produced by transesterification in which oil or fat is reacted with a monohydric alcohol in the presence of a catalyst.

The process of transesterification is affected by the mode of reaction, molar ratio of alcohol to oil, type of alcohol, nature and amount of catalysts, reaction time, and temperature. [8]

Various studies have been carried out using different oils as the raw material and different alcohols (methanol, ethanol, butanol), as well as different catalysts, notably homogeneous ones such as sodium hydroxide, potassium hydroxide, sulfuric acid, and supercritical fluids or enzymes such as lipases. Recent research has focused on the application of heterogeneous catalysts to produce biodiesel, because of their environmental and economic advantages. [9]

This thesis research work focuses on investigation of biodiesel production using heterogeneous catalyst.

1.2 Problem Statement

The depletion of world petroleum reserves and increased environmental concerns has stimulated the search for alternative renewable fuels that are capable of fulfilling an increasing energy demand. [1] The problems related with petroleum diesel is fluctuation of oil price ,shifting toward higher value and natural fossil fuel depletion ,instability of world political condition, high demand of energy ,as a whole, over the world.

In recent decades, research concerning and knowledge about the external benefits of renewable raw materials have intensified the efforts for sustainable energy sources. Biodiesel plays a major role in this field because of the world-wide research, development, and exploitation activities of this sustainable energy source.

Catalysts for transesterification can be classified into two kinds: homogeneous and heterogeneous. From the point of view of process, the major problems related with biodiesel production process using homogeneous catalysts such as sodium and potassium hydroxides are apparatus corrosion and catalyst separation. Furthermore, the problems of homogeneous catalyst are sensitivity to free fatty acid & water content of the feedstocks, removal of catalyst, formation of soap with high free fatty acid feedstock, large quantity of effluent water as a result of removal of catalyst, necessities pre-treatment of oil in case FFA content are higher and no scope for regeneration or re-utilization of the catalyst

A heterogeneous catalyst is insoluble and can be easily separated, thus simplifying the production and purification processes. In order to overcome the limitations of homogeneous catalysts, many efforts have focused on the development of heterogeneous catalyst. Solid acid and solid base are the main heterogeneous catalysts for biodiesel preparation.

1.3 Objective of the research

1.3.1 General objective

Investigation of biodiesel production using transesterification reaction with solid or heterogeneous catalyst at laboratory scale and to compare the physical properties with the standard biodiesel properties.

1.3.2 Specific objectives

In the heterogeneously catalyzed transesterification reaction, a number of operating parameters such as temperature, extent of catalyst loading, mode of mixing, alcohol/oil molar ratio and the time of reaction are important in the transesterification reaction.

This thesis research work covers the effect of temperature, effect of alcohol to oil molar ratio and effect of catalyst weight on the yield of biodiesel in its scope. Hence, effects of the following parameters on the yield of biodiesel production: mass ratio of catalyst to oil, molar ratio of methanol to oil, reaction temperature on biodiesel yield were the specific objectives.

The selected process parameters are temperature ranged from 318K to 333K, molar ratio of methanol to oil from 4:1 to 8:1, mass ratio of catalyst to oil from 3% to 5% and rotation speed at optimum biodiesel yield was produced at 600rpm. The reaction time and rotation speed was taken fixed at optimum points at which the biodiesel production becomes maximum. Hence, the rotation speed and reaction time was 600rpm and 3hr respectively to achieve high yield or maximum conversion.

2. LITERATURE 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. [2]

The manufacturing process is based on the transesterification of triglycerides by alcohols to fatty esters, with glycerol as a byproduct. [5] 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 (tallow). [1]

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. [8]

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. [3]

However when thinking about biodiesel production, cost plays an important role and Jatropha curcas bean oil is one of the lowest priced oils, which makes it quite effective to use. It has proven itself as one of the most beneficial of all oils to use however still there are researches to determine other variables that affect the yield oil as well.

Although Jatropha is indigenous to the southeastern Mediterranean Basin, Eastern Africa, and India, today it is widespread throughout tropical regions. In areas with a suitable climate, Jatropha establishes itself easily as an apparently "native" plant.

Jatropha curcas oil has a 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, seed is easier to plant and it costs less due to inedibility of its oil.

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 an azeotrope with water so it is expensive to purify the ethanol during recovery. If the water is not removed it will interfere with the reactions. [21] Methanol recycles easier because it doesn't form an azeotrope. 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 catalyses 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). [7]

Beside the solid acid or solid base catalyst, the other heterogeneous catalysts are enzymatic catalyst.

They have various races of enzymes (rizhomucor miehei, pseudomonas cepacia, caida antarctica) 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 lost 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.

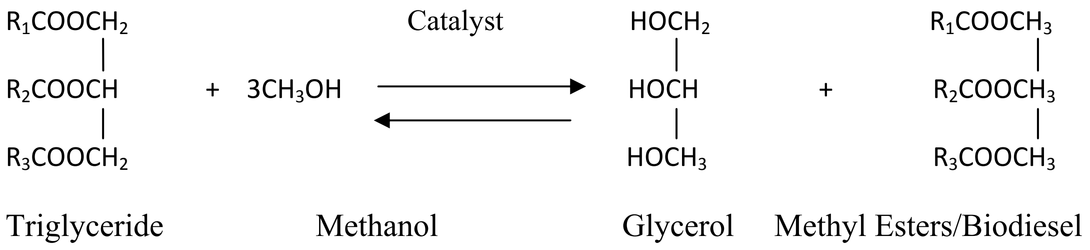
2.3 Chemistry of Biodiesel Production

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.

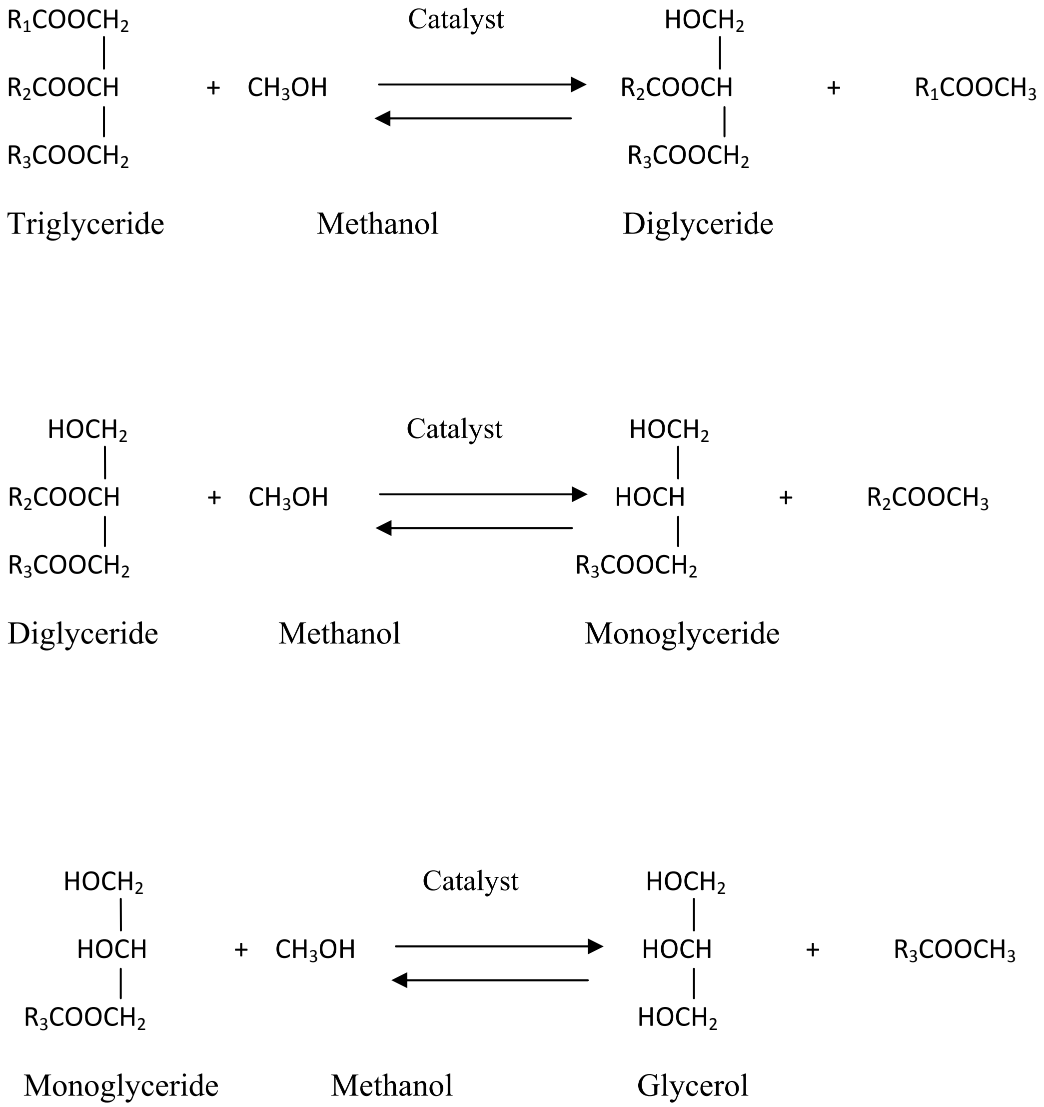
The overall reaction occurs in three stages is controlled by chemical equilibrium, as expressed by the reactions in scheme 1.

a) Overall Reaction: Transesterification



$$\begin{matrix} R_1COOCH_2 \\ | \\ R_2COOCH \\ | \\ R_3COOCH_2 \end{matrix} + 3CH_3OH \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} \begin{matrix} HOCH_2 \\ | \\ HOCH \\ | \\ HOCH_3 \end{matrix} + \begin{matrix} R_1COOCH_3 \\ | \\ R_2COOCH_3 \\ | \\ R_3COOCH_3 \end{matrix}$$

b) Stepwise consecutive and reversible reaction



Scheme 1: Transesterification reactions of glycerides with methanol (a) Overall reaction and (b) stepwise consecutive and reversible reactions, where; R_1, R_2 and R_3 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 transesterification 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 transesterification.

Otherwise, the formation of soaps occurs by reaction with the hydroxide catalyst, as it is given in scheme 2.

$$\underset{\text{FFA}}{R_1\text{-COO-CH}} + \underset{\text{Base}}{\text{NaOH}} \longrightarrow \underset{\text{Soap}}{R_1\text{-COONa}} + \underset{\text{Water}}{H_2O}$$

Scheme 2: Reaction between free fatty acid and base

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

2.4 Biodiesel Production Technologies

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

2.4.1 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.

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.

The transesterification 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. In turn, the economic indices are on the lower side because of lower equipment productivity and higher operation costs, such as manpower and automation.[11]

The replacement of a homogeneous catalyst by a heterogeneous one is highly desirable.

2.4.2 Catalytic Continuous Processes

The Catalytic continuous process technology of biodiesel production is a conceptual scheme of a continuous process working at low pressure that is capable of processing a feedstock with a larger amount of free fatty acids, such as unrefined non-edible vegetable oils, tallow fat and used cooking oil.

For this reason in the first reactor the esterification of free fatty acids with methanol is carried out. Then the transesterification reaction follows in the second reactor. A homogeneous catalyst is currently used, either as alkaline hydroxide or alkaline methoxide.

To ensure high yield in monoester and minimum amounts of mono - /di - /triglycerides minimum two reactors in series with glycerol intermediate separation should be employed. The reaction mixture is then submitted to phase separation in crude ester and glycerol. The separation can take place by decanting or by centrifugation.

The glycerol phase is treated with acid for soap removal and recovery as FFA. Then, the methanol is recovered by evaporation and recycled.

The crude ester follows the route of methanol separation. The material balance loop is closed by the recovery of excess methanol from water solution by distillation. [1]

Using a heterogeneous solid catalyst in the transesterification phase allows a substantial simplification of the process flow. [26] Two reactors are employed with intermediate glycerol separation. Excess methanol is recovered by multistage flash.

Phase separation of ester and glycerol are carried out by coalescence separation or centrifugation. It can be seen that the neutralization and washing steps are absent. Methanol can be recycled as vapor. [1]

2.4.3 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. Since the critical coordinates of methanol are $T_c = 239\ ^oC$ and $P_c = 80$ bar, raising the temperature and pressures at sufficiently high values is necessary. Studies conducted in Japan demonstrated the feasibility of producing biodiesel by the esterification of rapeseed with methanol without a catalyst working around 350 ° C and 200 bars at molar ratio methanol to oil of 42: 1 for reaction times below 4 min.

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 ratio to methanol, at 280 ° C and 12.8 MPa. Similar results have been reported with CO_2 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. [1]

2.4.4 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. [1]

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. [1]

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.

2.4.5 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. [1]

2.5 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. [2] 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. [2] There are different types of transesterification and they are discussed as follows.

2.5.1 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, CH_3ONa, CH_3OK and KOH. [6]

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. [8]

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.

2.5.2 Homogeneous acid-catalyzed transesterification

The liquid acid-catalyzed transesterification process is not much popular as the base-catalyzed process. Homogeneous acid catalyzed reaction is about 4000 times slower than the homogeneous base-catalyzed reaction. However, the performance of the acid catalyst is not strongly affected by the presence of FFAs in the feedstock. In fact, acid catalysts can simultaneously catalyze both esterification and transesterification.

Thus, a great advantage with acid catalysts is that they can directly produce bio-diesel from low-cost lipid feedstocks, generally associated with high FFA concentrations (low cost feedstocks, such as used cooking oil and greases, commonly have FFAs levels of >6%). For acid-catalyzed systems, sulfuric acid, HCl, BF_3, H_3PO4, and organic sulfonic acids, have been used by different researchers. [8]

2.5.3 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 bio-diesel. 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. [8]

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. [8]

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. [20]

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 $70^{O}C$ and the yield observed was 93.5% for 2.5hr reaction period. [27] 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 $70^{O}C$ for 2hr reaction period to obtain 93% yield of fatty acid methyl ester. [22]

The transesterification of sunflower oil was done at 1% catalyst weight and 12:1 molar ratio of methanol at a reaction temperature of 60 ^{O}C .The fatty acid methyl ester yield observed was 92%. [27] Another researcher also performed the transesterification of soybean oil using 8% catalyst weight and 12:1 molar ratio of methanol to oil for at a reaction period of half hour with $65^{O}C$ reaction temperature to obtain 97% yield. [23]

The key benefit solid catalyst is that no polluting by-products are formed, and does not mix with biodiesel with biodiesel product, elimination of several steps of washing /recovery of biodiesel/ catalysts, lower production costs.

The utilization of heterogeneous catalysts has higher life times, since the catalyst utilization time is higher than the homogeneous catalytic processes. This means less catalyst replacements in the reactor. These types of catalysts catalyze a reaction by chemical adsorption (the attraction of reactants to a surface of the catalysts) of the reactants on its surfaces.

The heterogeneous catalysts has not been consumed in the reaction, can be easily separated from products, products do not contain impurities of catalyst, the catalyst can be regenerated and reused, the final separation cost is reduced and environmentally friendly. [10]

2.5.4 Supercritical and subcritical alcohol transesterification

Transesterification of vegetable oil with non-catalytic supercritical methanol provides a new way of producing bio-diesel. Transesterification reaction in supercritical conditions was completed in minutes, while the conventional catalytic transesterification takes several hours.

Under supercritical conditions, the mixture becomes a single homogeneous phase, which will accelerate the reaction because there is no interphase mass transfer to limit the reaction rate.

The transesterification is completed via a methoxide transfer, whereby the fatty acid methyl ester and diglycerides are formed. In a similar way, diglyceride is transesterified to form methyl ester and monoglycerides which is converted further to methyl ester and glycerol in the last step.

The presence of water in the reaction system does not affect the yield of methyl esters under supercritical alcohol transesterification. [8] Synthesis of bio-diesel by supercritical methanol has a drawback with the high cost of apparatus due to the high temperature and pressure, which are not viable in the large scale practice in industry. [14]

So, researches have focused on how to decrease the severity of the reaction conditions. Co-solvents, such as carbon dioxide, hexane, propane and calcium oxide and subcritical alcohol with small amount of catalyst, added into the reaction mixture can decrease the operating temperature, pressure and the amount of alcohol. The supercritical methanol method with co-solvents like hexane and condensed CO_2 can improve the product yield. [8]

2.5.5 Enzymatic transesterification

Enzymatic transesterification using lipase looks attractive and encouraging for reasons of easy product separation, minimal wastewater treatment needs, easy glycerol recovery and the absence of side reactions.

Practical use of lipase in pseudo homogenous reaction systems presents several technical difficulties such as contamination of the product with residual enzymatic activity and economic cost. [12] In order to overcome this problem, the enzyme is usually used in immobilized form so that it can be reused several times to reduce the cost and also to improve the quality of the product. When free enzymes are used in a bio-diesel process, the enzymatic activity can be partially recovered in the glycerol phase. However, the build-up of glycerol limits the possible number of reuses.

Compared to chemical approach enzymatic approach for biodiesel production offers more advantages but cost of lipase is the major issue for the industrialization of lipase-mediated bio-diesel production. [13]Researchers reported that there are two ways to reduce the lipase cost. One is to reduce the production cost of the lipase, which can be realized through new lipase development, fermentation optimization, and downstream processing improvement. Another way is to improve/extend the operational life of the lipase, and this can be achieved through enzyme immobilization, alcoholysis reaction optimization, etc.

2.5.6 Microwave assisted transesterification

The use of microwave heating as a tool for preparative chemistry is continuing to grow. By using microwave irradiation it is often possible to reduce reaction times significantly as well as improve product yields. An alternative energy stimulant, ‘‘microwave irradiation’’ can be used for the production of the alternative energy source, bio-diesel.

Microwave irradiation activates the smallest degree of variance of polar molecules and ions such as alcohol with the continuously changing magnetic field. [15] The changing electrical field, which interacts with the molecular dipoles and charged ion, causes these molecules or ions to have a rapid rotation and heat, is generated due to molecular friction.

The preparation of bio-diesel using microwave offers a fast, easy route to this valuable biofuel with advantages of a short reaction time, a low oil/ methanol ratio, an ease of operation a drastic reduction in the quantity of by-products, and all with reduced energy consumption.

Aside from the great advantages of microwave-assisted reactions, there are also a few drawbacks. Microwave synthesis is not easily scalable from laboratory small-scale synthesis to industrial multi kilogram production.

The most significant limitation of the scale up of this technology is the penetration depth of microwave radiation into the absorbing materials, which is only a few centimeters, depending on their dielectric properties. The safety aspect is another reason for rejecting microwave reactors in industry.

2.5.7 Ultrasound assisted transesterification

Ultrasound has proven to be a very useful tool in enhancing the reaction rates in a variety of reacting systems. It has successfully increased the conversion, improved the yield, changed the reaction pathway, and/or initiated the reaction in biological, chemical, and electrochemical systems.

At high ultrasonic intensities, a small cavity may grow rapidly through inertial effects. As a result, some bubbles undergo sudden expansion to an unstable size and collapse violently, generating energy for chemical and mechanical effects. [17] The collapse of the cavitation bubbles disrupts the phase boundary and causes emulsification, by ultrasonic jets that impinge one liquid to another.

A low frequency ultrasonic irradiation could be useful for transesterification of triglyceride with alcohol. Ultrasonication provides the mechanical energy for mixing and the required activation energy for initiating the transesterification reaction. Ultrasonication increases the chemical reaction speed and yield of the transesterification of vegetable oils and animal fats into bio-diesel.

Ultrasonic assisted transesterification method presents advantages such as shorter reaction time and less energy consumption than the conventional mechanical stirring method, efficient molar ratio of methanol to TG, and simplicity. For the transesterification of 1 kg soybean oil conventional mechanical stirring method and ultrasonic cavitation method consume 500 and 250 W/kg of energy, respectively.

The limitation of ultrasonic assisted transesterification is the surface of the reactants must be accessible to transmit ultrasound and training skill is more extensive than with some other methods. It is difficult to make large scale or scale-up production.

2.6 Parameters Affecting Biodiesel Production

Transesterification has been described as a chemical reaction between triglycerides and alcohol in the presence of catalyst to produce mono-esters that are termed as biodiesel. Transesterification reaction is affected by various parameters. The reaction is either incomplete or the yield is reduced to a significant extent if the parameters are not optimized. The important process parameters, which affect the yield of the transesterification process, are discussed below.

2.6.1 Alcohol to Oil Molar Ratio

The stoichiometric transesterification requires 3 mol of the alcohol per mole of the triglyceride to yield 3 mol of the fatty esters and 1 mol of the glycerol. However, the transesterification reaction is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction close to completion in a forward direction.

The molar ratio of 6:1 or higher generally gives the maximum yield (higher than 98% by weight). Lower molar ratios require a longer time to complete the reaction. Excess molar ratios increase the conversion rate but leads to difficulties in the separation of the glycerol. At optimum molar ratio only the process gives higher yield and easier separation of the glycerol. The optimum molar ratios depend on the type and quality of the vegetable oil used. [3]

2.6.2 Catalyst

A catalyst is needed to improve the transesterification reaction and yield. 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% 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. [3]

2.6.3 Reaction 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 methanol (60 to 70°C) at atmospheric pressure. With further increase in temperature there is more chance of loss of methanol. Transesterification reaction has been reported to be influenced positively with increase in temperature.

2.6.4 Mixing Intensity

The mixing effect is more significant during the slow rate region of the transesterification reaction and when the single phase is established, mixing becomes insignificant. Understanding the mixing effects on the kinetics of the transesterification process is a valuable tool in the process scale-up and design.

2.6.5 Purity of Reactants

Impurities present in the vegetable oil also affect ester conversion levels significantly. The vegetable oil (refined or crude oil) is filtered before the transesterification reaction. The oil settled at the bottom of the tank during storage would give lower yield because of deposition of impurities such as wax and gums. [3]

2.7 Biodiesel Specifications and Properties

The fuel specification defines and sets the quality standards for biodiesel. It is based on the standard ASTM D 6751.The ASTM and EU biodiesel property specifications with the recommended test methods are given in Table 2.1.

The kinematic viscosity: "the resistance to flow of a fluid under gravity". 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. 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 1.9-6.0mm^2/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.

However, the acid value may increase with time as the fuel degrades due to contact with air or water. This test should be performed regularly as a part of the producer QC program. The requirement is a maximum of 0.8 mg of KOH/g.

Table 2.1: Standard Specifications of Biodiesel: USA and European

Property	Unit	USA	EU	
		ASTM D 6751	EN 14214	Recommended Test method
Density at 15^{0}C	Kg/m^3	-	860 – 900	ASTM D 4052
Kinematic viscosity at 40^{o}C	mm^2/s	1.9 -6.0	3.5 - 5.0	ASTM D 445
Flash point	^{o}C	≥ 120	≥ 130	ASTM D 93
Cloud point	^{o}C	-	-	ASTM D 2500
Sulfur content,100%	w%	≤ 0.05	≤ 0.01	ASTM D 5453
Sulphated Ash	wt%	≤ 0.02	≤ 0.02	ASTM D 874
Water content	mg/Kg	-	≤ 500	EN ISO 12937
Total contamination	mg/Kg	-	≤ 24	EN 12662
Water and sediment	% vol.	<=0.05		ASTM D 2709
Corrosion (Cu) at 50^{o}C	-	≤ No.3	class 1	ASTM D 130
Cetane number	-	≥ 47	≥ 51	ASTM D 613
Acid number	mg KOH/g	≤ 0.8	≤ 0.5	ASTM D 664
Oxidation Stability ,110^{o}C	hours		≥ 6	EN14112
Methanol content	wt%		≤ 0.2	EN 14110
Ester content	wt%		≥ 96.5	EN 14103
Carbon Residue,100%	wt%	0.05 max		ASTM D 4530
Triglycerides	wt%		≤ 0.20	EN 14105
Diglycerides	wt%		≤ 0.80	EN 14105
Monoglycerides	wt%			EN 14105
Free glycerol	wt%	≤ 0.02	≤ 0.02	ASTM D 6584
Total glycerol	wt%	≤ 0.24	≤ 0.25	ASTM D 6584
Iodine value	gI2/100g		≤ 120	EN 14111
Phosphorus	mg/Kg	≤ 10	≤ 10	ASTM D 4951

Source: Adopted from Biodiesel industries, Australia 2003

The flash point is defined as the “lowest temperature, at which the application of an ignition source causes the vapors of a specimen to ignite under specified conditions of test’’. This test, in part, is a measure of residual alcohol. The flash point is a determinant for flammability classification of materials. The typical flash point of pure methyl esters is greater than 200 ° C, classifying them as “non-flammable”.

However, during production and purification of biodiesel, not all the methanol may be removed, making the fuel flammable and more dangerous to handle and store if the flash point falls below 130ºC. Excess methanol in the fuel may also affect engine seals and elastomers and corrode metal components. Generally, a production quality control (QC) laboratory should include a flash point apparatus for quality control and as a means of detecting excess alcohol levels. The requirement is a minimum of 130°C.

The cloud point is “the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled down.” The cloud point is a critical factor in cold weather performance for all diesel fuels that can be predicted ± 5 % with knowledge of the esters composition, but producers are advised to be equipped to perform this test. Since the saturated methyl esters are the first to precipitate, the amounts of these esters, methyl palmitate and methyl stearate, are the determining factors for the cloud point.

The producer can modify the cloud point two ways. One is through the use of additives that retard the formation of solid crystals. The cloud point can also be modified by blending feedstocks that are relatively high in saturated fatty acids with feedstocks that have lower saturated fatty acid content. The requirement is to report the temperature for the customer.

The cetane number is “a measure of the ignition performance of a diesel fuel obtained by comparing it to reference fuels in a standardized engine test”. Cetane for diesel engines is analogous to the octane rating in a spark ignition engine. It is a measure of how easily the fuel will ignite in the engine.

The cetane number is seldom an issue because all of the common fatty acid esters have cetane numbers near or above 47. The cetane number can be predicted ± 10 % using the esters composition. It is unlikely that an individual producer will ever run cetane tests on-site because the equipment is extremely expensive. The requirement is the cetane number has to be above 47.

The water and sediment test is a measure of cleanliness of the fuel. It is particularly important because water can react with the esters, making free fatty acids, and can support microbial growth in storage tanks. Water is usually kept out of the production process by removing it from the feedstocks. However, some water may be formed during the process by the reaction of the sodium or potassium hydroxide catalyst with alcohol.

If free fatty acids are present, water will be formed when they react to either biodiesel or soap. Finally, water is deliberately added during the washing process to remove contaminants from the biodiesel. This washing process should be followed by a drying process to ensure the final product will meet the standard.

Sediments may plug fuel filters and may contribute to the formation of deposits on fuel injectors and other engine damage. Sediment levels in biodiesel may increase over time as the fuel degrades during extended storage.

The production QC lab should be equipped to perform this test on a routine basis. The requirement is a maximum of 0.05% volume.

The carbon residue is “In petroleum products, the part remaining after a sample has been subjected to thermal decomposition” is the carbon residue. The carbon residue is a measure of how much residual carbon remains after combustion. The test basically involves heating the fuel to a high temperature in the absence of oxygen. Most of the fuel will vaporize and be driven off, but a portion may decompose and pyrolyze to hard carbonaceous deposits.

This is particularly important in diesel engines because of the possibility of carbon residues clogging the fuel injectors. The most common cause of excess carbon residues is an excessive level of total glycerin. The requirement is a maximum of 0.05wt%.

Free glycerol is the glycerol present as molecular glycerol in the fuel. Free glycerol results from incomplete separation of the ester and glycerol products after the transesterification reaction. This can be a result of imperfect water washing or other approaches that do not effectively separate the glycerol from the biodiesel.

The free glycerol can be a source of carbon deposits in the engine because of incomplete combustion. The terms “glycerine,” “glycerin,” and “glycerol” are used interchangeably. The requirement is a maximum of 0.02wt%.

3. MATERIALS AND METHODS

3.1 Materials and Equipments

The major raw materials used during the experiment are Jatropha curcas oil, analytical grade (AG) methanol and sodium phosphate as a heterogeneous catalyst. The Jatropha seed was purchased from local market in Desie for the extraction of oil using hexane as solvent. The sodium phosphates (98% purity) were bought from South Korea samchun Reagent Chemical Co., Ltd. and used as catalysts without further processing.

The equipments used during the experimentations are Glass reactor equipped with mechanical stirrer, thermostat, and condenser, Centrifuge, Rotary Evaporator Hydrometer, Vibro viscometer, Bomb Calorimeter, Bunsen burner, conical flask, balance and burette.

3.2 Experimental Method

3.2.1 Jatropha Seed Preparation

The Jatropha seed were dried at 50^{O}c for 2hr to remove some moisture afterward all the seeds were de-hulled by using beco disk mill with disk space of 1.875 and the kernels were separated from the husk by sifting and stored in a plastic bag until the next process. Then, the kernels were dried at high temperature of 100-105ºC for 30 min under the oven. Finally, the clean kernels were grounded by using Fritsch cutting mill to 2.0 mm to increase the surface area for extraction.

Fig.3.1: Jatropha seed to the left, beco disk mill in the middle and Fritsch cutting mill to the right

Fig. 3.2: Jatropha seed Kernel and grounded Jatropha kernel

3.2.2 Oil Extraction

The grounded seed was used for oil extraction. The extraction method used was known as cold extraction. The grounded seed was mixed with the proper amount of solvent, hexane, in a batch vessel for 3 days with occasional agitation. During these days, the hexane extracts oil from the grounded kernel. Supernatant solution was collected which is the mixture of extracted oil and hexane after it is separated from the kernel cake by decantation. Since some amount of suspension is available within the supernatant solution, filtration is employed with the help of filter paper to remove all the suspension from the extracted oil.

After the separation was completed, all of the remaining solution was transferred to rotary evaporator and the mixture was distilled to separate hexane from the extracted oil.

Fig. 3.3 Rota vapor used to separate the hexane from the extracted Jatropha oil

Fig. 3.4: Crude Jatropha Curcas oil collected during extraction process

The amount of oil extracted was calculated from,

$$\%\ oil = \left(\frac{mass\, of\ oil}{initial\ mass\ of\ seed}\right) * 100 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

3.2.3 Purification of Crude Jatropha Oil

3.2.3.1 Degumming

The extracted crude Jatropha oil contains phosphatides, gums and other complex compounds which can promote hydrolysis (increase in free fatty acid) of vegetable oil during storage. During transesterification process, these compounds can also interfere. Therefore these compounds are removed by acid degumming process.

In this process, a combination of water and phosphoric acid (85%) were used. The oil was heated to 70 ºC under stirring at 1000 rpm in a jacketed glass vessel connected to a circulation thermostat, 3% of distilled water (which first was heated to approximately 90 ºC) and 0.2% of phosphoric acid (85%) was added.

The mixture was stirred for 1h. The white-formed precipitate was separated by centrifugation for 0.5h at 3500 rpm and the degummed oil was dried at 100 ºC for 0.5h.The experimental set up was done as follows:

Fig. 3.5 Experimental set up during degumming process for purification of crude Jatropha oil

Fig.3.6 Jatropha oil after Degumming on settling tank to separate the white and dark precipitates

3.2.3.2 Neutralization

NaOH (0.5 N) solution was added to the degummed oil (which was heated to approx. 70^0 c) constant stirring at 1000 rpm in a jacketed glass vessel connected to circulating thermostat) to neutralize the free fatty acids.

Sodium chloride (about 10% of the weight of the oil) was added to help settle out the soap formed. After 1hour mixing the mixture was transferred into a separating funnel and allowed to stand for 1h; the soap formed was separated from the oil.

Hot water was added again and again to the oil solution until the soap remaining in solution was removed. The neutralized oil was then drawn off into beaker.

The appropriate amount of alkaline solution (NaOH) required to neutralize the free fatty acid was calculated by the following chemical reaction. First of all, the composition of free fatty acid was determined from the acid value. The acid value is determined by using titration and the result was attached in appendix E.

3.2.4 Characterization of Purified Jatropha Oil (Physicochemical Properties)

3.2.4.1 Moisture Content Determination

The empty dish was weighed with and without the amount of kernel and dried in an oven at 105°C for 7hr, weighing each 2hr till constant weight is obtained and finally the weight was taken and compared with the initially recorded weight. The percentage weight in the seed was calculated using the formula:

$$Moisture\ \ Content = \left(\frac{(W_1 - W_2)}{W_2}\right) * 100 \quad \text{..} 3.2$$

Where W_1 = original weight of the sample before drying;

W_2 = Weight of the sample after drying.

3.2.4.2 Determination of Specific Gravity

The sample was filled into graduated cylinder (50 ml) and its temperature was recorded. Hydrometer was used to measure the SG of the oil at 20 °C specified. Hence, the density of the oil is determined using the specific gravity.

3.2.4.3 Determination of Kinematic Viscosity

Vibro viscometer was used to determine the viscosity of oil, and the sample was kept in the water thermostat bath until it reaches the equilibrium temperature of 40 ^{o}C.

After maintaining the equilibrium temperature, the Vibro viscometer tip was inserted to the sample and the reading was taken from the controller. The kinematic viscosity is then equal to the ratio of dynamic viscosity to density of the oil.

$$\mu = \frac{\nu}{\rho} \quad \text{......} 3.3$$

Where μ=kinematic viscosity, mm^2/s

ν=dynamic viscosity, mPa.sec and ρ=density, kg/m^3

3.2.4.4 Determination of Acid Value or Acid Number

To determine the Acid value, Standard alcoholic KOH solution (0.1 N) was prepared by dissolving KOH (pellet) with ethanol. The solution was filtered and stored in brown bottle for five days. Furthermore, a mixture of 95% ethanol and diethyl ether in a ratio of 1 to 1 by v/v was prepared by mixing 500 ml diethyl ether and 500 ml of ethanol.

A weighed quantity of the oil sample was dissolved in 25 ml of 1 to 1 mixture of ethanol and diethyl ether. The solution was titrated with 0.1N ethanolic KOH solution in presence of 5 drops of phenolphthalein as indicator until the end point (colorless to pink) is recognized. The volume of 0.1 N ethanolic KOH (V) for the sample titration was noted. The total acidity (acid number) in mg KOH/ gm was calculated using the following equation:

$$Acid\ Number = \frac{V * N * 56.1}{m} \quad \text{......} 3.4$$

Where V is the volume expressed in milliliter of 0.1N solution of ethanolic KOH

m is mass in gram of the test portion

N is concentration of ethanolic KOH

3.2.4.5 Determination of Saponification Number (SN)

The Saponification Number determination was conducted by dissolving the oil in an ethanolic KOH solution. This solution is then heated for half an hour so that the oil completely dissolves in the ethanolic KOH solution.

A weighted amount of oil (W) was added to 25 mL of 0.5N ethanolic potassium hydroxide solution and the reflux condenser was attached to the flask. The mixture was heated, and as soon as the ethanol boils, the flask was occasionally shaken using magnetic stirrer until the oil was completely dissolved, and the solution was boiled for half an hour.

After the oil was completely dissolved, 5 drops of phenolphthalein indicator was added and the hot soap solution obtained was slowly titrated with 0.5N hydrochloric acid (and volume V_a was recorded).

Then a blank determination was carried out upon the same quantity of potassium hydroxide solution at the same time and under the same conditions (and volume V_b was recorded). The final result was calculated using equation 3.5.

$$Saponification\ Number = \frac{56.1 * N * (V_b - V_a)}{W} \quad \text{..} 3.5$$

Where W= weight of oil taken in gram.

N= normality of HCL solution

V_a= volume of HCL solution used in the test in milliliter.

V_b= volume of HCL solution used in blank in milliliter.

3.2.5 Experimental Design for Biodiesel Production

In these work the biodiesel was prepared using purified Jatropha curcas oil and methanol with a heterogeneous catalyst of tribasic sodium phosphate bought from South Korea. Experimental design was analyzed and done by the Design-Expert 7.0.0 program.

The experimental design selected for this study is Central Composite Design (CCD) and the response measured is 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 oil and weight percentage of catalyst. 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 3.1 lists the range and levels of the three independent variables studied. The levels of the variables investigated are chosen by considering the operating limits of the biodiesel production process conditions.

A five-level-three-factor CCD was employed in the optimization study, requiring 20 experiments. The methanol-to-oil molar ratio, catalyst concentration and reaction temperature were the independent variables selected to optimize the conditions for FAME production of tri sodium phosphate-catalyzed transesterification. The 20 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 three variables.

Table 3.1: Independent variables and levels used in the central composite design for the alkali catalyzed Transesterification process Chosen for this Study

Variable (Factors)	Factor Coding	Unit	Levels				
			-2	-1	0	+1	+2
Reaction Temperature	x_1	^oC	40	45	52.5	60	65
Methanol to Oil ratio	x_2	-	2.64	4	6	8	9.4
Amount of Catalyst	x_3	wt %	2.32	3	4	5	5.7

Table 3.2 shows the complete experimental design matrix of CCD for the factorial design (n factors, each at two-level).The order in which the runs were made was randomized to avoid systematic errors.

Table3.2: Central Composite Design Arrangement (Experimental Design Matrix)

Run	Coded Factor			Actual Factors		
	X_1	X_2	X_3	Reaction temperature	Methanol to oil ratio	Catalyst to oil ratio
1	0	0	0	52.5	6	4
2	-2	0	0	40	6	4
3	+1	+1	+1	60	8	5
4	0	+2	0	52.5	9.4	4
5	0	0	0	52.5	6	4
6	+1	-1	+1	60	4	5
7	0	0	-2	52.5	6	2.32
8	0	0	0	52.5	6	4
9	0	0	+2	52.5	6	5.7
10	0	0	0	52.5	6	4
11	0	0	0	52.5	6	4
12	0	0	0	52.5	6	4
13	-1	+1	-1	45	8	3
14	-1	+1	+1	45	8	5
15	0	-2	0	52.5	2.64	4
16	-1	-1	+1	45	4	5
17	-1	-1	-1	45	4	3
18	+1	+1	-1	60	8	3
19	+1	-1	-1	60	4	3
20	+2	0	0	65	6	4

3.2.6 Experimental Setup

The batch transesterification reaction system employed in this work is shown in Figure 3.7. A 250ml glass reactor equipped with mechanical stirrer, thermostat, and condenser was used in all experiments. The reactor was connected to a water bath thermostat which was capable of controlling the temperature to within deviation of 1°C. A mechanical stirrer fitted with stainless steel propeller provided the mixing requirement.

Fig. 3.7 Experimental set-up for biodiesel production through transestrification

3.2.7 Biodiesel Production Procedure

Initially, about 100ml of Jatropha curcas seed oil was poured into a 250ml glass reactor. The reactor assembly was then heated to the desired temperature by using thermostat. A measured amount of methanol and heterogeneous catalyst was added to the reactor. The reaction was timed as soon as mechanical stirrer was turned on.

The Transesterification was carried out at optimum reaction time and rotation speed to achieve maximum conversion for 3h. The reaction parameters were chosen as follows: temperature ranged from 313 to 338K, molar ratio of methanol to oil from 4:1 to 8:1, mass ratio of catalyst to oil from 3% to 5%.

Finally, after transesterification was carried out, catalyst and glycerol part was separated from the biodiesel mixture by centrifugation for 2hr. Then, unreacted methanol and trace moisture was removed by rotary evaporator.

The end product, biodiesel was obtained as a clear amber-yellow liquid. These procedures are used for each experiments executed at different parameters using the experimental design matrix.

3.2.8 Feed Material Requirement for Biodiesel Production

100ml of purified Jatropha oil was used for each run. Hence, the amount of methanol and catalyst was calculated as follows using the process parameters.

The amount of methanol required when the molar ratio of methanol to oil ratio 6:1;

$$\frac{n\ methanol}{n\ \ oil} = 6 \qquad \text{.........} 3.6$$

Substituting mass for mole;

$$\frac{\frac{\rho meOH * Vmeoh}{MmeOH}}{\frac{\rho\ oil * Voil}{Moil}} = 6$$

$$\frac{\frac{0.79g/ml * VmeOH}{32.04g/mol}}{\frac{0.9g/ml * 100ml}{860g/mol}} = 6$$

Solving for V_{meOH}=25.5ml of methanol

The amount of catalyst required when the ratio of catalyst weight to oil is 5;

$$moil = \rho\ oil * Voil \ldots\ldots 3.7$$

$$moil = 0.90g/ml * 100ml$$

=90gm

$$\frac{mass\ of\ catalyst}{mass\ of\ oil} = 5\% \ldots\ldots 3.8$$

$$mass\ of\ catalyst = 5\% * mass\ of\ oil$$

=4.5gm of catalyst

Similarly, the amount of methanol and catalyst is calculated for all experiments. The tabulated result for different processes parameter was given in appendix C.

3.2.9 Methods for Biodiesel Characterization (Physico-Chemical Properties of Biodiesel)

Standard procedure was used to characterize the Physico-chemical properties of biodiesel. The method was given in Table 2.1 and they are discussed as follows.

3.2.9.1 Determination of Specific Gravity (SG) and Density, ASTM D 4052

The sample was filled into graduated cylinder and its temperature was recorded. Hydrometer was used to measure the SG of the fuels specified. The specific gravities were taken at temperatures of 15^{O}C.

$$\text{Specific Gravity} = \frac{\text{Density of oil}}{\text{Density of water}} \qquad 3.9$$

3.2.9.2 Determination of Kinematic Viscosity, ASTM D 445

The viscosity of the Jatropha curcas oil was measured using Vibro viscometer. Vibro Viscometer integrated with a water bath thermostat was used and the sample was kept in as shown in the Fig 3.8. The kinematic viscosity is then equal to ratio of dynamic viscosity to the density of the biodiesel observed. The apparatus brand name is AND SV-10 with the capacity to read the viscosity of a fluid from 0.3-10,000mPa.sec.The device will detect the viscosity with vibration. During vibration, there is a shear force between the tip and the fluid. It will read the dynamic viscosity which is resistance to flow. The observed kinematic viscosity was 30.9mm^2/sec which is in agreement with literature data.

Fig 3.8 Experimental set-up for viscosity determination

3.2.9.3 Determination of Acid Value or Acid Number, ASTM D 664

To determine the Acid value, Standard alcoholic KOH solution (0.1 N) was prepared by dissolving KOH (pellet) with ethanol. The solution was filtered and stored in brown bottle for five days. Furthermore, a mixture of 95% ethanol and diethyl ether in a ratio of 1 to 1 by v/v was prepared by mixing 500 ml diethyl ether and 500 ml of ethanol.

A weighed quantity of the oil sample was dissolved in 25 ml of 1 to 1 mixture of ethanol and diethyl ether. The solution was titrated with 0.1N ethanolic KOH solution in presence of 5 drops of phenolphthalein as indicator until the end point (colorless to pink) is recognized. The volume of 0.1 N ethanolic KOH (V) for the sample titration was noted. The total acidity (acid number) in mg KOH/ g was calculated using the following equation 3.4.The acid value was determined to know the amount of free fatty acid composition in the oil.

3.2.9.4 Determination of Saponification Number

A weighted amount of biodiesel (W) was added to 25 mL of 0.5N ethanolic potassium hydroxide solution and the reflux condenser was attached to the flask. The mixture was heated, and as soon as the ethanol boils, the flask was occasionally shaken using magnetic stirrer until the oil was completely dissolved, and the solution was boiled for half an hour.

After the oil was completely dissolved, 5 drops of phenolphthalein indicator was added and the hot soap solution obtained was slowly titrated with 0.5N hydrochloric acid (and volume V_a was recorded).

Then a blank determination was carried out upon the same quantity of potassium hydroxide solution at the same time and under the same conditions (and volume V_b was recorded). The final result was calculated using equation 3.5.

3.2.9.5 Determination of Heating Value (Calorific Value)

Calorific value (energy content or heat of combustion) of a fuel was determined by bomb calorimeter. Benzoic acid was used to standardize the calorimeter. One gram of sample was taken in a crucible and made into a pellet and the initial weight was noted. It was placed in the bomb, which is pressurized to 18atm of oxygen.

The bomb was placed in a vessel containing a measured quantity of water (2000g). The ignition circuit was connected and the water temperature noted. After ignition the temperature rise was noted every minute till a constant temperature was reached.

The pressure was released and the length of unburned fuse wire was measured. And the determination of the biodiesel’s calorific value was conducted following the same procedure for standardization, except for the sample preparation, which was Biodiesel. The calorific value was calculated from (Eq. 6): (Parr, 1987)

Including the corrections for heat transfer between the surrounding and the apparatus, heat liberated by the glowing wire etc, the heat value of the air- dried sample of the fuel is expressed according to the following formula.

$$HHV = \frac{[m_w * C_w + (m_c)_{app}](t_m + c - t_o) - \sum b}{M} \quad \text{...3.10}$$

Where: HHV= higher heating value [cal/g]

M =Mass of the fuel [g]

$m_w C_w$ = the mass and specific heat of the calorimeter water C_w = 1cal/g°C

t_o=first temperature reading of main test [°C]

t_m =last temperature reading of main test[°c]

c = Correction for heat exchange between calorimeter and the surrounding

Summation of b=correction for heat exchange between calorimeter and the surrounding, cal

The correction is calculated from the formula

$$C = m'\Delta n - (\Delta n + \Delta \nu)F \quad \text{..3.11}$$

Where m'= duration of main test [min]

Δn= Average temperature fall for every minute of the pre-test

Δv =Average temperature rise for every minute of the pre-test

The factor F can be approximated to

F = 1.0, if the temperature rise in 1st minute of the main test is higher than in the 2nd.

F = 1.25, if temperature rise in the 1st minute and 2nd minutes of the main test are about the same.

F = 1.5, if temperature rise in the 1st minute of the main test id less than in the 2nd minute

The correction summation of b consists of heat value added by glowing of the ignition wire 1cm = 1.5cal.

3.2.9.6 Determination of Iodine Value (IV)

The Iodine value of the biodiesel was determined using the empirical formula suggested by Dembirbes (1998) for determination of higher heating value. After rearrangement the iodine value was calculated from Eq. 3. 12.

$$\mathrm{HHV} = 49.43 - [0.041(\mathrm{SN}) + 0.015(\mathrm{IV})] \quad \text{...3. 12}$$

$$\mathrm{IV} = \frac{\mathrm{HHV} - 49.43 + 0.041(\mathrm{SN})}{0.015} \quad \text{...3.13}$$

3.2.9.7 Determination of Cetane Number (CN), ASTM D613

The cetane number of the biodiesel was determined using the empirical formula suggested by (Kalayasiri et al., 1996), using the result of Saponifcation number (SN) and the iodine value (IV) of the biodiesel.

$$\mathrm{CN} = 46.3 + (54.58/\mathrm{SN}) - 0.225(\mathrm{IV}) \quad \text{...3.14}$$

3.2.9.8 Determination of Flash Point, ASTM D 93

The flash point of the biodiesel was determined using open cup method. The cup was filled with the biodiesel up to the mark (about 75 ml) and the cup was heated by a Bunsen burner. Small open flame was maintained from an external supply of natural gas.

Periodically, the flame was passed over the surface of the oil. When the flash temperature was reached the surface of the oil catch flame, the temperature at the moment was noted and reported as flash point temperature.

3.2.9.9 Determination of Cloud Point, ASTM D 2500

An alternative procedure for measuring the cloud point of diesel/biodiesel fuels is ASTM D 5773. A summary of the procedure steps was the sample has to be cooled at a 2^{O}c rate and continuously monitored until the cloud appears and the temperature is recorded that corresponds to the first formation of a cloud in the fuel.

The cloud point is a measure of the temperature at which components in the biodiesel begin to solidify out of the solution.

4. RESULT AND DISCUSSION

4.1 Jatropha Seed Preparation, Oil Extraction, Purification and Characterization

4.1.1 Seed Preparation

13kg of Jatropha seeds were taken and dehusked using disk mill. Then, the husk is carefully removed and the kernels thus obtained were used for oil preparation. After sifting, 8kg of jatropha seed kernel was obtained.

$$\text{Hence, the ratio of kernel weight to the raw seed weight} = \frac{\text{mass of kernel}}{total\ mass} \quad \text{.....................................4.1}$$

$$= \frac{8kg}{13kg}$$

$$=0.62\%$$

Therefore, the kernel weight was 62 % of raw seed weight. The 8kg clean Jatropha seed kernels were grounded by using cutting mill to 2.0 mm to increase the surface area for extraction.

4.1.2 Moisture Content Determination

The amount of sample was weighted using a balance for each experiment. Then; it was dried in an oven at $110^{O}C$ for 8hours. 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 kernel seed average moisture content of 4.69%.The moisture content determination of the kernel conducted laboratory result was given in the table below as follows;

Table 4.1: Moisture content determination

Run	Sample weight(g)				Average Seed moisture content (% w/w)
	weight of the sample before drying	Weight of the sample after drying	Difference(before drying-after drying)	Moisture content(%w/w)	
1	3.156	3.011	0.14 5	4.59	4.69%
2	3.304	3.152	0.152	4.60	
3	3.421	3.246	0.174	5.10	
4	3.285	3.135	0.149	4.55	
5	3.114	2.954	0.160	5.13	
6	3.853	3.692	0.161	4.18	

4.1.3 Oil Extraction

The amount of Jatropha curcas grounded kernel collected from the cutting mill was used for oil extraction. From 7.6kg of the kernel, 3.2liter of Jatropha curcas crude oil was extracted using cold extraction method by using hexane as a solvent. Then, the density of the crude oil was measured using hydrometer in the lab and the reading observed was 920kg/m^3. The mass of the oil extracted will be calculated using the following equation:

$$m = \rho * V \quad \text{(4.2)}$$

$$= 920\,\frac{\text{kg}}{\text{m}^3} * 3.2\,liter * \frac{1m^3}{1000\,liter}$$

=2.9kg of Jatropha curcas crude oil was extracted

Yield of oil (Oil Content) within the grounded kernel seed was calculated as follows:

$$\text{Yield of oil} = \frac{\text{mass of crude oil extracted}}{\mathit{total\ mass\ of\ seed\ kernel}} * 100\% \quad \ldots\ldots\ldots\ldots 4.3$$

$$= \frac{2.9\text{kg}}{7.6\text{kg}} * 100 = 38.15\%$$

$$= 38.15\%$$

4.1.4 Purification

The total amount of crude Jatropha curcas oil obtained from extraction with hexane is 3.2 liter from 7.6kg of Jatropha seed kernel. The crude jatropha oil was degummed to remove phosphatides, gums and other complex compounds in the crude oil using 64ml of phosphoric acid and 96ml of distilled water. After degumming, 0.122g free fatty acid was neutralized, using 0.0176g of NaOH and 0.29g of sodium chloride to make the produced soap settle faster. The detailed calculation is given in appendix C.

4.1.5 Physico- Chemical Properties of Purified Oil

The specific gravity, density, kinematic viscosity, acid value, free fatty acid composition, saponification number, flash point and higher heating value of the purified Jatropha oil were determined and the results are given in Table 4.2.

The specific gravity of the Jatropha oil was in agreement with the result reported by Y.J.Franken as given in the appendix A. The kinematic viscosity of the crude Jatropha oil was higher than the result reported by Dennis Y.C. Leung , Xuan Wu, M.K.H. Leung (Applied Energy2008) which was 29.4 mm ^{2}/sec. The variation in viscosity is occurred from the dependence of chemical composition of the crude oil on agro climatic conditions.

Table 4.2 Physico-chemical properties of purified jatropha oil

Property	Experimental Result	Unit
Specific Gravity	0.9	-
Density at 15^0C	0.9	g/ml
Kinematic viscosity at 40^oC	30.9	mm^2/s
Acid Value	8.4	mg KOH/g oil
Composition of Free Fatty Acid	4.21	%
Saponification Number	205	mg KOH/g oil
Flash point	240	^{o}C
Higher Heating Value	39.95	MJ/kg
Iodine value	73.3	g I2/100g

The acid value of the crude Jatropha oil was in agreement with the value reported by Munch and Kiefer (1986) which was (3-38 mgKOH/gm) but there is deviation with the result reported by Y.J.Franken.

The Saponifcation number of the crude oil is higher that the result reported by Munch and Kiefer (1986) which was (188-193 mg KOH/gm), the rise in Saponifcation number was caused by the variation of fatty acid composition depending on the agro climatic condition.

The HHV of jatropha oil was found to be 39.95MJ/kg which was in agreement with the value found in literature.

4.2 Analysis on Biodiesel Production

The transesterification was carried out at reflux of methanol, using a 250ml capacity glass reactor which is equipped with a stirrer, condenser and thermostat. The statistical analysis of the biodiesel was discussed below.

4.2.1 Statistical Analysis on Factors Affecting Biodiesel Yield

The experimental design selected for this study is Central Composite Design (CCD) and the response measured is the yield of fatty acid methyl esters (FAME). The three transesterification process variables studied are reaction temperature, ratio of methanol to and weight percentage of catalyst.

The Design-Expert 7.0.0 program was used in the regression analysis and analysis of variance (ANOVA). The Statistical software program was used to generate surface plots, using the fitted equation obtained from the regression analysis, holding one of the independent variables constant.

Experiments were carried out to validate the equation, using combinations of the independent variables, which were not part of the original experimental design, but within the experimental region.

The response of the transesterification process was used to develop a mathematical model that correlates the yield of FAME to the transesterification process variables studied. Design Expert software version 7.0.0 was used for the regression analysis of the experimental data and also for evaluation of the statistical significance of the equation developed.

The central composite design conditions and responses, and the statistical analysis of the ANOVA are given in Tables 4.3 and 4.4, respectively. The multiple regression coefficients were obtained by employing a least square technique to predict a quadratic polynomial model for the FAME content (Table 4.4).The actual yield of biodiesel produced at different process parameters was calculated and is given in appendix c.

The model was tested for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared (R^2), adjusted R-Squared and predicted R-Squared having a value of 0.9966, 0.9936 and 0.9788, respectively.

Table 4.3: Experimental and predicted values of biodiesel yield

Run	Reaction Temperature	Molar ratio of methanol to oil	Amount of Catalyst	Experimental Biodiesel Yield Value	Predicted Biodiesel Yield Value	Residual
1	52.5	6	4	85	86.068	-1.06811
2	40	6	4	48.2	47.7419924	0.4580076
3	60	8	5	93	93.8902135	-0.890214
4	52.5	9.4	4	87.86	87.5518234	0.3081766
5	52.5	6	4	86	86.0681097	-0.06811
6	60	4	5	96	95.0832748	0.9167252
7	52.5	6	2.3	80.38	80.9281741	-0.548174
8	52.5	6	4	85.42	86.0681097	-0.64811
9	52.5	6	5.7	88.58	88.0979319	0.4820681
10	52.5	6	4	86.56	86.0681097	0.4918903
11	52.5	6	4	87.3	86.0681097	1.2318903
12	52.5	6	4	86.14	86.0681097	0.0718903
13	45	8	3	64.76	65.6299811	-0.869981
14	45	8	5	70.68	70.4631446	0.2168554
15	52.5	2.6	4	84.66	85.0342826	-0.374283
16	45	4	5	68	69.0162059	-1.016206
17	45	4	3	62.38	61.4430424	0.9369576
18	60	8	3	94	92.9370501	1.0629499
19	60	4	3	91.22	91.3901113	-0.170111
20	65.3	6	4	92.1	92.6241136	-0.524114

The yield of the transesterification processes were calculated as sum of weight of FAME produced to weight of jatropha oil used, multiplied by 100.The formula is given as:

$$\text{Yield of FAME} = \frac{\text{weight of fatty acid methyl ester}}{\textit{weight of oil used}} * 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.4$$

4.2.1.1 Development of Regression Model Equation

The model equation that correlates the response (yield of jatropha oil to FAME) to the transesterification process variables in terms of actual value after excluding the insignificant terms was given below. The predicted model for percentage of FAME content (R) in terms of the coded factors is given by Eq. 4.5.

$$\begin{aligned}\text{Yield of FAME(\%)} = {} & +86.07 + 13.34 * A + 0.75 * B + 2.13 * C - 0.66 * A * B - 0.97 * A * C \\ & - 0.68 * B * C - 5.62 * A^2 + 0.080 * B^2 - 0.55C^2 \quad \ldots\ldots\ldots\ldots\ldots 4.5\end{aligned}$$

Where A=reaction temperature

B=molar ratio of methanol to oil

C=weight of catalyst amount

4.2.1.2 Model Adequacy Check

The quality of the model developed could be evaluated from their coefficients of correlation. The value of R-squared for the developed correlation is 0.9966. It implies that 99.66% of the total variation in the yield of FAME is attributed to the experimental variables studied. The graph of the predicted values obtained using the developed correlation versus actual values is shown in Figure 4.1.

A line of unit slope, i.e. the line of perfect fit with points corresponding to zero error between predicted values and actual values is also shown in Figure 4.1. This plot therefore visualizes the performance of the correlation in an obvious way.

The results in Figure 4.1 demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit. This result indicates that it was successful in capturing the correlation between the three transesterification process variables to the yield of FAME.

The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in Table 4.3. Based on a 95% confidence level, the model was tested to be significant as the computed F value (327.82) is much higher than the theoretical $F_{0.05\ (9,\ 10)}$ value 3.02 and the p value less than 0.05. Besides that, each term in the model was also tested to be significant at a 95% confidence level as the computed F values for the respective terms are higher than the theoretical $F_{0.05\ (1,\ 10)}$ value (4.96) and the p values were all less than 0.05. Values of p greater than 0.05 indicates that the model terms are not significant. Thus, from these statistical tests, it was found that the model is adequate for predicting the yield of FAME within the range of variables studied.

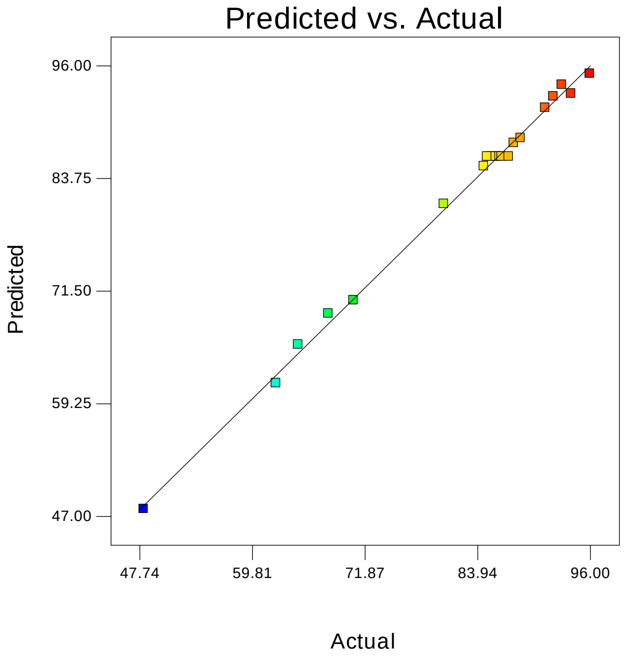


Fig 4.1: Predicted versus Actual Yield of FAME

Table 4.4: Analysis of Variance (ANOVA) for the Regression Model Equation and Coefficients

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Model	2976.574765	9	330.73053	327.820945	< 0.0001	**
A-Reaction Temperature	2431.601695	1	2431.6017	2410.20981	< 0.0001	**
B-Methanol to Oil ratio	7.650657067	1	7.6506571	7.58335082	0.0203	*
C-Catalyst to Oil ratio	62.05183928	1	62.051839	61.5059416	< 0.0001	**
AB	3.4848	1	3.4848	3.45414266	0.0927	
AC	7.5272	1	7.5272	7.46097986	0.0211	*
BC	3.7538	1	3.7538	3.72077615	0.0826	
A^2	454.5591707	1	454.55917	450.560211	< 0.0001	**
B^2	0.091150545	1	0.0911505	0.09034865	0.7699	
C^2	4.356174912	1	4.3561749	4.3178517	0.0644	*
Residual	10.08875528	10	1.0088755			
Lack of Fit	6.75855528	5	1.3517111	2.02947429	0.2279	not significant
Pure Error	3.3302	5	0.66604			
Cor Total	2986.66352	19				

Where * significant, ** highly significant

The Values of "Prob > F" less than 0.0500 indicate model terms are highly significant. In this case A, B, C, AC and A^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

This shows that the temperature,methanol to oil ratio, catalyst and the interaction between temperature and catalyst affects the yield much significantly.

The "Lack of Fit F-value" of 2.03 implies the Lack of Fit is not significant relative to the pure error. Non-significant lack of fit is good because we want the model to fit.

4.2.2 Effect of Transesterification Process Variables

Based on the analysis of variance, the transesterification reaction was significantly affected by various interactions between the process variables. On the other hand, significant individual process variables that affect the transesterification reaction is reaction temperature, A, ratio of methanol to oil, B, and catalyst amount, C. This result demonstrated the advantage of using design of experiments in capturing the interaction between variables that affects the transesterification reaction.

4.2.2.1 Effect of Individual Process Variables

Figure 4.2 shows the effect of reaction temperature on the yield of the transesterification reaction. It can be seen that with increasing reaction temperature, increases the yield. As seen in Figure 4.2, the yields of fatty acid methyl ester (FAME) were increase significantly.

The increase in the yield of FAME at higher reaction temperature is due to higher rate of reaction. Is it well reported in the literature that the rate constants of the transesterification reaction is strongly influenced by the reaction temperature. Due to higher rate constant at higher temperature, this will lead to higher rate of reaction and eventually higher FAME yield.

The transesterification reaction is basically diffusion controlled. At lower reaction temperature, the lower viscosity of Jatropha oil might cause poor diffusion between the phases that will lead to slower rate of reaction.

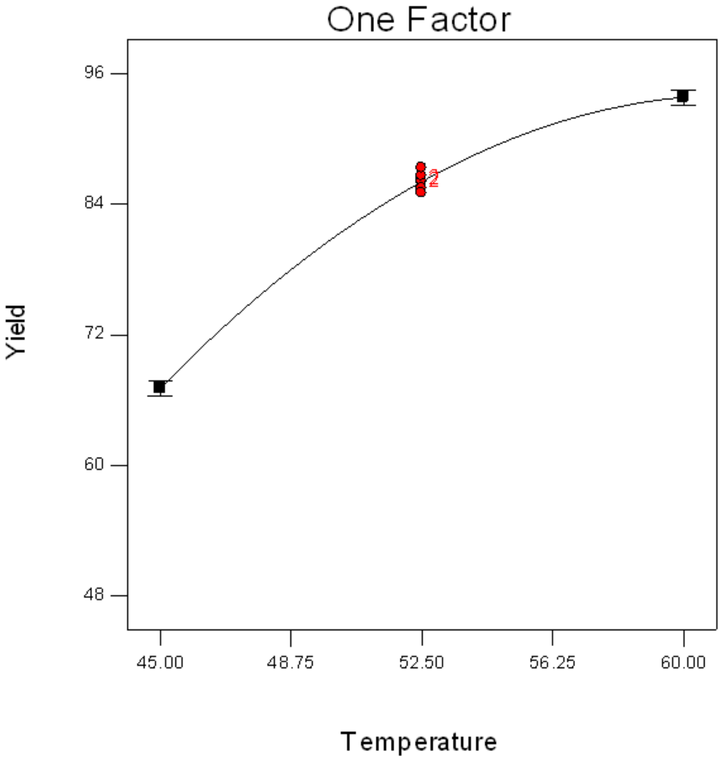


Fig 4.2: Biodiesel yield versus reaction temperature at methanol to oil ratio of 6 and 4 % catalyst amount.

The transesterification process consists of a sequence of three consecutive reversible reactions where the triglyceride is successively transformed into diglyceride, monoglyceride and finally into fatty acid methyl esters (FAME) and glycerin.

The ratio of methanol to oil is one of the important factors that affect the conversion of triglyceride to FAME. Stoichiometrically, three moles of methanol are required for each mole of triglyceride, but in practice, a higher molar ratio is required in order to drive the reaction towards completion and produce more FAME as products. The results obtained in this study are in agreement with this, as shown in Figure. 4.3, where at higher methanol to oil ratio, the biodiesel yield was increased. Higher ratio of methanol used could also minimize the contact of access triglyceride molecules on the catalyst's active sites which could decrease the catalyst activity.

Besides that, an increase in the ratio of methanol could also lead to the increase in the purity of the FAME layer which would also be responsible for the observed increased in FAME yield.

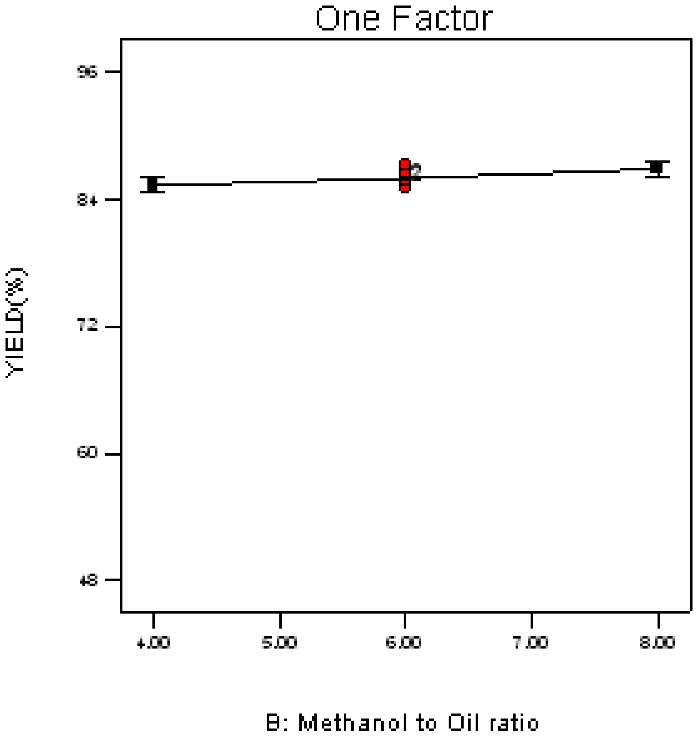


Fig 4.3: Biodiesel yield versus methanol to oil ratio at reaction temperature of 52.5°c and 6 % catalyst amount.

From Fig. 4.4 the effect of one factor which is methanol to oil ratio is not highly significant. This shows that the interaction between the transesterification processes parameter was significant. This result agrees with the ANOVA out put for the regression model equation and coefficient.

Figure 4.4 illustrates the effect of mass ratio of catalyst to oil on biodiesel yield. When the mass ratio of catalyst to oil was improved from 2% to 4%, the active sites of the solid catalyst was increased; accelerating transesterification reaction whereby increasing biodiesel yield.

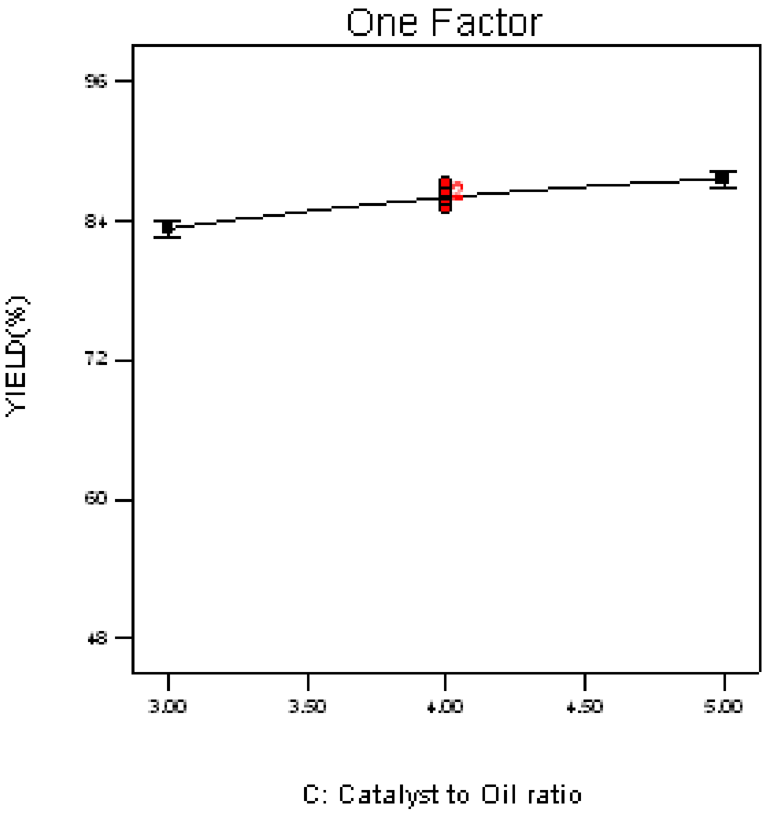


Fig 4.4: Biodiesel yield versus catalyst to oil ratio at reaction temperature of 52.50°c and methanol to oil ratio of 6.

4.2.2.2 Effect of Interaction between Process Variables

The process variables were found to have significant interaction effects. Figure 4.5, 4.7 and 4.9 shows the interaction between catalyst ratio and reaction temperature, wt% of catalyst and methanol to oil ratio and reaction temperature to methanol to oil molar ratio, respectively, on the yield of FAME.

Generally, an increase in reaction temperature is found to increase the yield of FAME in all three cases. This is due to similar explanation given in the previous section.

Another notable observation is that at lower range of reaction temperature, higher wt% of catalyst and higher ratio of methanol to oil, always resulted in FAME yield higher than when using lower wt% of catalyst and lower ratio of methanol to oil.

However, at higher range of reaction temperature, totally opposite is observed. Reactions carried out using lower ratio of methanol to oil and lower wt% of catalyst is found to have higher yield as compared to reactions using lower reaction temperature, higher ratio of methanol to oil and higher wt% of catalyst.

The former observation can be easily explained as higher reaction period will ensure the transesterification reaction goes to completion, excess methanol will drive the reaction forward and higher wt% of catalyst used will increase the availability of active sites for the reaction to occur.

However, at higher range of reaction temperature, the observations showed that using a combination of both, higher reaction temperature and higher ratio of methanol to oil or higher wt% of catalyst used is not beneficial in increasing the yield of FAME.

This is probably because at these conditions, the higher reaction temperature is already sufficient to push the reaction forward.

This phenomena is further supported by the fact that reaction temperature is the most significant process variable that effect the yield of the FAME as indicated by the highest F value in the ANOVA (Table 4.4).

The RSM was used to optimize the conditions of conversion for Jatropha biodiesel and to understand the interaction of the factors affecting Jatropha biodiesel production. Figures 4.5, 4.7 and 4.9 show surface plots between the independent and dependent variables for different fixed parameters.

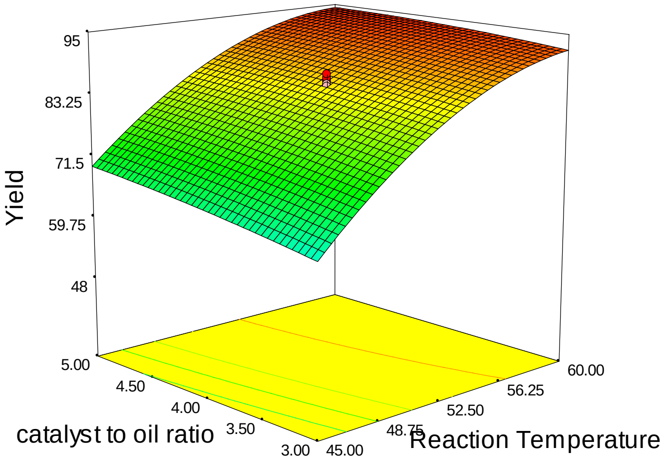


Fig 4.5: Surface plot of the interaction effect of temperature and catalyst ratio versus yield when the molar ratio of methanol to oil is 6.

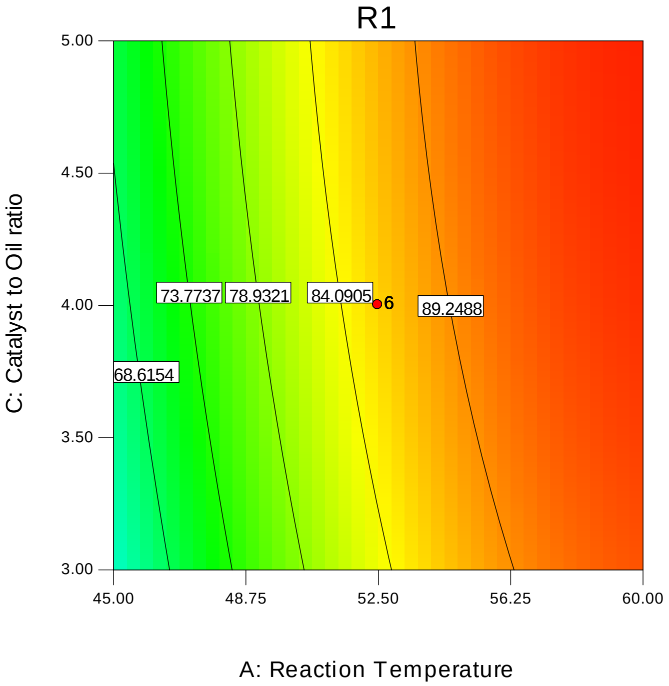


Fig 4.6: Contour plot of the interaction effect of temperature and catalyst ratio versus yield when the molar ratio of methanol to oil is 6.

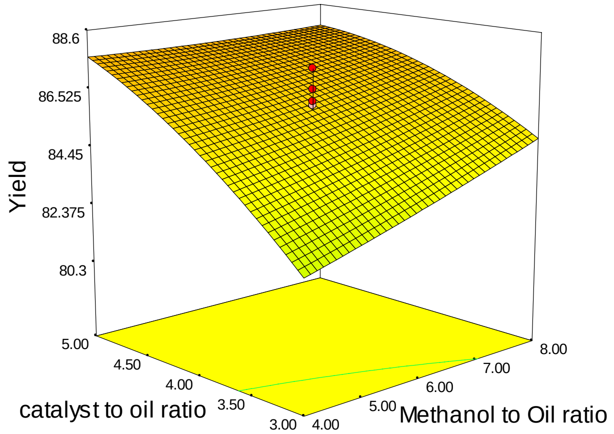


Fig 4.7: Surface plot of the Interaction effect of catalyst ratio and methanol ratio versus yield when the reaction temperature is 52.5°C.

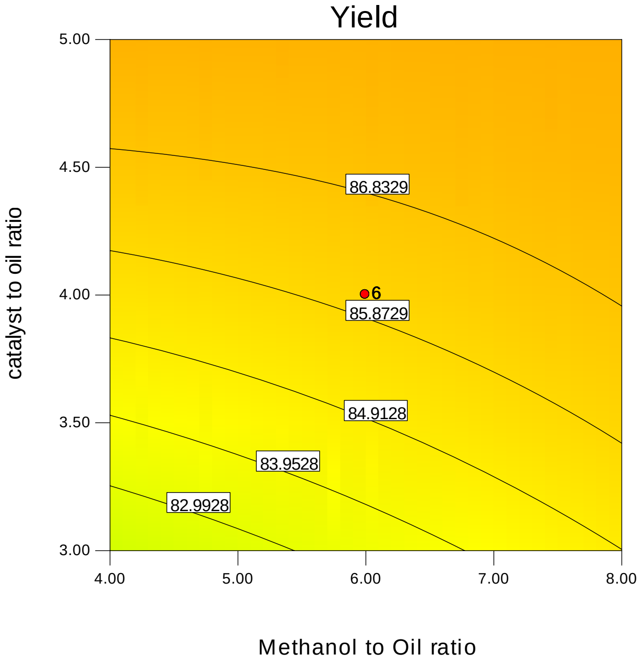


Fig 4.8: Contour plot of the Interaction effect of catalyst ratio and methanol ratio versus Yield when the reaction temperature is 52.5°C.

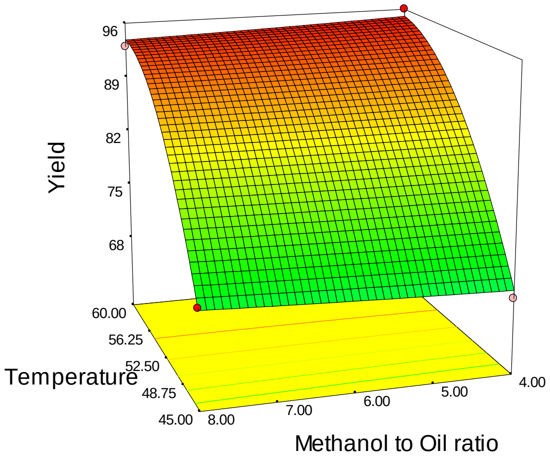


Fig 4.9: Surface plot of the interaction effect of temperature and methanol ratio versus yield when the catalyst amount is 5%.

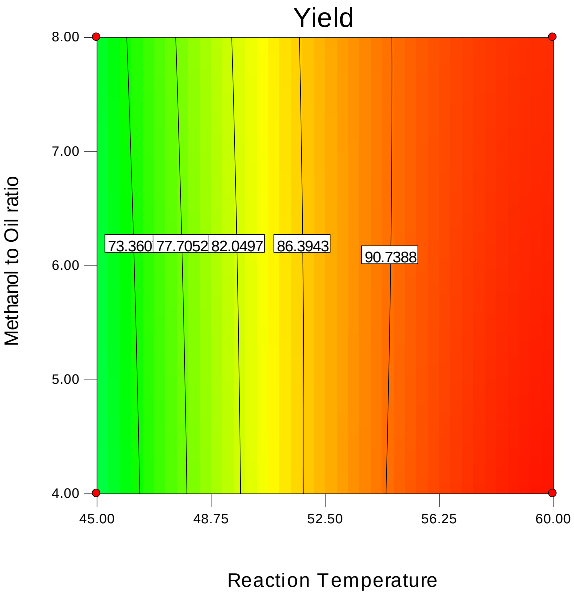


Fig. 4.10: Contour plot of the interaction effect of temperature and methanol ratio versus yield when the catalyst amount is 5%.

Figure 4.7 show the interaction between methanol to oil ratio and wt% of catalyst used, respectively on the yield of FAME. The drop in FAME yield at higher methanol to oil ratio with lower catalyst ratio could also due to catalyst leaching and deactivation. Therefore, at higher methanol to oil ratio, more catalyst might get deactivated and caused a drop in FAME yield.

From Figure 4.7, the % FAME amount increased with increasing catalyst concentration at a low methanol-to-oil molar ratio. From Figure 4.9, the % FAME amount increased with the increasing methanol-to-oil molar ratio for a low reaction temperature. From Figure 4.5, the % FAME amount increased with increasing reaction temperature at a high catalyst concentration.

4.2.2.3 Optimization of Process Variables

The results above have shown that the three transesterification process variables and the interaction among the variables affect the yield of FAME. Therefore, the next step is to optimize the process variables in order to obtain the highest yield using the model regression developed.

Using the optimization function in Design Expert, it was predicted that at the following conditions; 60^{o}C of reaction temperature, methanol to jatropha oil ratio of 4 and 5 wt% of catalyst, an optimum FAME yield of 95.08% can be obtained. In order to verify this prediction, experiments were conducted and the results were comparable with the prediction. It was found that the experimental value of 94.98% of FAME content agreed well with the predicted value. Therefore, this study shows that tribasic sodium phosphate is a potential catalyst for the production of biodiesel from jatropha oil via heterogeneous transesterification.

The optimization result also tells the same result as the ANOVA output. The ANOVA output shows that the transesterification process is highly and significantly affected by the temperature, catalyst weight and the interaction between the temperature and the catalyst.

4.3 Physico- Chemical Properties of Biodiesel

4.3.1 Specific Gravity (Density)

The density of the biodiesel produced was performed and observed to be in the range 860-900kg/m^3 at different transesterification process parameters. When we compare the average of the results with the ASTM D6751 for biodiesel 870–890 kg/m3 is acceptable.

4.3.2 Viscosity

The viscosity is a very important property related to the biodiesel utilization in direct injection diesel engines. High values of viscosity give rise to a poor fuel atomization, incomplete combustion, and carbon deposition on the injectors.

Therefore, the biodiesel viscosity must be low. In appendix c, the calculations and values of viscosity at temperature of 40 °C are listed. But in Table 4.5 the result of density and viscosity are given.

As it can be observed in Fig.4.11, for this range of temperature, the viscosities decreased with the increase of reaction temperature. The variables studied showed a similar behavior; that is, as ethyl esters yield increased, the viscosity decreased. Consequently, the viscosity, as the other properties, is related with the grade of conversion achieved that is depending on the final yield.

The viscosities of the biodiesel produced at lower temperature are higher than that of the corresponding experiments conducted with the same feed ratio but at higher temperature. This is due to effects of the operating parameters that affect the transesterification reaction.

Table 4.5: Experimental results of density and viscosity of biodiesel

Run	Reaction temperature, ^{o}C	Molar ratio of methanol to oil	Catalyst weight, g	Density, kg/m^3	Viscosity ,mm^2/sec
1	52.5	6	4	870	5.55
2	40	6	4	900	18.3
3	60	8	5	860	4.6
4	52.5	9.4	4	870	4.96
5	52.5	6	4	870	5.47
6	60	4	5	860	4.74
7	52.5	6	2.3	870	5.48
8	52.5	6	4	870	5.51
9	52.5	6	5.7	870	4.92
10	52.5	6	4	870	5.56
11	52.5	6	4	880	5.95
12	52.5	6	4	870	5.95
13	45	8	3	880	15.1
14	45	8	5	880	15.4
15	52.5	2.6	4	880	7.87
16	45	4	5	880	16.4
17	45	4	3	880	16.9
18	60	8	3	870	4.85
19	60	4	3	870	4.89
20	65	6	4	860	4.41

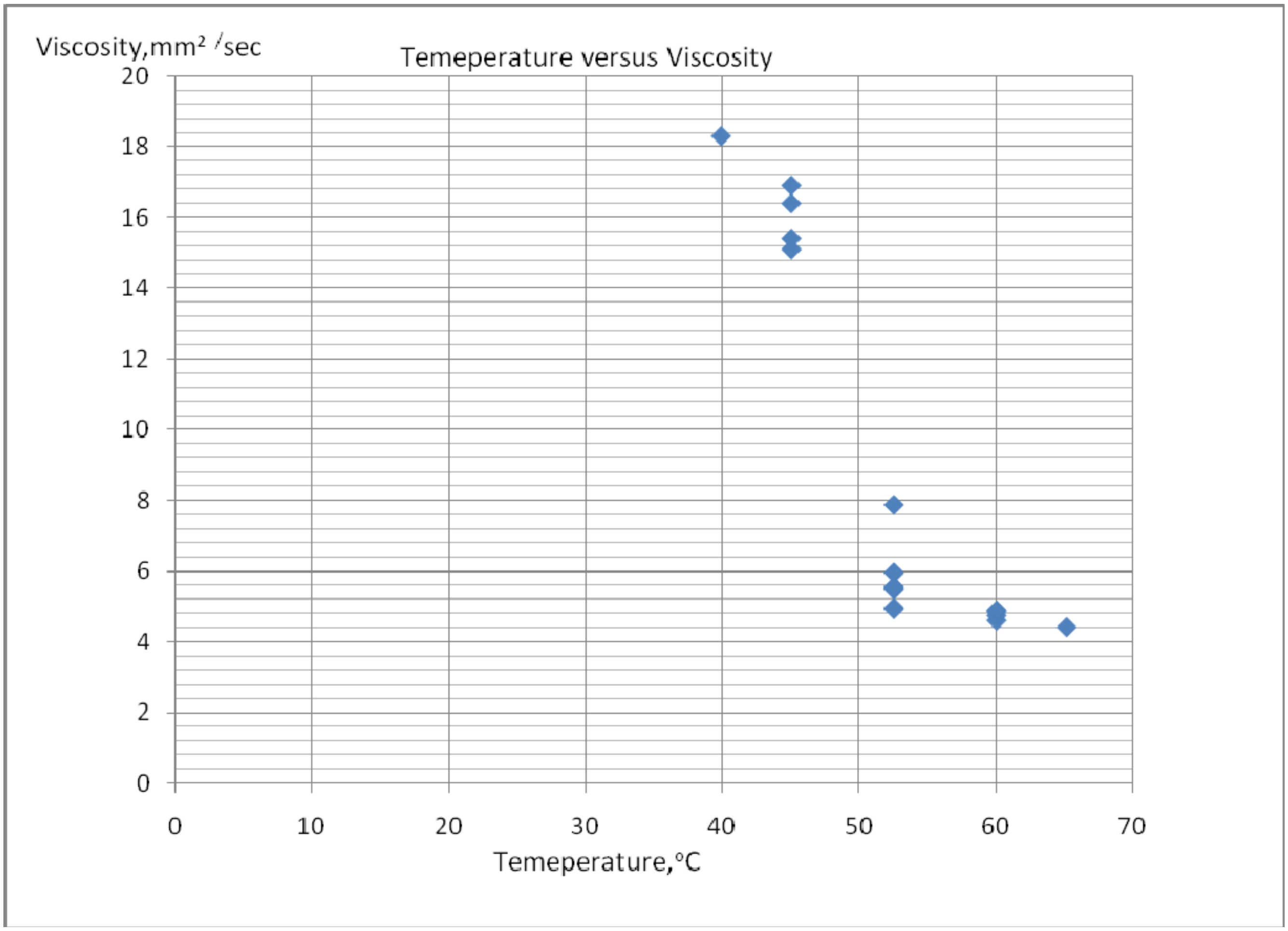


Fig. 4.11 Effect of temperature on viscosity of biodiesel

Transesterification reaction is responsible for minimizing the viscosity of vegetable oil in order to apply it as a fuel for engines yet it is significantly affected by temperature. The experimental result observed from expt't 2, 13,14,16,17 proof this idea. This experimental runs are out of the ASTM range (1.9-6mm^2/sec) for requirement of biodiesel viscosity.

Therefore, the viscosity of the biodiesel samples decreased as the operating temperature increased because as the temperature increase the transesterification reaction is facilitated.

4.3.3 Acid Value and FFA Composition

The Acid value of the biodiesel produced was found to be 0.163-0.78 mgKOH/g. The result of which indicates that acid value of the diesel decreased significantly after transesterification reaction. Jatropha oil biodiesel has acid values within the standard specification limit (max 0.8, ASTM D664). Furthermore, higher acid value resulted in low yield of biodiesel.

Table 4.6 Acid value and FFA composition of Biodiesel

Run	Reaction temperature, °C	Molar ratio of methanol to oil	Catalyst weight, g	Acid value, mgKOH/g	FFA composition
1	52.5	6	4	0.5965	0.298
2	40	6	4	0.7986	0.399
3	60	8	5	0.2239	0.112
4	52.5	9.4	4	0.3781	0.189
5	52.5	6	4	0.5843	0.292
6	60	4	5	0.1638	0.082
7	52.5	6	2.3	0.6034	0.302
8	52.5	6	4	0.5965	0.298
9	52.5	6	5.7	0.3208	0.16
10	52.5	6	4	0.5024	0.251
11	52.5	6	4	0.4614	0.231
12	52.5	6	4	0.5119	0.256
13	45	8	3	0.744	0.372
14	45	8	5	0.6894	0.345
15	52.5	2.6	4	0.6006	0.3
16	45	4	5	0.7276	0.364
17	45	4	3	0.7877	0.394
18	60	8	3	0.2061	0.103
19	60	4	3	0.3003	0.15
20	65	6	4	0.2416	0.121

4.3.4 Flash Point

The flash point measures the tendency of the sample to form a flammable mixture with air under controlled conditions. This is the property that must be considered in assessing the overall flammability hazard of a material. The flash point of FAME (B100) is greater than or equal to 130°C according to ASTM and jatropha methyl ester result observed was ≥ 176. The higher flash point of biodiesel is important advantage. The results are given in Table 4.7.

Table 4.7 Flash point of Biodiesel

Run	Reaction temperature, °C	Molar ratio of methanol to oil	Catalyst weight, g	Flash point, °C
1	52.5	6	4	209
2	40	6	4	187
3	60	8	5	220
4	52.5	9.4	4	197
5	52.5	6	4	210
6	60	4	5	230
7	52.5	6	2.3	185
8	52.5	6	4	215
9	52.5	6	5.7	225
10	52.5	6	4	209
11	52.5	6	4	210
12	52.5	6	4	214
13	45	8	3	176
14	45	8	5	180
15	52.5	2.6	4	225
16	45	4	5	190
17	45	4	3	205
18	60	8	3	224
19	60	4	3	195
20	65	6	4	218

Flash point is used in safety regulations to define “flammable” and “combustible” materials. Higher values indicate materials that are less likely to ignite accidentally. ASTM D 974 and ASTMD 93 require a minimum of 52°C for diesel and 130°C for biodiesel.

4.3.5 Higher Heating Value

It is the amount of heat released during the combustion of certain fuel. The heating value depends on the composition of the fuel. Since all the oils have very nearly the same carbon, hydrogen and oxygen contents the gross and net heating values of each fuel per unit mass will be close to each other. Biodiesel has lower energy content (lower heating value) than conventional diesel fuel. The detailed calculation is presented in appendix c. The ASTM value of the HHV is between 40-42MJ/kg. The results are given in Table 4.8.

Table 4.8Higher Heating Value for Selected Experiment run

Run	Reaction Temperature, °C	Molar ratio of methanol to oil	Catalyst weight, g	HHV ,cal/g	HHV ,MJ/kg
3	60	8	5	9688.6	40.54
6	60	4	5	9826.4	41.11
9	53	6	5.68	9524.7	39.85
18	60	8	3	9585.1	40.1
19	60	4	3	9770.4	40.88
20	65	6	4	9704.5	40.6

4.3.6 Saponification Value

According to the experiment conducted the saponification number (SN), were determined and the results are given in Table 4.9. The detailed calculation is given in appendix c.

Table 4.9: Saponification value of fatty acid methyl ester

Run	Reaction Temperature, ^{o}C	Molar ratio of methanol to oil	Catalyst weight, g	SV,mg/g
1	52.5	6	4	183
2	40	6	4	195
3	60	8	5	197
4	52.5	9.4	4	192
5	52.5	6	4	172
6	60	4	5	198
7	52.5	6	2.3	182
8	52.5	6	4	185
9	52.5	6	5.7	193
10	52.5	6	4	186
11	52.5	6	4	190
12	52.5	6	4	192
13	45	8	3	199
14	45	8	5	186
15	52.5	2.6	4	183
16	45	4	5	183
17	45	4	3	175
18	60	8	3	195
19	60	4	3	187
20	65	6	4	184

4.3.7 Iodine Value

Is a measure of total unsaturated (double bonds) within the FAME product. Iodine absorption occurs at double bond positions thus a higher IV indicates a higher quantity of double bonds in the sample and greater potential to polymerize in engine and hence lesser stability. The process of transesterification reduces the iodine value to a small extent. The ASTM requirement is a maximum of 115. The results are given in Table 4.10.

Table 4.10 Empirically determined Iodine value of methyl ester fatty acid

Run	Reaction Temperature, ^{o}C	Molar ratio of methanol to oil	Catalyst weight, g	IV, g I_2/100g
3	60	8	5	54.45
6	60	4	5	13.261
9	53	6	5.7	111.08
18	60	8	3	88.78
19	60	4	3	58.955
20	65	6	4	85.537

4.3.8 Cetane Number

Cetane number is a measure of the readiness of a fuel to auto-ignite (conceptually similar to the octane scale used for gasoline). When injected in to a diesel engine. It relates to the delay between when fuel is injected in to the cylinder and when ignition occurs. Cetane number (CN) or aniline point is a relative measure (the scale) of the interval between the beginnings of injection and auto-ignition of the fuel. Fuels with low CN will result in difficult starting, noise and exhaust smoke. In general, diesel engines will operate on fuels with cetane number > 47 (ASTM D613). Determination using empirical formulas (Kalayasiri et al., 1996) which is given in materials and methods part, using the results for Saponification number (SN) and Iodine value (IV) of the oil, the CN was calculated. The results are given in Table 4.11.

Table 4.11 Empirically determined Cetane Number of Biodiesel

Run	Reaction Temperature	Molar ratio of methanol to oil	Catalyst weight	CN
3	60	8	5	86.257
6	60	4	5	76.849
9	53	6	5.7	99.572
18	60	8	3	94.265
19	60	4	3	88.752
20	65	6	4	95.209

4.3.9 Cloud Point

The cloud point is the temperature at which a cloud of wax crystals first appears in a liquid upon cooling. A fuel property that is particularly important for the low temperature operability of diesel fuel is the cloud point.

Therefore, it is an index of the lowest temperature of the fuel’s utility under certain applications. Operating at temperatures below the cloud point for a diesel fuel can result in fuel filter clogging due to the wax crystals. As described in ASTM D 2500, the cloud point is determined by visually inspecting for a haze in the normally clear fuel, while the fuel is cooled under carefully controlled conditions.

Cloud Point data consistently over predict the cold temperature limit at which start-up or performance problems may be expected to occur. The results are given in Table 4.12.

Table 4.12 Experimental Result Cloud Point of Biodiesel

Run	Reaction Temperature, °C	Molar ratio of methanol to oil	Catalyst weight, g	Cloud point, °C
1	52.5	6	4	3
2	40	6	4	4
3	60	8	5	3
4	52.5	9.4	4	5
5	52.5	6	4	3
6	60	4	5	3
7	52.5	6	2.3	5
8	52.5	6	4	3
9	52.5	6	5.7	5
10	52.5	6	4	3
11	52.5	6	4	3
12	52.5	6	4	3
13	45	8	3	4
14	45	8	5	4
15	52.5	2.6	4	5
16	45	4	5	4
17	45	4	3	4
18	60	8	3	2
19	60	4	3	2
20	65	6	4	2

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this research, the use of heterogeneous catalysts for biodiesel production has been investigated. Three transesterification parameters affecting the yield of biodiesel; reaction temperature, molar ratio of methanol to oil and catalyst concentration has been studied The outputs of the experiments conducted have been analyzed by employing analysis of physicochemical parameters.

The result obtained shows that biodiesel production using heterogeneous catalyst, is a considerable potential in biodiesel production process, mainly because of catalyst regeneration (decrease of catalyst cost),Simplification of separation process (decrease of production cost) and decrease of wastewater (development of environmental friendly process).

Based on the experimental results obtained, it is found that all the process variables exhibited significant interaction effect on the yield of fatty acid methyl ester. This shows the capability of design of experiment analysis in successfully capturing these effects.

Of all the variables studied, temperature, methanol to oil molar ratio, mass weight of catalyst and the interaction between temperature and catalyst weight had more influence on the yield of the reaction. 333K of reaction temperature, methanol to Jatropha oil ratio of 4 and 5 wt% of catalyst, an optimum fatty acid methyl ester yield of 95.10% was obtained.

The experimental results show that sodium phosphate has excellent activity during transesterification. As a solid catalyst, sodium phosphate can decrease the waste water treatment and the steps of purification. It has a potential for industrial application in the transesterification of Jatropha oil to biodiesel. Hence, sodium phosphate has good catalytic performance.

Therefore, it can be concluded that sodium phosphate is an effective catalyst for the production of biodiesel from jatropha oil via heterogeneous transesterification. An increase in the biodiesel caused an increase in the catalyst content.

The drop in fatty acid methyl ester yield at higher methanol to oil ratio with lower catalyst ratio could also be due to catalyst leaching and deactivation. The fatty acid methyl ester amount increased with increasing catalyst concentration at a low methanol-to-oil molar ratio. The fatty acid methyl ester amount increased with the increasing methanol-to-oil molar ratio for a low reaction temperature. The fatty acid methyl ester amount increased with increasing reaction temperature at a high catalyst concentration.

Physicochemical properties determined for the biodiesel produced meet the ASTM specification except viscosity for some experiments conducted at low reaction temperature.

5.2 Recommendation

Further research has to be conduct on the analysis of jatropha oil transesterification to biodiesel via heterogeneous catalysis using gas chromatogram or high performance liquid chromatography since it will help to know the exact composition of fatty acid methyl ester and biodiesel conversion.

Beside this, reusability is one of the most important properties of a solid catalyst. To reduce the production cost of biodiesel, the catalyst has to be recycled. So that the catalyst was regenerated and used again and again until the point at which we can get optimum yield. Hence, further research has to be done on catalyst reusability.

Moreover, I recommend further study on blending the biodiesel with diesel and engine tests has to be carried out with biodiesel produced via heterogeneous transesterification.

Since ethanol is available in Ethiopia in the future, I recommend future work on investigation of biodiesel production using heterogeneous catalyst and ethanol.

Additionally, I recommend that preliminary design of pilot plant, process development and scale-up has to be performed.

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APPENDICES

Appendix A: Composition of Jatropha Oil

Table A1: Fatty Acid Composition of Jatropha oil

Fatty Acid	Systemic Name	Formula	Structure	Wt %
Myristic	Tetradecanoic	$C_{14}H_{28}O_2$	14:0	0-0.1
Palmitic	Hexadecanoic	$C_{16}H_{32}O_2$	16:0	14.1-15.3
Palmitoleic	cis-9-Hexadecenoic	$C_{16}H_{30}O_2$	16:1	0-1.3
Stearic	Octadecanoic	$C_{18}H_{36}O_2$	18:0	3.7-9.8
Oleic	Cis-9-Octadecenoic	$C_{18}H_{34}O_2$	18:1	34.3-45.8
Linoleic	Cis-9,cis-12-octadecadienoic	$C_{18}H_{32}O_2$	18:2	29.0-44.2
Linolenic	Cis-6,cis-9,cis-12-octadecatrienoic	$C_{18}H_{30}O_2$	18:3	0-0.3
Arachidic	Eicosanoic	$C_{20}H_{40}O_2$	20:0	0-0.3
Behenic	Docosanoic	$C_{22}H_{44}O_2$	22:0	0-0.2

Adapted from Berchmans and Hirata, 2007

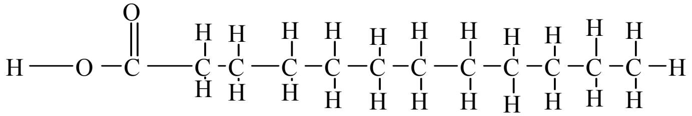
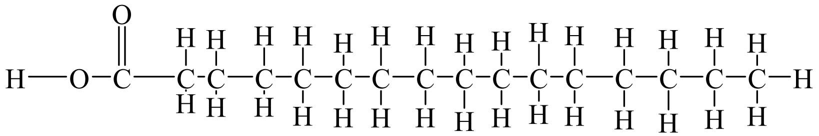
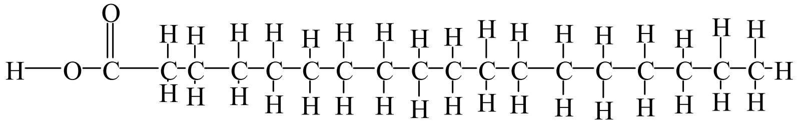
xx: y indicates xx carbons in the fatty acid chain with y double bond

Table A2: Fatty acid composition of different oil

Fatty Acid	Jatropha curcas oil	Sunflower oil	Soybean oil	Palm oil
oleic 18:1	44.7	21.1	23.4	39.2
Linoleic 18:2	32.8	66.2	53.2	10.1
Palmitic 16:0	14.2		11	44
Stearic 18:0	7	4.5	4	4.5
Palmitoleic 16:1	0.7			
Linolenic 18:3	0.2		7.8	0.4
Arachidic 20:0	0.2	0.3		
Margaric 17:0	0.1			
Myristic 14:0	0.1		0.1	1.1
Caproic 10:0				
Caprylic 8:0				
Lauric 12:0				0.2
Capric 6:0				
Saturated	21.6	11.3	15.1	49.9
Monounsaturated	45.4	21.2	23.4	39.2
Polyunsaturated	33	66.2	61	10.5

From Edem, D.O. (2002)

Table A3: Description of the main fatty acid contents of vegetable oils

SATURATED			
Fatty acid	STRUCTURAL FORMULA	SYMBOL	Molecular formula
Lauric acid	 $H-O-\overset{\overset{O}{\|}}{C}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$	C12:O	$C_{12}H_{24}O_2$
Palmitic acid	 $H-O-\overset{\overset{O}{\|}}{C}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$		
Stearic acid	 $H-O-\overset{\overset{O}{\|}}{C}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$	C18:O	$C_{18}H_{36}O_2$

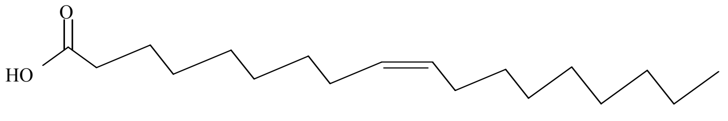
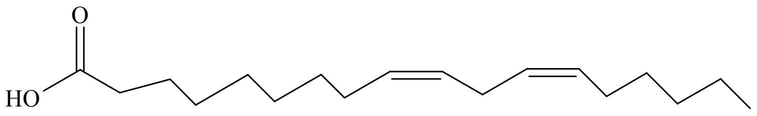
UN SATURATED			
Fatty acid	STRUCTURAL FORMULA	SYMBOL	Chemical formula
Oleic acid		C18:1	$C_{18}H_{34}O_2$
Linoleic acid		C18:2	$C_{18}H_{32}O_2$

Table A4: Jatropha curcas oil Characteristics

Property	Range
Specific gravity(g/cm3)	0.860-0.933
Calorific value(MJ/kg)	37.87-42.05
Pour Point	-3
Cloud Point	2
Flash Point	210-240
Cetane Value	38-51
Saponification number(mg/g)	102.9-209
Viscosity at30oC(cSt)	37-54,8
Free fatty acids %(kg/kg *100)	0.18-3.40
Unsaponifiable %(kg/kg *100)	0.79-3.80
Iodine number(mg iodine/g)	92-112
Acid number(mg KOH/g)	092-6.16
Monoglycerides(kg/kg *100)	up to 1.7
Diglycerides(kg/kg *100)	2.5-2.7
Triglycerides(kg/kg *100)	88.2-97.3
Carbon residue(kg/kg *100)	0.07-0.64
Sulfur content(kg/kg *100)	0-0.13

Source: [25]

Appendix B: Standard Specifications of Biodiesel

Table B1: Specification of EN 14214 comparing to conventional diesel

Properties	Diesel	Biodiesel
density,288K	0.82 -.86	0.86 -0.90
viscosity,313K	2.0 -4.5	3.5 -5.0
Flash point, K	> 377	> 130
Sulfur, % mass	< 0.2	< 0.01
sulphated ash (% mass)	< 0.01	< 0.02
water (mg/Kg)	< 200	< 500
Carbon residues (% weight)	< 0.3	< 0.03
Cetane number	> 45	> 51
Acid Value(mg KOH/g)		< 0.8
Methanol(% mass)	-	< 0.2
MG content (% mass)	-	< 0.8
DG content (% mass)	-	< 0.2
TG content (% mass)	-	< 0.4
free glycerin (% mass)	-	< 0.02
Total glycerin	-	< 0.25
Iodine number	-	<120
Cloud Point		Report to the customer
Pour point		Report to customer
Phosphorus (mg/Kg)	-	< 10

Table B2: Jatropha curcas oil methyl ester literature characteristics

Property	Range
density(g/cm3)	0.864-0.875
calorific value(MJ/kg)	38.45-41
Flash point	170-192
Cetane Value	50-56.1
saponification number(mg/g)	202.6
viscosity at30oC(cSt)	4.84-5.65
iodine number(mg iodine/g)	93-106
acid number(mg KOH/g)	0.06-0.5
monoglycerides(kg/kg *100)	0.24
diglycerides(kg/kg *100)	0.07
triglycerides(kg/kg *100)	-
carbon residue(kg/kg *100)	0.02-0.5
sulfur content(kg/kg *100)	0.0036
sulphated ash %(kg/kg *100)	0.005-0.010
Methyl ethyl ester content %((kg/kg *100))	99.6
Methanol %((kg/kg *100))	0.06-0.09
water % (kg/kg *100)	0.07-0.10
free glycerol	0.015-0.030
total glycerol	0.088-0.100

Source: [25]

Table B3: Physico-Chemical Properties of Biodiesel from Different oil raw material Source: [2]

Feed stock	Kinematic Viscosity (cst at 40oC)	Density (g/cm3)	Saponification number, mg/g	Iodine value, g I_2/100g	Acid value(mg KOH/g)	Cetane Number	Heating value(MJ/kg)
soybean	4.08	0.885	201	138.7	0.15	52	40
rapeseed	4.3-5.83	0.88-0.888			0.25-0.45	49-50	45
sunflower	4.9	0.88	200	142.7	0.24	49	45.3
Palm	4.42	0.86-0.9	207	60.07	0.08	62	34
peanut	4.42	0.883	200	67.45		54	40.1
Corn	3.39	0.88-0.89	202	120.3		58-59	45
camelina	6.12-7	0.882-0.88		152-157	0.08-0.52		
Canola	3.53	0.88-0.9	182	103.8		56	45
Cotton	4.07	0.875	204	104.7	0.16	54	45
pumpkin	4.41	0.8837	202	115	0.48		38
jatropha curcas	4.78	0.8636	202	108.4	0.496	61-63	40-42
pongamina pinnata	4.8	0.883			0.62	60-63	42
Sea mango							
palanga	3.99	0.869					41
Tallow		0.856	244.5	126	0.65	59	
nile tilapia				88.1	1.4	51	
Poultry		0.867	251.23	130	0.25	61	
used cooking oil	4				0.15		

Appendix C: Experimental Result

Table C1: Viscosity of jatropha curcas oil

Dynamic viscosity,mpa.sec at 40^{o}C					Dynamic Viscosity Avg.	Density kg/m^3	Kinematic viscosity,mm^2/sec
26.4	28.1	28.7	29.2	29.8	28.4	900	30.9

Table C2: Saponification value of jatropha curcas oil

Run	N $_{HCL}$	$V_{b\ HCL}$	Va $_{HCL}$	V_b-V_a ,ml	mass of Oil, g	SV, mg/g
1	0.46	31.9	15.9	16	2	206.448
2	0.46	31.9	16.1	15.8	2	203.8674
3	0.46	31.9	16	15.9	2	205.1577
						205.16

Table C3: Acid Value of jatropha curcas oil

N $_{KOH}$	V $_{KOH}$,ml	mass of oil, g	AV, mg KOH/g	FFA Composition
0.073	4.14	2	8.477271	4.2386355
0.073	4	2	8.1906	4.0953
0.073	4.2	2	8.60013	4.300065
			8.422667	4.2113335

Table C4: Calibration of bomb calorimeter

m' min	Δn	Δv	F	C	Unburnt wire	Sum of b	to	tm	tm+C-to, min	m_c of apparatus
10	0.0025	0.0085	1.25	0.0113	0	21	1.51	4.17	2.67125	359.5694899

Table C5: Heating Value of Jatropha curcas oil

m' min	Δn	Δv	F	C	to	tm	tm+C-to, min	Unburnt wire	Sum of b	HHV cal/g	HHV MJ/kg
9	3.5E-07	0.011	1.25	0.0137	1.52	4.75	3.243747	4	15	9548.52	39.95

Table C6: Experimental Processes Conditions for Biodiesel Production

Factors	Run #1		Run #2		Run #3	
Reaction Temperature	52.5	°C	39.9	°C	60	°C
Methanol to oil ratio	6	25.5ml	6	25.5ml	8	34ml
Catalyst to oil ratio	4	3.6g	4	3.6g	5	4.5g
	Run #4		Run #5		Run #6	
Reaction Temperature	52.5	°C	52.5	°C	60	°C
Methanol to oil ratio	9.4	40ml	6	25.5ml	4	17ml
Catalyst to oil ratio	4	3.6g	4	3.6g	5	4.5g
	Run #7		Run #8		Run #9	
Reaction Temperature	52.5	°C	52.5	°C	52.5	°C
Methanol to oil ratio	6	25.5ml	6	25.5ml	6	25.5ml
Catalyst to oil ratio	2.32	2.1g	4	3.6g	5.68	5.1g
	Run #10		Run #11		Run #12	
Reaction Temperature	52.5	°C	52.5	°C	52.5	°C
Methanol to oil ratio	6	25.5ml	6	25.5ml	6	25.5ml
Catalyst to oil ratio	4	3.6g	4	3.6g	4	3.6g
	Run #13		Run #14		Run #15	
Reaction Temperature	45	°C	45	°C	52.5	°C
Methanol to oil ratio	8	34ml	8	34ml	2.64	11.22 ml
Catalyst to oil ratio	3	2.7g	5	4.5g	4	3.6g

Factors	Run #16		Run #17		Run #18	
Reaction Temperature	45	^{o}C	45	^{o}C	60	^{o}C
Methanol to oil ratio	4	17ml	4	17ml	8	34ml
Catalyst to oil ratio	5	4.5	3	2.7g	3	2.7g
	Run #19		Run #20			
Reaction Temperature	60	^{o}C	65	^{o}C		
Methanol to oil ratio	4	17ml	6	25.5ml		
Catalyst to oil ratio	3	2.7g	4	3.6g		

Table C7: Fatty Acid methyl ester (Biodiesel) composition for different processes variables

Run	Reaction Temperature	Methanol to oil ratio	Catalyst weight	Oil Input	Biodiesel Output	FAME Composition
1	52.5	6	4	100	85	85
2	40	6	4	100	48.2	48.2
3	60	8	5	100	93	93
4	52.5	9.36	4	100	87.86	87.86
5	52.5	6	4	100	86	86
6	60	4	5	100	96	96
7	52.5	6	2.3	100	80.38	80.38
8	52.5	6	4	100	85.42	85.42
9	52.5	6	5.7	100	88.58	88.58
10	52.5	6	4	100	86.56	86.56
11	52.5	6	4	100	87.3	87.3
12	52.5	6	4	100	86.14	86.14
13	45	8	3	100	64.76	64.76
14	45	8	5	100	70.68	70.68
15	52.5	2.64	4	100	84.66	84.66
16	45	4	5	100	68	68
17	45	4	3	100	62.38	62.38
18	60	8	3	100	94	94
19	60	4	3	100	91.22	91.22
20		6	4	100	92.1	92.1

Table C 8: Fatty Acid methyl ester (Biodiesel) density and viscosity for different processes variables

Run	A	B	C	DV1	DV2	DV3	DV4	DV5	DVavg	ρ	(DV/D)	KV
1	52.5	6	4	4.74	4.78	4.82	4.86	4.93	4.83	870	0.0055	5.55
2	40	6	4	16.37	16.39	16.44	16.5	16.53	16.4	900	0.0183	18.3
3	60	8	5	3.97	3.96	3.93	3.95	3.98	3.96	860	0.0046	4.6
4	52.5	9.4	4	4.19	4.26	4.31	4.39	4.42	4.31	870	0.005	4.96
5	52.5	6	4	4.65	4.71	4.78	4.8	4.84	4.76	870	0.0055	5.47
6	60	4	5	3.91	3.97	4.08	4.11	4.31	4.08	860	0.0047	4.74
7	52.5	6	2.3	4.68	4.72	4.75	4.82	4.87	4.77	870	0.0055	5.48
8	52.5	6	4	4.71	4.74	4.76	4.84	4.9	4.79	870	0.0055	5.51
9	52.5	6	5.7	4.13	4.22	4.29	4.37	4.4	4.28	870	0.0049	4.92
10	52.5	6	4	4.77	4.81	4.83	4.87	4.91	4.84	870	0.0056	5.56
11	52.5	6	4	5.19	5.21	5.23	5.25	5.28	5.23	880	0.0059	5.95
12	52.5	6	4	5.11	5.16	5.19	5.21	5.23	5.18	870	0.006	5.95
13	45	8	3	13.25	13.29	13.3	13.3	13.35	13.3	880	0.0151	15.1
14	45	8	5	13.48	13.51	13.55	13.6	13.61	13.5	880	0.0154	15.4
15	52.5	2.6	4	6.87	6.89	6.92	6.96	6.99	6.93	880	0.0079	7.87
16	45	4	5	14.37	14.41	14.47	14.5	14.56	14.5	880	0.0164	16.4
17	45	4	3	14.81	14.84	14.87	14.9	14.96	14.9	880	0.0169	16.9
18	60	8	3	4.17	4.18	4.19	4.25	4.32	4.22	870	0.0049	4.85
19	60	4	3	4.15	4.2	4.24	4.31	4.36	4.25	870	0.0049	4.89
20	65	6	4	3.89	3.83	3.75	3.74	3.77	3.8	860	0.0044	4.41

Where DV=Dynamic Viscosity, mPa.sec and KV=Kinematic Viscosity, mm^2/sec

ρ=Density, kg/m^3 and KV=Kinematic Viscosity= (DV/ρ)*1000

Table C9: Fatty Acid Methyl ester Acid Value and FFA Composition Experimental Result

Run	N of KOH	V KOH	V2,ml	V3, ml	mass of oil, g	AV1	AV2	AV3	Average AV, mg KOH/g	FFA Composition
1	0.073	1.46	1.44	1.47	10	0.59	0.602	0.598	0.5965	0.298
2	0.073	1.9	2	1.95	10	0.82	0.799	0.778	0.7986	0.399
3	0.073	0.55	0.55	0.54	10	0.23	0.221	0.225	0.2239	0.112
4	0.073	0.92	0.94	0.91	10	0.38	0.373	0.377	0.3781	0.189
5	0.073	1.42	1.43	1.43	10	0.59	0.586	0.582	0.5843	0.292
6	0.073	0.99	0.11	0.1	10	0.05	0.041	0.405	0.1638	0.082
7	0.073	1.45	1.48	1.49	10	0.61	0.61	0.594	0.6034	0.302
8	0.073	1.46	1.45	1.46	10	0.59	0.598	0.598	0.5965	0.298
9	0.073	0.78	0.78	0.79	10	0.32	0.324	0.319	0.3208	0.16
10	0.073	1.2	1.22	1.26	10	0.5	0.516	0.491	0.5024	0.251
11	0.073	1.12	1.11	1.15	10	0.45	0.471	0.459	0.4614	0.231
12	0.073	1.2	1.3	1.25	10	0.53	0.512	0.491	0.5119	0.256
13	0.073	1.8	1.83	1.82	10	0.75	0.745	0.737	0.744	0.372
14	0.073	1.67	1.7	1.68	10	0.7	0.688	0.684	0.6894	0.345
15	0.073	1.45	1.47	1.48	10	0.6	0.606	0.594	0.6006	0.3
16	0.073	1.78	1.76	1.79	10	0.72	0.733	0.729	0.7276	0.364
17	0.073	1.92	1.94	1.91	10	0.79	0.782	0.786	0.7877	0.394
18	0.073	0.5	0.52	0.49	10	0.21	0.201	0.205	0.2061	0.103
19	0.073	0.74	0.71	0.75	10	0.29	0.307	0.303	0.3003	0.15
20	0.073	0.58	0.6	0.59	10	0.25	0.242	0.238	0.2416	0.121

Table C 10: Heating Value (Calorific value) of Selected Experimental Run Result

Run	m' min	Δn	Δv	F	C	To	tm	tm+C-to, min	Unburnt wire, m	Sum of b	HHV cal/g	HHV MJ/kg
3	10	0.005	0.0077	1.25	0.03	1.75	5.01	3.29238	2.2	17.7	9688.6	40.54
6	10	0.003	0.0074	1.25	0.02	1.56	4.88	3.33875	2.78	16.83	9826.4	41.11
9	10	0.004	0.0076	1.25	0.03	1.5	4.711	3.2365	2.72	16.92	9524.7	39.85
18	10	0.002	0.0016	1.25	0.01	1.54	4.786	3.25713	2.46	17.31	9585.1	40.1
19	10	0.001	0.0013	1.25	0.01	1.59	4.899	3.31993	2.5	17.25	9770.4	40.88
20	10	0.001	0.0014	1.25	0.01	1.5	4.787	3.2975	2.64	17.04	9704.5	40.6

Table C 11: Experimental Result of Saponification value of Biodiesel

Run	N of HCL	Vb HCL	Va HCL 1	Va HCL 2	(Vb-Va)1 ml	(Vb-Va)2 ml	mass of Oil, g	SV1	SV2	SV , mg/g
1	0.46	31.9	17.8	17.7	14.1	14.2	2	181.9	183.2	183
2	0.46	31.9	16.8	16.8	15.1	15.1	2	194.8	194.8	195
3	0.46	31.9	16.5	16.8	15.4	15.1	2	198.7	194.8	197
4	0.46	31.9	17	17.1	14.9	14.8	2	192.3	191	192
5	0.46	31.9	18.6	18.5	13.3	13.4	2	171.6	172.9	172
6	0.46	31.9	16.6	16.6	15.34	15.3	2	197.9	197.4	198
7	0.46	31.9	17.7	17.9	14.24	14	2	183.7	180.6	182
8	0.46	31.9	17.7	17.5	14.2	14.4	2	183.2	185.8	185
9	0.46	31.9	17	17	14.94	14.9	2	192.8	192.3	193
10	0.46	31.9	17.3	17.7	14.64	14.2	2	188.9	183.2	186
11	0.46	31.9	17.1	17.2	14.78	14.7	2	190.7	189.7	190
12	0.46	31.9	17.1	16.9	14.78	15	2	190.7	193.5	192
13	0.46	31.9	16.6	16.4	15.3	15.5	2	197.4	200	199
14	0.46	31.9	17.5	17.5	14.4	14.4	2	185.8	185.8	186
15	0.46	31.9	17.7	17.8	14.2	14.1	2	183.2	181.9	183
16	0.46	31.9	17.7	17.7	14.2	14.2	2	183.2	183.2	183
17	0.46	31.9	18.4	18.2	13.5	13.7	2	174.2	176.8	175
18	0.46	31.9	16.6	16.9	15.26	15	2	196.9	193.5	195
19	0.46	31.9	17.4	17.4	14.46	14.5	2	186.6	187.1	187
20	0.46	31.9	17.4	17.9	14.5	14	2	187.1	180.6	184

Appendix D: GC Analysis of Biodiesel from Literature

Table D1: Chromatograph of a reference rapeseed Biodiesel

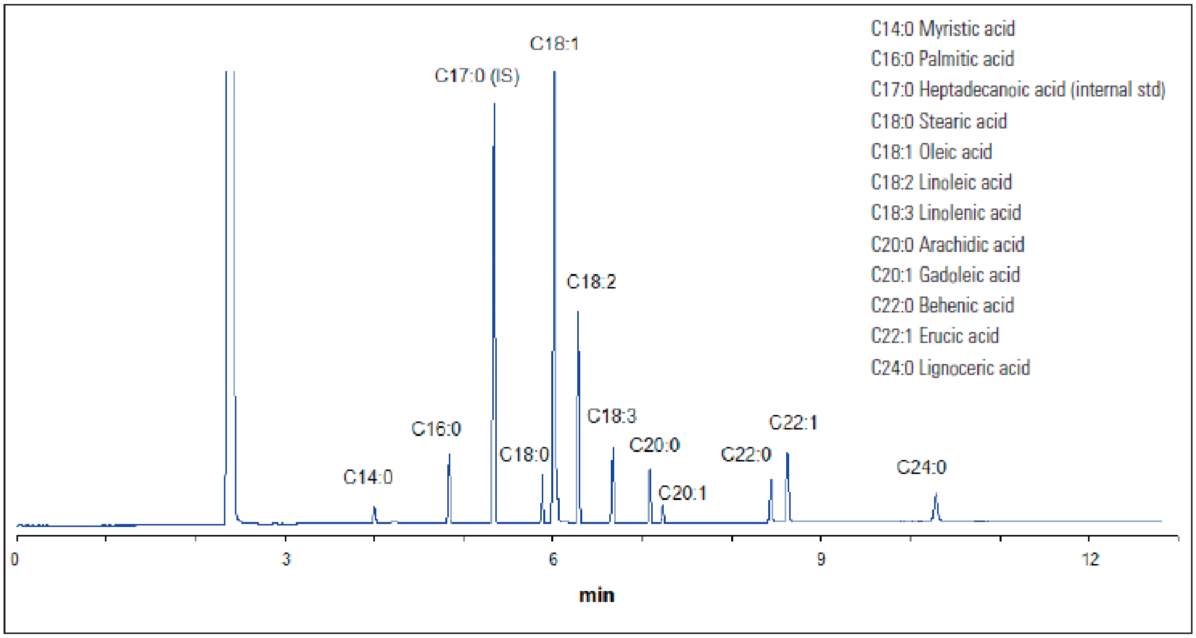


Figure 3: Chromatogram of a reference rapeseed biodiesel

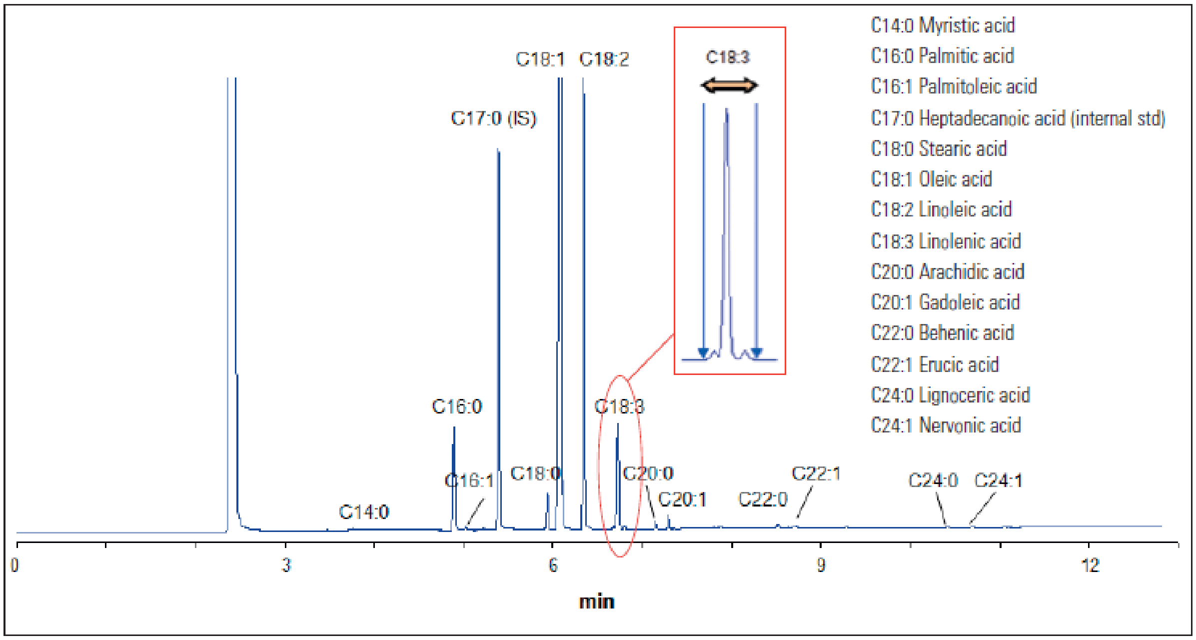


Figure 4: Chromatogram of an unknown biodiesel

Appendix E: Calculation Part

E1: Purification of the Crude Oil

The total amount of crude Jatropha curcas oil obtained from extraction with hexane is 3.2 liter out of 7.6kg of Jatropha seed kernel.

Degumming

It is the removal of phosphatides, gums and other complex compounds the extracted crude Jatropha oil. Hence, based on the method discussed in previous chapter; 3% of distilled water and 2% of phosphoric acid by volume is required for degumming the crude Jatropha oil.

Hence, amount of phosphoric acid required=amount of Jatropha oil*2%

=3.2liter*0.02

=0.064liter or 64ml

Amount of distilled water required= amount of Jatropha oil*3%

=3.2 liter*0.03

=0.096liter or 96ml

Neutralization

This step is used to neutralize the free fatty acids using appropriate amount of NaOH. Sodium chloride (about 10% of the weight of the oil) was added to help settle out the soap formed.

Amount of sodium chloride (makes the soap to settle faster) =10% of oil

=0.29g

The appropriate amount of alkaline solution (NaOH) required to neutralize the free fatty acid was calculated by the following chemical reaction. First of all, the composition of free fatty acid was determined from the acid value.

The acid value is determined by using titration.

R1-COO-CH	+	NaOH		R1-COONa	+	H20
FFA		Base	⟶	Soap		Water

Recall Eq. 3.4

$$Acid\ Number = \frac{V * N * 56.1}{m}$$

Where

V = the titrant volume expressed in milliliter of 0.1N solution of ethanolic KOH at which the end point is observed=3ml

m = mass in gram of the sample weight=2g

N = concentration of ethanolic KOH=0.1

Substituting numerical values,

AV= (3*0.1*56.1)/2 =8.4mg of KOH/g of oil

AV=FFA*2

% composition of FFA=AV/2=4.21, Hence, there are 0.122g of FFA in the oil which will affect the transesterification reaction during biodiesel production. This free fatty acid was removed by using stoichiometric amount of sodium hydroxide. Hence, amount of NaOH required to neutralize the free fatty acids is 0.0176g.

E2: Physico- Chemical Properties of Purified Oil

Saponification Value

The saponification number was determined by using titration. I prepared the solution with the required concentration. Since we don't know the exact concentration, we have to standardize the solution. Hence, primary and secondary standardization was used.

Mass of KOH=N*equivalent weight*Volume of solution in liter
=0.5mol/lit*56.11g/mol*1lit
=28.055gm

Mass of HCL= N*equivalent weight*Volume of solution in liter
=0.5*36.5*1
=18.25gm

V_{HCL}=m/ρ=18.25/1.16 =15.73ml

0.53 gm of sodium carbonate was dilute in 100ml distilled water was used as a primary standard with a known concentration which is 0.1 normality.

25ml solution of sodium carbonate was taken and titrated with HCL solution to determine the concentration using 3 drops of methyl orange as indicator. The Volume was noted as the end point appears.

$$V_1N_1=V_2N_2 \qquad \text{Eq.4.1}$$

$$N_2= (V_1N_1)/V_2 =25*0.1/5.4 =0.46$$

Another experiment was done to validate the concentration;

$$N_2=25*0.1/5.5=0.4545$$

$$N_3=25*0.1/5.4 =0.46$$

Then the average concentration becomes;

$$N_{HCL}=0.46$$

Similarly, HCL is used to standardize the ethanolic alcohol solution.25ml of ethanolic KOH was titrated against HCL using 3 drop methyl orange as indicator to determine the exact concentration of ethanolic KOH.The volume of HCL was noted.

$$N_{31}= (V_2N_{2)}/V_3 =34.7*0.46/25 =0.634$$

$$N_{32}= (33.9*0.46)/ 25=0.619$$

$$N_{33}= (33.8*0.46) /25 =0.623$$

$$N_{KOH}=0.625$$

5gm of oil was dissolved in ethanolic KOH and titrated with HCL. Blank titration was done titrating ethanolic KOH against HCL. In both cases, the volume of HCL was recorded. Hence, the Saponification value observed was 205.16 which is in agreement with literature data. The experimental result was attached in appendix c.

DECLARATION

I declare that the thesis for the M.Sc. degree at the University of Addis Ababa, hereby submitted by me, is my original work and has not previously been submitted for degree at this or any other university, and that all resources of materials used for this thesis have been duly acknowledged.

Name: **Temesgen Mathewos Fitamo**
Signature: ___________________
Date of Submission:___________________

This thesis has been submitted for examination with my approval as a university advisor.

Name: **Dr. Ing Nurelegn Tefera**
Signature: ___________________
Date:___________________