ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING

PRODUCTION AND CHARACTERIZATION OF BIODIESEL FROM JATROPHA CURCAS SEED BY USING K_2O/FLY ASH AS A CATALYST

BY

TINSU GEBREYOHANS

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Advisor	Signature	Date
Dr. Berhanu Assefa	_____	_____
Internal Examiner	Signature	Date
Dr. Beteley Tekola	_____	_____
External Examiner	Signature	Date
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School Chairperson	Signature	Date

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I declare that, this thesis entitled "*production and characterization of biodiesel from Jatropha curcas seed using K_2O/fly ash as a catalyst*" has not been submitted in any form for another degree, diploma or an award at any university or other institution of the tertiary education. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature and discussions. Information taken from published and unpublished work of others has been acknowledged in the text and a list of references is given. The work was under the guidance of Professor Belay Woldeyes (Dr.Ing) instructor in Addis Ababa University, School of Chemical and Bio Engineering.

Name: Tinsu Gebreyohans

Signature: _____

Date of Submission: _____

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ABSTRACT

The fly ash based catalyst was prepared using the wet impregnation procedure with different loadings of potassium hydroxide. The prepared catalyst was characterized by powder X-ray diffraction (XRD) and Fourier transformed infrared spectroscopy (FTIR). The K_2O/fly ash based catalyst at a reaction temperature of 60ºC, molar ratio of methanol to oil of 6:1 and reaction time of 2 hours exhibited maximum oil conversion (94.5%)due that this catalyst was selected for the whole experimental study. Biodiesel was produced via transesterification reaction process using K_2O/fly ash as a heterogeneous catalyst, and purified Jatropha curcas seed oil which is extracted from the Jatropha seed bought from Awash Melkasa. To obtain a high percentage yield of biodiesel fuel that comply the specification of standard methods, some important variables such as molar ratio of methanol to oil (6:1-12:1), reaction temperature of (50-60ºC) and catalyst loading of (2-4Wt.%) was investigated and an optimum biodiesel (FAME) yield of 92.68% was obtained At the following conditions; 60ºC of reaction temperature, molar ratio of methanol to oil of 6.5:1 and 3.44wt.% of catalyst, which indicating that K_2O/fly ash based catalyst has the potential as a heterogeneous catalyst. The biodiesel produced was tested and important fuel properties of the methyl esters (Biodiesel) compared well with ASTM biodiesel standard. The experimental design and statistical analysis were done by Design-Expert 7.0.0 program. Response surface methodology (RMS) employing the central composite design (CCD) was used to optimize the biodiesel production.

Keywords: Fly ash, Transesterification, Jatropha oil, Biodiesel

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ACRONYMS

ANOVA	Analysis of Variance
ASTM	American Society for Testing and Material
AV	Acid Value
FA	Fly Ash
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography-Mass Spectroscopy
LIDI	Leather Industry Development Institute
RSM	Response Surface Method
SEM	Scanning Electron Microscope
SV	Saponification Value
XRD	X-ray Diffraction

1. INTRODUCTION

Energy is the most necessary demand for human existence. There are many reasons for the search of an alternative fuel where an increased demand for fossil fuels in all sectors of human life and those fossil fuel resources are non-renewable. Different alternatives such as wind, solar, hydro, nuclear, biofuel, and biodiesel have been suggested. But biodiesel is still in the research and development stage in our country.

Biodiesel or methyl ester is a fuel from vegetable oils that have properties similar to diesel derived from fossils. Biodiesel can be used either pure or blended with diesel without changes on other machines that use it. The use of biodiesel as an energy is demanding to be realized. Because, besides being a solution to the scarcity of fossil energy in the future, biodiesel also be renewable, can decompose (biodegradable), has the lubrication properties of the piston engine because it includes a group of nondrying oil, is able to reduce emissions carbon dioxide and the greenhouse effect. Biodiesel is also environmentally friendly because emissions gas is much lower than diesels derived from fossil which is free of sulfur, lower smoke number, burn completely, and does not produce toxins (Dhewayani 2017).

The satisfactory replacement of diesel derived from fossil with biodiesel is feasible only if it meets two basic requirements: first if its easy availability and environmentally friendly and second being economically reasonable. Thus, feedstock for biodiesel production could be divided into different categories such as edible oils, non-edible oils, waste oils, animal fats, and algal lipids. There is a growing interest in using Jatropha curcas oil as the feedstock for biodiesel production because it is non-edible and thus does not compromise the edible oils, which are mainly used for food consumption. Non-edible oils are not suitable for human consumption because of the presence of toxic components. Further, Jatropha Curcas seed has a high content of oil and the biodiesel produced has similar properties to that of petroleum-based diesel (Helwani et al. 2013).

The uses of fossil fuels as sources of energy are increasingly coming under inspection. Fossil fuels are non-renewable and as such are unsustainable long-run sources of energy. In addition to this, consumption of fossil fuels is a major source of air pollution and a significant contributor to greenhouse gas emissions. These apparent costs have caused many to look towards as an

alternative source of transport fuel energy worldwide. The uses of fossil fuels as sources of energy are increasingly coming under inspection.

Ethiopia is among 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.

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. 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. 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 such as fly ash to produce biodiesel, because of their environmental and economic advantages.

This thesis is aimed to study the effect of K_2O/fly ash catalyst loading to the transesterification yield and conducted by several factors and variables.

1.1. Statement of the Problem

One of the most promising options of substituting the imported petroleum products is to rely on the production of biofuel from indigenous biomass. Biodiesel (fatty acid methyl ester) can be produced from non-edible, locally available vegetable oil via transesterification reaction using alcohol in the presence of catalyst. In this regard, so many efforts have been made to solve the dependency on fossil fuel and to have an eco-friendly energy option. Specially giving emphasis to convert wastes to useful and renewable energy source is our country main focus.

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. The problems related with petroleum diesel is a 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 worldwide 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 the process, the major problems related to 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 is higher and no scope for regeneration or re-utilization of the catalyst.

A K_2O/fly ash based 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 K_2O/fly ash catalyst.

1.2. Objectives

1.2.1. General Objectives

The general objective of this study is to produce biodiesel from Jatropha curcas seed oil by using K_2O/fly ash as a catalyst.

1.2.2. Specific Objectives

- To extract Jatropha oil from Jatropha curcas seed and characterize the physicochemical properties (density, viscosity, acid value, and free fatty acid composition and saponification number).
- To prepare K_2O/fly ash base catalyst for transesterification of Jatropha seed oil.
- To Trans-esterify Jatropha oil to biodiesel using K_2O/fly ash as a catalyst.
- To investigate the main and interaction effect of transesterification reaction parameters (molar ratio of methanol to oil, reaction temperature, and catalyst loading) on the yield of FAME produced from Jatropha oil using response surface method.
- To characterize the fuel properties of the produced biodiesel such as density, kinematic viscosity, acid value, FFA composition, saponification number, flash point and fatty acid methyl ester composition.
- To generate model equation and determine the optimal operating condition aiming for maximum percentage yield of FAME.

1.3. Significance of the Study

After the study is effectively completed, it will be helpful to produce biodiesel from Jatropha seed oil using methanol and fly ash catalyst, which is locally available from such as sugar factories and Jatropha can be abundantly cultivated and grown, non-edible and good for production of biodiesel. This helps to encourage rural communities to cultivate more Jatropha plants to sustain their earnings. Biodiesel has no sulfur and nitrogen oxide emissions during combustion as raw materials are agricultural products, which are free of sulfur and nitrogen molecules.

In addition, the study will be used as a reference material for Jatropha and plant cultivation owners who are interested to produce biodiesel from Jatropha seed oil using the provided process technology and additional raw materials at small scale.

2. LITERATURE REVIEW

2.1. General Overview of Biodiesel Production

Biodiesel is an alternative diesel, which can be produced from renewable biological sources such as vegetable oils. It is biodegradable and nontoxic has low emission profiles and therefore, is environmentally beneficial (Krawczyk. T. 1996).

Biodiesel is a biomass-derived fuel, safer, cleaner, renewable, non-toxic and biodegradable direct substitute of petroleum diesel in compression-ignition engines, but more expensive. Biodiesel is a mono-alkyl-ester mixture obtained from natural oils, currently produced by a process called transesterification, where new or used oil (sunflower, jatropha, colza, soybean, or even animal fat) is first filtered.

Then pre-processed with alkali to remove free fatty acids, then mixed with an alcohol (usually methanol) and a catalyst (usually sodium or potassium hydroxide); the oil's triglycerides react to form esters and glycerol. 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 (F. Narasimharao et al. 2007).

The manufacturing process is based on the transesterification of triglycerides by alcohols to fatty esters, with glycerol as a byproduct. In this way, highly viscous triglycerides are converted into long-chain monoesters presenting much lower viscosity and better combustion properties. Homogeneous or heterogeneous catalysis is 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 (Demirbas 2008).

2.2. Raw Materials for Biodiesel Production

Biodiesel is an alternative diesel fuel that is produced from vegetable oils and animal fats. Biodiesel is produced from high free fatty acid feedstocks such as recycled oils and fats. Vegetable oils and animal fats are triglyceride molecules in which three fatty acid groups are esters attached to one glycerol molecule (Demirbas 2008). Table 2.1 shows main groups and types of oils that could be used in biodiesel production.

Table 2.1: Oil species for biodiesel production (Demirbas 2008)

Group	Source of oil
Major oils	Coconut (Copra), corn (maize), cottonseed, canola (a variety of rapeseed), olive, peanut (groundnut), sunflower, sesame, soybean, and sunflower
Nut oils	Almond, cashew, hazelnut, macadamia, pecan, pistachio and walnut
Other edible oils	Amaranth, apricot, argan, artichoke, avocado, babassu, bay laurel, beech nut, ben, Borneo tallow nut, carob pod (algaroba), cohune, coriander seed, false flax, grape seed, hemp, kapok seed, lallemantia, lemon seed, macauba fruit (Acrocomia sclerocarpa), meadowfoam seed, mustard, okra seed (hibiscus seed), perilla seed, pequi, (Caryocar brasiliensis seed), pine nut, poppyseed, prune kernel, quinoa, ramtil (Guizotia abyssinica seed or Niger pea), rice bran, tallow, tea (camellia), thistle (Silybum marianum seed), and wheat germ
Inedible oils	Algae, babassu tree, copaiba, honge, jatropha or ratanjyote, jojoba, Karanja or honge, mahua, milk bush, nagchampa, neem, petroleum nut, rubber seed tree, silk cotton tree, and tall

Vegetable oils are a renewable and potentially inexhaustible source of energy with energy content close to diesel fuel. Refined oils and fats contain large amounts of free fatty acids (M. Canakci, and J. Van Gerpe 2005).

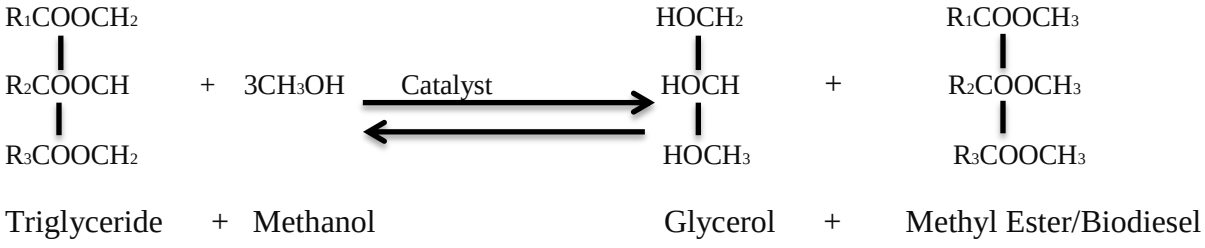
The advantages of vegetable oils as diesel fuel are liquidity, ready availability, renewability, lower sulfur and aromatic content, and biodegradability (Fang *et al*. 2007). The main disadvantages of vegetable oils as diesel fuel are higher viscosity, lower volatility, and the reactivity of unsaturated hydrocarbon chains.

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 this scheme.

Overall Reaction: Transesterification



Triglyceride + Methanol Glycerol + Methyl Ester/Biodiesel

Scheme: Transesterification reactions of glycerides with methanol Overall reaction

2.4. Extraction of Oil Seeds

2.4.1. Pressing

Pressing of oil-bearing materials for the production of oil has been known for several hundred years and only after World War II this process was replaced by solvent extraction. Today, more than 98% of the oil production worldwide is carried out by solvent extraction, but for specialty oils, such as extra virgin olive oil or virgin rapeseed oil, oils produced in rural areas, or for pre-pressing before solvent extraction, this old technique is still in use.

The aim of the pressing process is to separate the oil phase from the solid phase of the seed material. In large-scale facilities, two different pressing techniques are used for the separation of oil from the seed. The first one is pre-pressing of the flaked seeds which leave about 15–20% oil in the press cake. Today, this is the commonly used technique, which is followed by the extraction of the press cake by the solvent. The advantage of pre-pressing is that a press cake is formed from the small flakes which allow a good solvent contact and percolation in the extractor. The result is an optimized removal of oil

from the seeds (Matthäus 2012). Extraction by combining screw press and solvent extraction has the economic advantages of low costs using a screw press and higher oil yield using solvent extraction.

The other technique is a more extensive pressing of the oilseed without further extraction by the solvent. This straight pressing is interesting for oilseeds with high oil content, where it is no problem to get over the release of some percent of oil in the residue. Nowadays, this method is used only barely in large-scale facilities since it is not possible to reduce the oil content to less than 5% oil in the press cake by this technique. From an economic point of view, this is not sufficient for this type of oil mill. Nevertheless, this technique has the advantages of lower investment and maintenance costs and of achieving higher oil quality (Matthäus 2012).

2.4.2. Extraction by Solvent

Extraction by the solvent is recommended if it is necessary to reduce the oil content in the raw material to lower than 2%. This means the aim of extraction by the solvent is to remove as much oil as possible from the oilseed. From an economic point of view, pre-extraction by screw presses is advisable, because equipment and maintenance for solvent extraction are very costly. In most cases, hexane is used as solvent, because it is cheap, has good oil solubility at relatively low temperature, has an appropriate boiling temperature, is noncorrosive to metal, does not react chemically with the oil, is stable under the process conditions, is not mixable with water, which eases the separation of water from the seeds, and it is easily and completely removed from the residue with low energy input and without impairment of the raw oil. Nevertheless, this solvent also has some disadvantages with regard to its potential danger from which results in high requirements concerning the equipment. Hexane is highly flammable and mixtures of air and hexane are explosive, which entail the risk of fire and explosion if the plant does not consider appropriate cautionary measures. From this, it is urgently recommended to use explosion-proofed electrical equipments, to avoid the possibility that hexane being accumulated at deeper locations since hexane is heavier than air and to avoid hexane coming into contact with hot components of the extraction apparatus. Despite such measures every year some solvent-extraction plant explodes somewhere in the world. Often, plants purge all vessels with an inert gas to reduce the risk of fire or explosion.

Because of this disadvantage, also some other solvents such as hydrogen sulfide or trichloroethylene are in the discussion, but finally, the advantages of hexane overbalance the disadvantages in comparison to the other solvents. Hydrogen sulfide has a high toxicity, a low boiling point, and an extremely high vapor pressure. The heat of evaporation of trichloroethylene is higher than that of hexane, considering the density.

During solvent extraction of the oilseed, an intensive contact between solvent and press cake is necessary to achieve an exhaustive removal of oil. For this, the solvent is heated to 50–60°C, but it is important to avoid boiling when hot press cake comes into contact with the solvent. Since press cake comes hot from the pressing process, a further temperature supply is only necessary when the extractor starts working. Temperature is important for the extraction since viscosity of the solvent is reduced and the solubility of the extract increases with higher temperatures. The result is a higher rate of extraction. Additionally, the composition of the extract is influenced by the extraction temperature. While most oils mainly consist of triacylglycerides, minor components such as phospholipids, chlorophyll, free fatty acids, color pigments, and degradation products of oxidative reactions are co-extracted by the solvent. This amount of minor components increases drastically with the temperature. For example, an increase in temperature from 40 to 58°C raises the content of phospholipids in rapeseed oil from 0.2 to 0.8% (Matthäus 2012). This should be taken into consideration, because removal of minor components during refining is costly.

2.4.3. Extraction by Carbon Dioxide

One alternative to the commonly used extraction methods is the extraction by carbon dioxide under supercritical conditions. Under these conditions, if temperature (>31.1°C) and pressure (>73 atm) both increase, carbon dioxide adopts properties midway between a gas and a liquid, with comparable dissolving power as n-hexane. Carbon dioxide has the following advantages: it is not toxic, is easy to remove from the oil and the meal, and it is nonflammable. Additionally, depending on the conditions, the temperature of the process is relatively low. Thus, the method is very gentle to minimize deteriorations of the product during extraction and the amount of minor compounds co-extracted with the oil from the seeds is reduced since carbon dioxide is highly selective for triacylglycerides. The disadvantage of carbon dioxide is that the application is very expensive, which makes the use only interesting for specialty oils produced in low amounts and

sold at a high price. Another drawback is the difficulty to use supercritical carbon dioxide in a continuous extraction procedure, which would be preferred for large-scale processing (Booth 2004). Recently, a gas-assisted oilseed pressing has been developed that extracts the oilseed by a mechanical solid-fluid separation aided by the application of a dense gas. The gas is contacted with the oilseed before or during pressing in order to achieve lower residual oil contents. Especially the use of carbon dioxide showed good results regarding oil yield. For rapeseed, a considerable increase in oil yield from 27 to 71% was found (Voges et al. 2007). In this system, the gas is injected into the press resulting in a lowering of the viscosity and an easier drainage of the oil from the material. The system works hexane-free, allows the extraction of oil under more gentle and low-temperature conditions, and may result in higher quality of the resulting oil. A higher oil yield than under normal pressing conditions can be expected.

2.5. Current Technologies in Biodiesel Production

There are many current technologies or procedures employed in the production of Biodiesel. The viscosities of animal fats and vegetable oils are reduced in order to use them as diesel engine fuels. The procedures involved in these processes vary as mentioned below:

2.5.1. Direct Use and Blending

Crude vegetable oils are found not much encouraging to be used directly as diesel engine fuels. Hence, crude vegetable oils are mixed directly or diluted with diesel fuel to improve the viscosity and to be used for diesel engines. Energy consumption in the case of these oils are found equivalent to diesel fuel. The ratios of oil to diesel 1:10 – 2:10 was found successful (Fukuda et al. 2001). But at the end, the use of direct oils or blend of oils was not satisfactory with regard to direct or indirect usage as diesel fuels. Polymerization during storage and combustion, carbon deposits and lubricating oil thickening are the problems encountered generally (Ma F and Hanna MA 1999).

2.5.2. Micro-emulsions of Oil

The fuels of this kind are also termed as hybrid fuels. The problem of high vegetable oil viscosity can be overcome by micro-emulsification. A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions in the range of 1–150 nm, formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic

amphiphiles (Ma F and Hanna MA 1999).They exist as the components namely an oil phase, an aqueous phase and a surfactant. The maximum viscosity limitation required for diesel engines can be met by micro-emulsions with butanol, hexanol, and octanol (Jain S. and Sharma MP 2010).

2.5.3. Pyrolysis of Oils

Pyrolysis is the conversion of an organic compound into another organic compound by means of heat with the help of catalyst. Animal fats, vegetable oils, natural fatty acids or methyl esters of fatty acids can be used as pyrolyzed material. In the case of animal fats and vegetable oils conversion, triglycerides play an important role and thus the thermal cracking reactions. It is a promising technology for biodiesel production. The pyrolysis reactions can be divided into catalytic and non-catalytic reactions. The points to be considered are the expensive equipment for the process and all possibilities of more gasoline production than diesel fuel (Jain S and Sharma MP 2010).

2.5.4. 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^{o}C 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 means to reduce significantly the operating temperature. For example, soybean oil could be converted with

methanol into biodiesel with 98% yield by using propane, at least in 0.05 molar ratios to methanol, at 280°C and 12.8 MPa. Similar results have been reported with 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 (Demirbas 2008).

2.5.5. 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 270ºC and pressures from 70 to 200 bar 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 (Demirbas 2008).

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 270ºC 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 the 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 the second reactor is sent to the distillation column, from which water and methanol are recovered and recycled (Demirbas 2008).

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 require moderate energy. By heat integration, the utility consumption could be kept at low level.

2.5.6. Transesterification of Oils

The most important and effective current technology for biodiesel production is the transesterification of oils with alcohol to give biodiesel as main product and glycerin as by-product.

The current technologies in use for production of biodiesel are catalytic and non-catalytic transesterification methods.

2.6. Types of Transesterification Reactions

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 (F. Narasimharao et al. 2007). There are different types of transesterification and they are discussed as follows.

2.6.1. Catalytic

The transesterification of vegetable oils by heating with an alcohol and using a catalyst is carried out in this process. Two types of catalysts are used in catalytic technique; one is by homogeneous catalysts and the other one by the heterogeneous catalyst. In the catalytic methods, the selection of suitable catalyst is more important to reduce the cost of production.

The homogenous catalytic methods are again sub-divided into two methods; one is homogenous base catalytic transesterification and the other, homogenous acid catalytic transesterification.

2.6.1.1. Homogenous Base Catalytic Transesterification

At present, this process is the most employed in commercial sectors. It uses homogenous catalysts such as alkaline metal alkoxides and hydroxides, as well as sodium or potassium carbonates. In the method of basic methanolysis, almost in all the cases sodium hydroxide or potassium hydroxide have been used, both in concentration from 0.4% to 2% w/w of oil. The reasons these catalysts preferred are best operative conditions, high conversion rate in minimum time, good catalytic activity and economical.

2.6.1.2. Homogeneous Acid Catalytic Transesterification

An acid catalyst is used for the processing of triglycerides for biodiesel production. Sulphuric acid, sulphonic acid and hydrochloric acid are used as acid catalysts. The process starts by mixing the oil directly with the acidified alcohol, and then the separation and transesterification occur in one step, with the alcohol acting both as a solvent and as an esterification reagent(Cerveró et at. 2008).

2.6.1.3. Heterogeneous Catalytic Transesterification

These catalysts can act in different phases which can help in easy separation. The expensive method of homogeneous catalysts has called for heterogeneous methods. No soap formation takes place in heterogeneous processes.

There are two more divisions in heterogeneous catalyst run reactions; they are heterogeneous solid base catalysts and heterogeneous solid acid catalysts. The former catalysts are base or basic oxides coated over large surface area. Solid-base catalysts are more active than solid-acid catalyst. The most common solid-base catalysts are Basic zeolites, alkaline earth metal oxides and hydrotalcite. Solid base can leads to the heterogeneous catalytic process, which promises the cost reasonable biodiesel production (Kouzu M. and Hidaka J.S 2011).

Heterogeneous solid acid catalysts have different acid sites with varying strengths of Bronsted or Lewis acidity, compared to the homogeneous acid catalysts. Heterogeneous Solid acid catalysts, such as Nafion-NR50, sulfated zirconia and tungstated zirconia have been chosen to catalyze biodiesel forming transesterification due to the presence of sufficient acid site strength (Dalai and Meher LC. 2006).

2.6.1.4. Fly ash Catalyzed Transesterification

The use of fly ash catalysts could be an attractive solution. Fly ash catalysts can be separated more easily from reaction products. Undesired saponification reactions can be avoided by using fly ash 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 fly ash catalyst on the production process are catalyst regeneration (decrease of catalyst cost), utilization of lower quality feedstocks 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 (Gerhard Knothe et al. 2005).

But in case of fly ash catalysts, catalysts present in different phases from reactants, providing a surface at which a reaction occurs.

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 (Raheman H. 2007).

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 (Adebowale K.O. and Adedire C.O. 2006).

The transesterification of sunflower oil was done at 1% catalyst weight and 12:1 molar ratio of methanol at a reaction temperature of 60ºC. The fatty acid methyl ester yield observed was 92. (Raheman H. 2007). 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 (Sujatha M. and Mukla N. 1996).

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 fly ash catalysts has higher lifetimes since the catalyst utilization time is higher than the homogeneous catalytic processes. This means fewer 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 fly ash catalysts have 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, and the final separation cost is reduced and environmentally friendly (J. Van Gerpen et al. 2004).

2.6.1.5. 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 (Kwan-Young Lee. et al. 2009). 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 biodiesel production. 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.

2.6.1.6. Microwave-Assisted Transesterification

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 electrical field. The changing electrical field, which interacts with the molecular dipoles and charged ion, causes these molecules or ions to have a rapid rotation and heat, is generated due to molecular friction. The preparation of biodiesel 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 (Knothe G. et al. 2005).

2.6.1.7 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. 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 triglycerides, and simplicity (Knothe G. et al. 2005).

2.6.1.8. Two-Step Acid - Base-Catalyzed Transesterification

This process involves a two-step process for the production of biodiesel from oils having high FFA. Initially, the acid catalyzed esterification reaction takes place to convert the FFA present in

the oil to esters. After the reduction of FFA, transesterification reaction was carried out, in which the pre-treated oil reacts with methanol using conventional base catalysts. This method of biodiesel production alleviates the drawbacks of the esterification process -requires longer time reaction to come to completion and transesterification problem of soap formation process (Wang Y. et al. 2007).

2.6.2. Non-catalytic

There are few non-catalytic methods too. These processes render production of biodiesel through a conventional transesterification system complicated, thus giving a reason to investigate the production of biodiesel from triglycerides via non-catalytic reactions. Supercritical alcohol esterification and BIOX co-solvent transesterification are included in the non-catalytic processes (Ahmad Abbaszaadeh et al. 2012).

2.7. 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.

A. Alcohol to Oil Molar Ratio

The stoichiometric transesterification requires 3 moles of the alcohol per mole of the triglyceride to yield 3 moles of the fatty esters and 1 mole 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 lead 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 (Erin Robinson & Chris Rolland 2006).

B. 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. The 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 (Erin Robinson & Chris Rolland 2006).

C. 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 by an increase in temperature.

D. 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.

E. 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 (Erin Robinson & Chris Rolland 2006).

2.8. Biodiesel Quality Parameters

A. Specific gravity (density)

Specific gravity is the ratio of the density of a liquid to the density of water. This property is important because it influences the efficiency of atomization of the fuel and it is a quality indicator for automotive, aviation and marine fuels, where it affects storage, handling and combustion properties (Shivakumar et al. 2011).

B. Water content

Determination of water content in fuel oil is important because the presence of water can promote organic growth which results in blockage of automotive filters. Further, in transesterification, the presence of water in raw materials results in soap formation (Ma F, and Hanna MA. 1999).

C. Viscosity

Viscosity refers to the thickness of the oil (flow properties) and is determined by measuring the amount of time taken for a given measure of oil to pass through an orifice of a specified size. Viscosity affects injector lubrication and fuel atomization. Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. Fuel atomization is also affected by fuel viscosity. Diesel fuels with high viscosity tend to form larger droplets on injection, which can cause poor combustion, increased exhaust smoke and emissions. The viscosity of biodiesel and biodiesel blends also increases more rapidly than diesel as the temperature is decreased. Certain impurities also tend to significantly increase the viscosity of biodiesel (Knothe and Steidley 2005).

D. Acid Number (acid value)

Acid value is defined as the amount of potassium hydroxide (KOH) in milligrams required to neutralize one gram of chemical substance. It is the measure of free fatty acid in a mixture of compounds (Berrios M and Skeleton RL. 2008).

Acid number (value) determines the acidic or basic constituents in petroleum products and lubricants. For biodiesels, the acid number is an indicator of the quality of the product. Specifically, it detects the presence of any unreacted fatty acids still in the fuel, or of any acids that were used in processing. This is also an indication of the condition of the stability of the fuel because the acid number increases as the fuel ages. (National Renewable Energy Laboratory, Colorado, USA, September 2001). The acid number is a measure of acids in the fuel. These acids emanate from two sources: (i) acids utilized in the production of the biodiesel that is not completely removed in the production process; and (ii) degradation by oxidation. For biodiesel blends, the acid number will change as a result of the normal oxidation process over time. Once purchased, biodiesel fuel blends that will not be utilized immediately should be monitored for

changes in acid number as an indicator of fuel degradation (Engine manufacturers association 2006).

E. Total Fatty Acids

Total Fatty Acid is the analysis of the number of fatty acids present in the biodiesel. It is an indication of the conversion efficiency of the original feedstock. Gas Chromatographic Analysis of Fatty Acids indicates the composition of each of the biodiesels. The largest fraction of fatty acids for each of the biodiesels is a potential indication of the rest of the properties. The methyl esters follow some patterns. The soy, canola, and two yellow greases FEME are mostly oleic and linoleic acid (C18, one and two double carbon bonds), while the two largest components of the lard, edible tallow, and inedible tallow ME are oleic and palmitic acid (C18, one C:C bond, and C16, saturated). Free glycerin and total glycerin (by the Christina Planc method) is a good indicator as to the cleanup of the fuel, or of the degree of completion during the reaction. As such, it should remain in the specifications for biodiesel (Neff et al. 2000).

F. Cloud Point

Cloud point is the temperature at which oil starts to solidify. While operating an engine at temperatures below oil's cloud point, heating will be necessary in order to avoid waxing of the fuel. Small crystals of fuel begin to form in the liquid causing haziness as the sample is cooled. It is an indicator of the utility of petroleum oil for some applications. In the case of biodiesel, the haze is made up of crystallized fuel molecules, specifically crystallized stearic and/or palmitic methyl esters (Knothe and Dun, 2001). Using a product below its cloud point may reduce the lubricating properties, and may plug filters. For biodiesel, the settled material may not cause lubrication problems, but the remaining liquid may have lower properties relative to the fully mixed fuel. The pout point and cloud point are both higher for biodiesel fuel than for gasoline-based diesel, indicating the biodiesel will tend to gel at higher temperatures than diesel, causing engine problems (Lee et al. 1996, Heraud, A. 1999).

G. Calorific Value or Heat of Combustion

Heating Value of Heat of Combustion is the amount of heating energy released by the combustion of a unit value of fuels. One of the most important determinants of heating value is moisture content. Air-dried biomass typically has about 15-20% moisture, whereas the moisture

content for oven-dried biomass is negligible. Moisture content in coals varies in the range 2-30%. However, the bulk density (and hence energy density) of most biomass feedstocks is generally low, even after densification-between about 10 and 40% of the bulk density of most fossil fuels. Liquid biofuels however, have bulk densities comparable to those for fossil fuels. The energy content of biodiesel and diesel is 37MJ/Kg and 45MJ/Kg respectively (Freedman et. al. 1989).

H. Pouring Point

Pour point refers to the temperature at which the oil in solid form stars to melt or pour. In cases where the temperatures fall below the melting point, the entire fuel system, including all fuel lines and fuel tank will need to be heated (Lee et al, 1996, Heraud, A. 1999).

I. Flash Point (FP)

The flash point temperature of diesel fuel is the minimum temperature at which the fuel will ignite (flash) on the application of an ignition source. Flashpoint varies inversely with the fuel's volatility. Minimum flash point temperatures (Standard) are required for proper safety and handling of diesel fuel. Biodiesel and diesel have a common boiling point, but biodiesel has a higher flash point because biodiesel has a high number of FAMEs, which are generally not volatile. Thus, biodiesel is safer to handle at higher temperature than diesel (National Renewable Energy Laboratory 2006).

J. Cetane Number

Cetane number is a measure of the self-ignition quality of the fuel. Higher Cetane numbers indicate shorter times between the injection of the fuel and its ignition. Higher numbers have been associated with reduced engine roughness and with lower starting temperatures for engines No. 2 diesel fuel usually has a cetane rating between 45 and 50 while vegetable oil is 35 to 45. Biodiesel is usually 50 to 60. The ignition quality affects engine performance, cold starting, warm up and engine combustion roughness. Cetane rating is related to the volatility of the fuel where more volatile fuels have higher ratings. A high cetane fuel also may lead to incomplete combustion and smoke if the fuel ignites too soon by not allowing enough time for the fuel to mix with air for complete combustion. Fuels with low Cetane Numbers will result in difficult staring, noise and exhaust smoke. In general, diesel, much like octane numbers measure the

ignition of gasoline. These numbers represent the measure of a fuel's willingness to ignite. Biodiesel has a higher cetane number than that of diesel, largely because of its higher oxygen content (Jackson MA and King JW. 1996). It is important to note that biodiesel's cetane number can vary widely, based on differences in fatty acid composition of the feedstock oil and the saturation level of the fatty acids (Saka S, Kusdiana D. 2001).

K. Iodine Value of Oils and Fatty Acids

Iodine value measures the amount of iodine required to saturate the olefinic bonds. The iodine value is an indicator of the unsaturation of the fuel, which has been linked with the formation of engine deposits and problems in storing the fuel. It has been suggested that values over 115 may be unacceptable; the biodiesels easily meet this requirement. The Iodine value is determined by measuring the number of double bonds in the mixture of fatty acid chains in the fuel by introducing iodine into 100 grams of the sample under test and measuring how many grams of that iodine is absorbed. Iodine absorption occurs at double bond positions-thus a higher iodine number indicates a higher quality of double bonds in the sample, greater potential to polymerize 29 and hence less stability. One can hence see that the process of transesterification (conversion of plant oil into biodiesel) reduces the iodine value to a small extent (National Renewable Energy Laboratory 2006).

2.9. Properties of Biodiesel from Various Sources

The viscosity, density and flash point of the raw materials used for the production of biodiesel are lowered in the process. The chemical composition of the biomass used is directly related to some important properties of the diesel oil, such as viscosity, melting point, thermal stability, and cetane index. Therefore, it is possible to assume the property values of biodiesel produced from a specific vegetable oil. The study by, evaluated the properties of biodiesel oils from varieties of biomass sources such as castor, soybean, cotton and canola (M.C.G. Albuquerque et al. 2009).

Table 2.2: Oil properties from Various Sources (Alnuami W. et al. 2014)

Properties	Units	Jatropha oil	Palm oil	Soybean oil	Waste cooking oil
Kinematic viscosity at 38ºC	mm^2/s	49.93	39.6	32.6	36.4
Cetane number	-	40-45	42.0	37.9	49.0
Heating value	MJ/kg	-	-	39.6	-
Flash point	^{o}C	240	267	254	485
Cloud point	^{o}C	-	31.0	-	-
Density	g/ml	0.9186	0.9180	0.9138	0.8830
Carbon residue	Wt.%	0.10	0.23	0.25	0.46

In another study by, high amounts of free fatty acids determine the quality of biodiesel to be produced. Oils containing hydroxyl group compounds possess high viscosity due to the presence of hydrogen bonding. The physico-chemical properties of Jatropha and castor oils were assessed for their potential in biodiesel. This research study has shown that high amounts of Free fatty acids in oils has produced low-quality diesel oil and vice versa. In both the cases of jatropha and castor oils, the FFA is neutralized to improve the quality of biodiesel (Aldo Okullo et al. 2012).

One more research study on evaluating different materials for biodiesel production by (Aldo Okullo et al. 2012), has given a clear idea on the properties of the oils and the respective produced biodiesel properties. The below tables provide the information on the same.

Table 2.3: Biodiesel properties from Various Sources (Alnuami W. et al. 2014)

Property	Jatropha	Soybean	Palm oil	WCO	Biodiesel standards		
					ASTM D 6751-02	DIN EN 14214	Diesel fuel
Density at 20ºC, kg/m^3	880	885	880	884	870-900	875-900	850
Viscosity at 40ºC, mm^2/s	2.37	4.5	5.7	4.5	1.9-6	3.5-5.0	2.60
Cloud point, ºC	-	1	13	1	-	-	4
Flashpoint, ºC	135	178	164	180	≥130	≥120	68
Acid value mgKOH/g	≤0.800					≤0.500	
Pour point	2	-7	12	-5.0	-15 to 10	-15 to 10	-20
Water, %	0.025	-	-	0.4	0.03	0.05	0.02
Sulfur, PPM	-	-	-	-	50	50	500
Carbon residue, wt.%	0.2	-	-	0.3	-	0.3	0.17
Cetane number	61	45	62	57.2	48-60	49	49
Calorific value, Mj/kg	39.2	33.5	33.5	32.9	38-42	-	42

3. MATERIALS AND METHODS

3.1. Materials

The major raw materials used during the experimental work were Jatropha curcas seed, analytical grade (AG) methanol and K_2O/fly ash as a heterogeneous catalyst, potassium hydroxide, sodium hydroxide, Phosphoric acid, ethanol, diethyl ether, phenolphthalein indicator, hydrochloric acid. The Jatropha seeds were collected from Awash Melkasa agricultural Research Center, Adama wereda, and the fly ash was collected from Wonji/Shoa sugar factory. All the other chemicals were analytical grade reagent and bought from different chemical stores in Addis Ababa.

3.2. Equipment

The equipments used during the experimentations includes mechanical press, 500 ml round bottom three-necked glass reactor for transesterification reaction, this reactor equipped with mechanical stirrer (to increase mixing efficiency between oil and alcohol) and a reflux condenser (to reduce the loss of methanol by evaporation), water bath, condenser, crusher, glove, separating funnel, digital weight balance, muffle furnace, oven, pestle and mortal, magnetic stirrer, Bunsen burner, different size conical and Erlenmeyer flasks, beakers, hot plate-MSH-20D, measuring cylinders, burette, micropipettes, XRD, FTIR, GC-MS.

The experimental work was started in December and end in April a total of six months was spent for the laboratory works. Preparation of the solid fly ash based catalyst, sieving, washing, drying, loading with KOH and aging, calcining and catalytic activity determination of the catalyst were done at School of Chemical and Bio Engineering Laboratory, AAiT. Extraction of Jatropha oil using mechanical pressing apparatus was done at Ministry of Water, irrigation and electricity, alternative energy technology and promotion directorate workshop and laboratory section. Jatropha oil purification, characterization of the purified oil, production and characterization of the biodiesel was also done at School of Chemical and Bio Engineering Laboratory. XRD and FTIR Analysis of the fly ash catalyst were conducted in Addis Ababa University, college of natural science in the department of chemistry. Fatty acid composition analysis of the produced biodiesel using GC-MS was done at Leather industry development institute (LIDI). The overall structure of the experimental works is shown in figure 3.1.

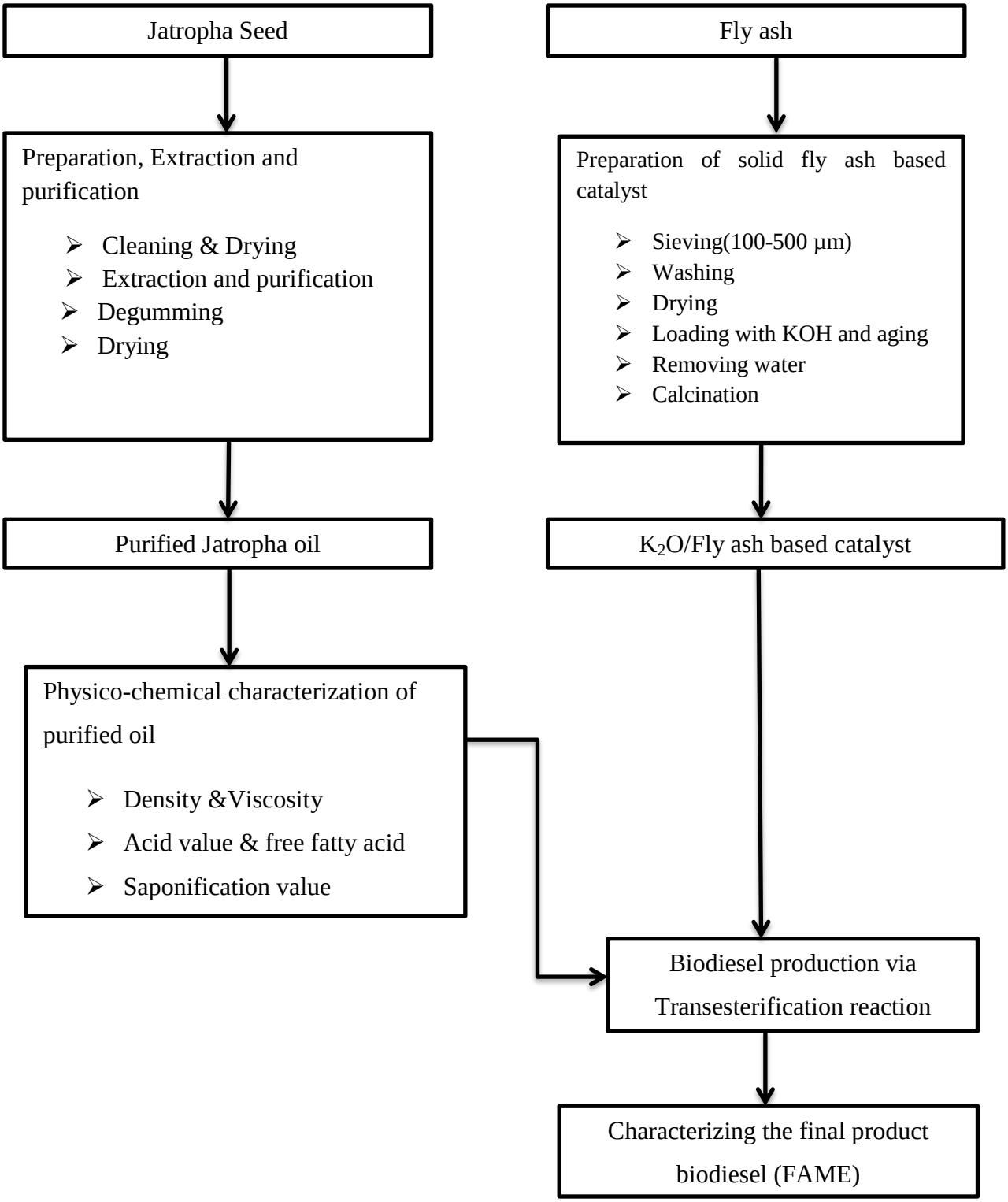


Figure 3.1: Framework of the experiment

3.3. Experimental Method

3.3.1. Preparation of K_2O/Fly ash based Catalyst

The catalysts were prepared using the established method of wet impregnation. The Bagasse fly ash collected from wenji/shoa sugar factory was sieved (100-500 µm), washed using distilled water, and then dried it at 105ºC for 24 hours using hot air oven to remove the water. The dried fly ash cooled in a desiccator for 30 minutes and stored in air-tight plastic bags to avoid any adsorption of moisture on the surface.

Then the dried fly ash was weighed and loaded with 8M, 10M, 12M, 14M and 16M potassium hydroxide slowly with constant stirring and aging for 24 hours. The KOH loaded fly ash was heating to remove the water using hot plate and then it was calcined at 500ºC for 5 hours. This method is similar to the one reported by (Babajide et al. 2010). The calcined material was milled in a ceramic pestle and mortar into a fine powder. These fly ash-based catalysts loaded with 8M, 10M, 12M, 14M and 16M KOH were prepared and labeled as A, B, C, D, E respectively.

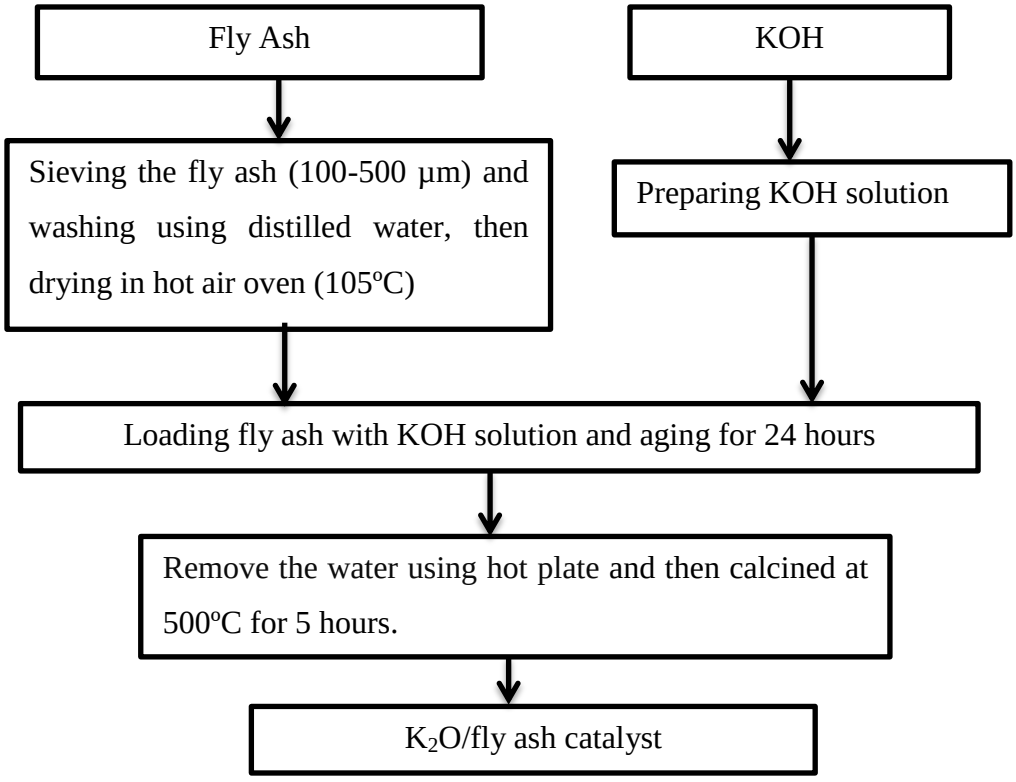


Figure 3.2: Flow sheet for the preparation of solid fly ash based catalyst

3.3.2. Characterization of K_2O/fly ash catalyst

3.3.2.1. Determination of Catalytic Activity

To evaluate the catalytic activity of the catalysts prepared, transesterification reaction was performed under constant input operating variables, using 50 ml oil, molar ratio of methanol to oil of 6:1, catalyst to oil weight ratio of 4%, reaction temperature of 60ºC, and 2 hour reaction time. The best performing catalyst that provide highest percentage yield of biodiesel was then selected for this experiment work.

3.3.2.2. Fourier Transform Infrared Spectroscopy

Various characteristic functional groups were identified by using the Fourier transformed infrared spectroscopy (FTIR). Functional group analysis of the fly ash and prepared fly ash based catalyst was done using Fourier-Transformed Infrared spectroscopy (FTIR). The FTIR spectra were recorded on spectrum 65 FTIR (PerkinElmer) equipped with KBr beam splitter. The instrument used was able to record spectra from wave numbers of 4000 to 400 cm^{-1}. Spectrum is produced as a result of the absorption of infrared radiation. The functioning group is determined based on the interpretation of the infrared spectrum obtained by comparing it with the standard spectrum group frequencies.

3.3.2.3. X-ray Diffraction (XRD)

XRD is one of the most commonly used techniques for either crystalline or amorphous phase identification. In this technique, the catalyst sample is irradiated with X-ray of a known wavelength (λ). The X-ray diffraction (XRD) patterns of fly ash catalyst were obtained using MiniFlex 300/600, Japan operated at 40 kV and 15 mA, using Ni-filtered Cu-Ka radiation (1.54059-1.54441). The samples were placed on a sample holder made up of silicon wafer and the measurements were taken continuously from 10^o to 70^o angles over the range of 2θ. The resultant intensity data was processed by using origin 8 software to draw graph and analyze the peak position.

3.3.3. Extraction and Purification of Jatropha Oil

3.3.3.1. Preparation of Jatropha Seed

Jatropha seeds were first cleaned from dirty, dust, sand and small stones. Then the prepared Jatropha seeds were sun dried for three days. The cleaned seeds were weighted and 6 kg Jatropha seeds were further dried by the sun for an hour to remove the rest of their moisture content. Then the dried seed was prepared for Mechanical press extraction process.

3.3.3.2. Extraction of Jatropha Oil

Mechanical press apparatus method was applied for Jatropha oil extraction. For the mechanical press extraction method, 6 kg of dried Jatropha seed was used. After extraction, the oil and solid suspension was separated using a centrifuge at 2500 rpm for 30 minutes. Finally, the oil was ready for purification.

(a)

(b)

Figure 3.3: a) Mechanical press machine b) crude Jatropha oil

3.3.3.3. Purification of Crude Jatropha Oil

- **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 70ºC under stirring at 500 rpm, 3% of distilled water (which first was heated to approximately 90ºC) and 2% of phosphoric acid (85%) was added. The mixture was stirred for 1hr. The white-formed precipitate was separated by centrifugation for half an hour at 2500 rpm and the degummed oil was dried at 105ºC for 30 minutes.

Figure 3.4. Degummed Jatropha oil

3.3.4. Characterization of Physico-chemical Properties of Purified Jatropha Oil

3.3.4.1. Moisture Content Determination of Jatropha Seed

The empty dish was weighed with and without the amount of kernel and dried in hot air oven at 110ºC for 8 hours, weighing every 2 hours until 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:

$$moisture\ content = \left[\frac{(W1 - W2)}{W1}\right] * 100\% \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

Where W1 = original weight of the sample before drying;

W2 = Weight of the sample after drying

3.3.4.2. Determination of Density

The density of Jatropha oil was determined using density meter. The oil was injected using a syringe to the density meter and the density meter was recorded for the density of purified oil at15ºC.

3.3.4.3. Determination of Kinematic Viscosity

Vibro viscometer was used to determine the viscosity of the oil. The sample was kept in the water thermostat bath until it reaches the equilibrium temperature of 40ºC. After maintaining the equilibrium temperature, the vibro viscometer tip was inserted into the sample and the reading was taken from the controller. This was done in triplicate and the average dynamic viscosity was recorded. The kinematic viscosity is then equal to the ratio of dynamic viscosity to the density of the oil.

3.3.4.4. Determination of Acid Value (AV)

The acid value determination was conducted by placed 3.0 g of the oil in a 250 ml conical flask and warmed, and then 25 ml of methanol was added with thorough stirring, followed by two drops of phenolphthalein indicator and drops of 0.14 M of potassium hydroxide solution. The content was titrated until a permanent light pink color. The endpoint was thus recorded. The acid value was calculated using Equation below.

$$Acid\ value = \frac{Titer\ value * N * 56.1}{Weight\ of\ oil\ sample} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

Where Titer value is the volume expressed in a milliliter of a 0.14 M solution of KOH

N is a concentration of KOH

3.3.4.5. Determination of Free Fatty Acid (FFA)

The free fatty acid of the oil extracted from the Jatropha seeds was determined using the expression given in equation below.

$$FFA = \frac{AV}{1.99} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.3$$

3.3.4.6. Determination of Saponification Number (SN)

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

A weighed amount of oil (2 gm) was added to 25 mL of 0.5 M potassium hydroxide solution and the reflux condenser was attached to the flask. The mixture was heated, and as soon as the solution starts to boil, 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 were added and the hot soap solution obtained was slowly titrated with 0.53 M hydrochloric acid (and volume V1 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 V2 was recorded). The final result was calculated using the equation below.

$$\text{Saponification Number} = \frac{56.1 * N * (V2 - V1)}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.4$$

Where W= weight of oil taken in gram.

N= normality of HCl solution

V_1= volume of HCl solution used in the test in a milliliter.

V_2= volume of HCl solution used in blank in a milliliter.

3.3.5. Biodiesel Production via Transesterification Reaction

Transesterification process, which is the process of converting extracted oil into biodiesel, was carried out in this work by reacting the extracted Jatropha oil with methanol in the presence of solid K_2O/fly ash as a catalyst to produce methyl ester and glycerol. Keeping reaction time and stirring rate constant at 2 hours and 500 rpm respectively. Three different biodiesel production conditions were varied as follows: molar ratio of methanol to oil from 6:1 to 12:1, reaction temperature ranged from 50ºC to 60ºC, the mass ratio of catalyst loaded from 2% to 4%.

For the biodiesel production experiments, we used the following amounts of reactants and catalyst: 50ml of Jatropha oil, from 6:1 to 12:1 methanol and from 2 to 4 wt.% solid fly ash catalyst. At the first step of the experiment, solid fly ash catalyst was added to the methanol and stirred until fully mixed. Then, 50 ml of Jatropha oil was measured using a measuring cylinder and heated until 55-60ºC. After reaching the desired temperature, solid fly ash-methanol mixture was added to the continuously mixed and heated oil (at 500 rpm and 55-60ºC temperature). The reaction was carried out for 2 hours.

After the reaction finished, the reaction mixture was let to settle until the biodiesel light layer completely separated from the glycerin heavy layer. It took 24 hours to separate glycerin and biodiesel layers. The biodiesel layer was separated by removal of the glycerin layer. Afterward, the biodiesel was prepared to the washing procedure. For the washing process, hot distilled water was added to the biodiesel in order to extract contaminants. The mixtures were allowed to separate, forming a top biodiesel layer and a bottom aqueous layer, due to the difference in densities and immiscibility. After complete separation, the aqueous layer is removed and the washing process is repeated until the aqueous layer shows no contamination. The next step is the drying process. The drying process was done by heating the biodiesel sample to a temperature of 110ºC, it was heated for about 60 minutes until all the water evaporated and separated from the sample.

(a) (b)

Figure 3.5: (a) experimental setup for transesterification reaction (b) produced biodiesel

3.3.6. Feed Material Requirement for Biodiesel Production

50 ml 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;

$$\frac{n\ methanol}{n\ oil} = 6 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.5$$

Substituting mass for mole;

$$\frac{(\rho methanol * Vmethanol)/Mmethanol}{(\rho oil\ Voil)/Moil} = 6$$

$$\frac{(0.79\ gm/ml * Vmethanol)/(32.04\ gm/mol)}{(0.91\frac{gm}{ml} * 50ml)/(860gm/mol)} = 6$$

Solving for Vmethanol =13 ml of methanol

The amount of catalyst required when the ratio of catalyst weight to oil is 1: 100.

M oil = ρ oil * Voil 3.6

M oil = 0.91 gm/ml *50 ml =45.5 gm

Mass of catalyst = 4% * mass of oil =1.82 gm of catalyst

Similarly, the amount of methanol and catalyst is calculated for all experiments.

3.3.7. Experimental Design for Biodiesel Production

In this work, the biodiesel was produced using purified Jatropha curcas oil and methanol with a solid fly ash heterogeneous catalyst. The 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).

The three transesterification process variables studied are a molar ratio of methanol to oil, reaction temperature and the catalyst load. The reaction time and rotational speed of stirrer were set at 2 hours and 500 rpm respectively. Atmospheric pressure is used for all the runs.

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 experimental study, 20 experimental runs were conducted. The molar ratio of methanol to oil, reaction temperature, and catalyst load were the independent variables selected to see the optimum conditions for biodiesel (FAME) production using solid fly ash catalyzed transesterification. The 20 experimental runs were carried out and data were statistically analyzed by the Design-Expert program to find the suitable model for the percentage of 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 Transesterification reaction.

Variables	Units	Levels				
		-1.68	-1	0	+1	+1.68
Molar ratio of methanol to oil	mole/mole	3.95	6	9	12	14.05
Reaction temperature	^{o}C	46.59	50	55	60	63.41
Catalyst load	Wt.%	1.32	2	3	4	4.68

The table below shows the complete experimental design matrix of CCD. The order in which the runs were made was randomized to avoid systematic errors.

Table 3.2: Central Composite Design Arrangement (Experimental Design Matrix)

Run	Actual factor		
	Molar ratio of methanol to oil, (Mole/Mole)	Reaction temperature (ºC)	Catalyst load (Wt.%)
1	9	55	1.32
2	9	55	4.68
3	12	60	4
4	9	55	3
5	3.95	55	3
6	14.05	55	3
7	9	46.59	3
8	12	60	2
9	9	55	3
10	12	50	2
11	9	55	3
12	6	50	4
13	9	55	3
14	9	63.41	3
15	6	60	2
16	12	50	4
17	6	60	4
18	6	50	2
19	9	55	3
20	9	55	3

3.3.8. Characterization of Physico-Chemical Properties of Biodiesel

3.3.8.1. Determination of Density

The density of biodiesel was determined using density meter. The biodiesel was injected using a syringe to the density meter and the density meter was recorded for density of biodiesel at 20ºC.

3.3.8.2. Determination of Kinematic Viscosity

Vibro viscometer was used to determine a viscosity of the biodiesel. The sample was kept in the water bath heated by thermostat until it reaches the 40ºC (equilibrium temperature). After maintaining the equilibrium temperature, the vibro viscometer tip was inserted in the sample and the reading was taken from the controller. The dynamic viscosity was recorded and the Kinematic viscosity was calculated.

3.3.8.3. Determination of Acid Value

To determine the Acid value, Standard alcoholic KOH solution (0.01M) was prepared by dissolving KOH (pellet) with ethanol.

The solution was filtered and stored in a 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 (2 gm) 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 0.01 M ethanolic KOH solution in presence of 5 drops of phenolphthalein as indicator until the endpoint (colorless to pink) is recognized. The volume of 0.01 M ethanolic KOH (V) for the sample titration was noted. The total acidity (acid number) in mgKOH/g was calculated using the following equation. The acid value was determined to know the amount of free fatty acid composition in the oil.

$$Acid\ value = \frac{V * N * 56.1}{m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 3.7$$

Where V is the volume expressed in a milliliter of 0.01 M solution of ethanolic KOH

m is mass in gram of the test portion

N is a concentration of ethanolic KOH

3.3.8.4. Determination of Saponification Number

A weighted amount of biodiesel (W) was added to 25 mL of 0.5 M 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 were added and the hot soap solution obtained was slowly titrated with 0.53 M hydrochloric acid (and volume Va 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 Vb was recorded). The final result was calculated using the equation below.

$$\text{Saponification Number} = \frac{56.1 * N * (Vb - Va)}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.8$$

Where W = weight of oil taken in gram.

N = normality of HCl solution

Va = volume of HCl solution used in the test in a milliliter.

Vb = volume of HCl solution used in blank in a milliliter

3.3.8.5. Determination of Flash Point

The 250 ml conical flask was filled to a certain level with the biodiesel and heated at a slow constant rate on a hot plate. The flashpoint was taken as the lowest temperature when the application of the test flame caused the vapor above the biodiesel sample to ignite.

3.3.8.6. Determination of Free Fatty Acid composition (FFA)

The free fatty acid composition of the biodiesel produced from the Jatropha seeds oil via transesterification reaction using solid fly ash catalyst was determined using the expression given in equation 3.3.

3.3.8.7. Determination of Higher Heating Value

Calorific value (energy content or heat of combustion) of a fuel was determined using bomb calorimeter. Benzoic acid was used to standardize the calorimeter. 1 gm 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 was pressurized to 18atm (18.2385 bar) of oxygen. The bomb was placed in a vessel containing 2000 gm of water. The ignition circuit was connected and the water temperature noted. After ignition a 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.

3.3.8.8. Gas Chromatography-Mass Spectroscopy (GC-MS)

GC analysis of biodiesel was performed with Agilent 7890A Gas Chromatography. Sample analysis was carried out on packed column- Agilent Technologies (30 m × 0.250 mm, 0.25 μm). Samples were injected by a sampler injector at an oven temperature of 325 to 350ºC for a total run time of 50 minutes. The data, obtained using Agilent 5975C Mass spectroscopy system EMS detector and processed using Chemstation software, were used to obtain fatty acid methyl ester composition of biodiesel.

4. RESULTS AND DISCUSSION

4.1. Catalyst Characterization

4.1.1. Determination of Catalytic Activity

Based on the transesterification reaction conducted the catalyst that gives high percentage yield of biodiesel was selected.

Table 4.1: Biodiesel yield from transesterification reaction using the prepared catalysts

Run	Molar ratio of methanol to oil, mole/mole	Reaction temperature, ^{o}C	Reaction time, hrs	Catalyst load, Wt.%	Catalyst type	Yield of FAME, %
1	6	60	2	4	A	86.8
2	6	60	2	4	B	88.6
3	6	60	2	4	C	94.5
4	6	60	2	4	D	82.2
5	6	60	2	4	E	80

Based on this study the little amount of KOH loaded catalyst makes yield to be lower. The increase of the KOH loading increases the reaction rate so that the yield of biodiesel produced also increases. However, when the amount of KOH loaded increases the yield of biodiesel produced start to decrease. The reason behind this decrement can be explained by looking into the intrinsic behavior of the fly ash based catalysts.

It is known that surface area, porosity, and number and strength of the active site are an important parameter for the efficiency of the heterogeneous catalyst. Any activity with a negative effect on those parameter leads to a reduction in catalytic activity and hence the yield. Catalyst with pore diameter lower than the critical diameter of triglyceride, defined as the diameter of the smaller cylinder through which that molecule can pass without distortion, inhibits the diffusion through the pore. Thus, mainly external active catalytic surface takes part in the reaction, which leads to the reduction in catalytic activity. The micropore volume of the fly ash catalyst decreased monotonously with the potassium oxide loading even for high loadings. The decrease

of surface area and micropore volume with increasing potassium loading could be assigned to a decrease of the available void volume (Babajide et al. 2010).

In this experiment as well, probably increasing of KOH beyond 12M might lead to a reduction in pore diameter which results in diffusion resistance through the pore. In addition, at higher loading, the active site of the catalyst has a probability of agglomerating (covering of active site) which reduces the available active surface area for the reaction. Consequently, incomplete reaction might occur which is responsible for reduction in yield of biodiesel in the higher KOH loading case.

4.1.2. Fourier Transform Infrared Spectroscopy Analysis

Functional group analysis of the fly ash and solid fly ash catalyst was done using Fourier transformed infrared spectroscopy (FTIR). The FTIR spectra were recorded on spectrum 65 FTIR (PerkinElmer) equipped with KBr beam splitter.

4.1.2.1. Fly Ash

The result of infrared spectroscopic for fly ash is shown in figure 4.1 The IR spectrum of fly ash shows transmission bands at 3442, 2884, 1625, 1053, 846 cm^{-1}. The main peak is at 1053 cm^{-1}.

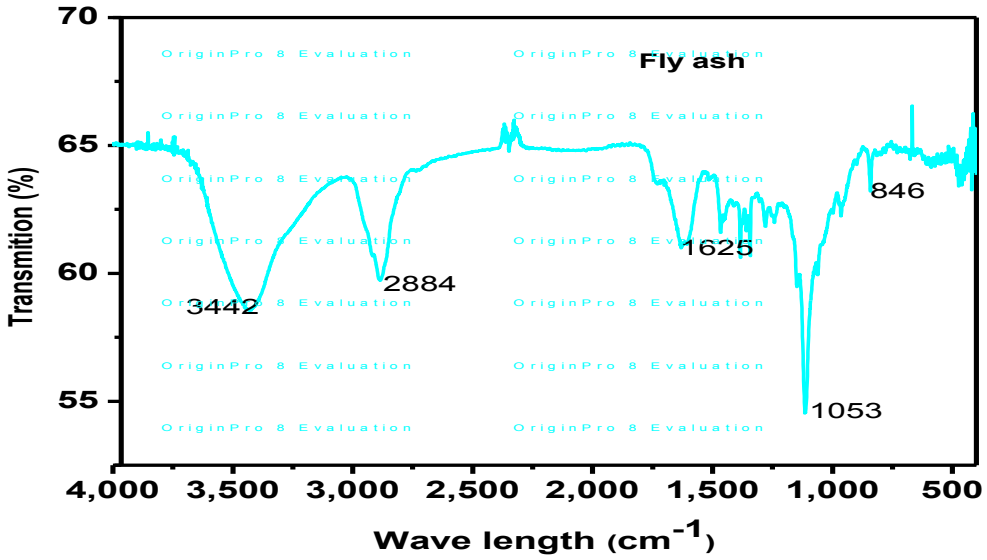


Figure 4.1: Spectra of fly ash

4.1.2.2. K_2O/Fly Ash Based Catalyst

The K_2O/fly ash based catalyst spectra obtained is illustrated in Figure 4.2 the most important transmission bands are at 3432, 1624, 1455, 1384, 1029 and 458 cm^{-1}.

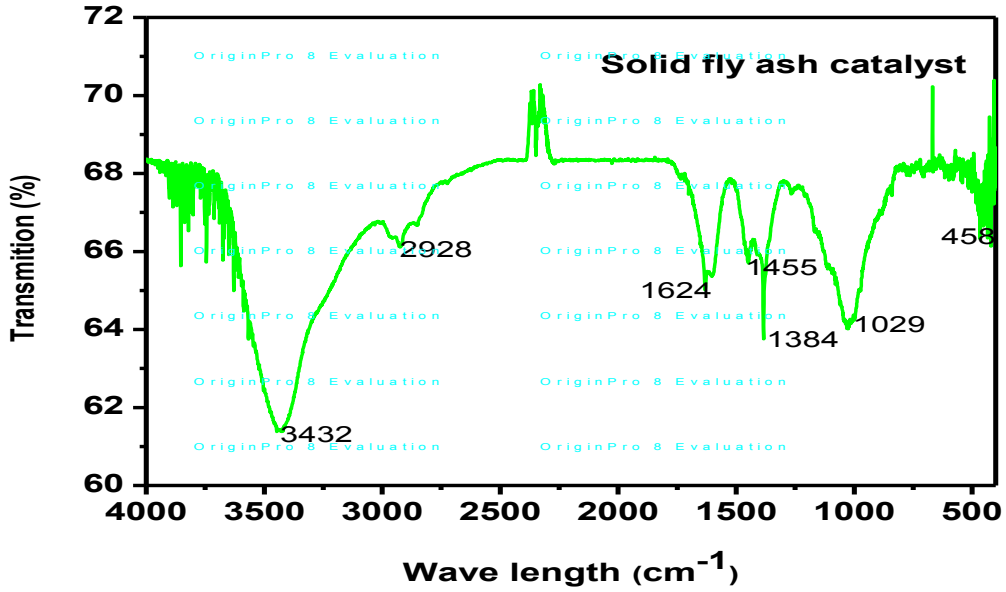


Figure 4.2: Spectra of K_2O/fly ash based catalyst

The spectrum for fly ash (Figure 4.1) shows the three wide bands characteristic of aluminosilicates: the band appearing at 1053 cm^{-1} was associated with T-O (T = Al, Si) asymmetric stretching vibrations. An adsorption peak observed at 1384-1455 cm- 1 with the potassium impregnated fly ash catalyst shows the presence of weak aliphatic bonds associated with N-O bond (Babajide et al. 2010).

The main feature of the FTIR spectra of fly ash shows a broad band at 1053 cm^{-1} depicts the presence of Al, Si asymmetric stretching vibrations. The intensity of this band is proportional to the reactivity of fly ash. In fly ash materials impregnated with KOH, a large broad band at around 3432 cm^{-1} is attributed to the presence of the O-H stretching frequency of silanol groups bonded to the inorganic structure, and also hydrogen bonds between adsorbed water and silanol group. Peaks appearing at 1384-1455 cm^{-1} shows the presence of potassium (S. Alehyen, M. EL Achouri 2017).

4.1.3. X-ray Diffraction (XRD) of K_2O/Fly Ash Catalyst

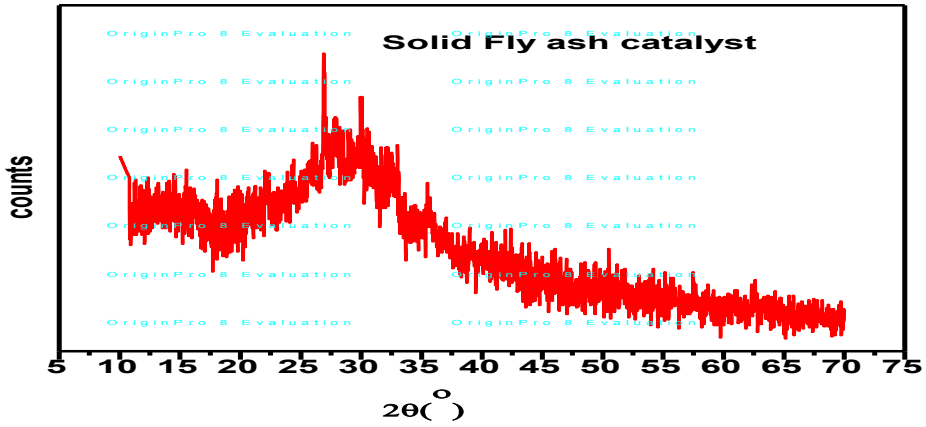


Figure 4.3: XRD patterns of K_2O/fly ash catalyst

From the XRD patterns of fly ash based catalyst illustrated in figure 4.3, it was found that the predominant phase were quartz (SiO_2) with major peaks at 20.86, 26.9, 30.1 and 36.5 degrees 2θ and intense peaks of mullite ($3Al_2.SiO_2$) at 42.4 degrees 2θ. This fly ash based catalyst shows that the characteristic peaks of crystalline phases with: quartz and mullite. A crystalline hump is observed in the diffraction pattern between 2θ values of approximately 20° to 40° (Kotwal MS. et at. 2009)

4.2. Purification of Jatropha Cured Oil

In order to remove impurities, gums like substances and to purify the Jatropha seed oil, we have done degumming and neutralization processes. The total amount of crude Jatropha oil obtained from extraction with mechanical press method was 3 liters from 6 kg of dried Jatropha seed.

- **Degumming**

It is the removal of phosphatides, gums and other complex compounds from the extracted crude Jatropha oil. Hence, based on the method discussed in the previous chapter; 3% of distilled water and 2% of phosphoric acid by volume is required for degumming the crude Jatropha oil. This degumming process uses 60 ml phosphoric acid and 90 ml distilled water.

4.3. Characterization of Physico-chemical Properties of Purified Jatropha Oil

4.3.1. Moisture Content Determination

The amount of sample was weighted using a balance for each experiment. Then; it was dried in an oven at 110ºC for 8 hours. Again, the weight of the sample after drying was measured. The moisture content of kernel was 5.01%.

Table 4.2: Moisture content determination of Jatropha kernel

Run	Weight of the sample before drying (gm)	weight of the sample before drying (gm)	Difference(before drying-after drying)	Moisture content (%)
1	25.34	24.07	1.27	5.01

4.3.2. Physico-chemical Properties of Purified Jatropha Oil

The density, viscosity, acid value, free fatty acid composition and saponification number of purified Jatropha oil were determined. The value of thus physicochemical was shown in the table below.

Table 4.3: Physico-chemical properties of purified Jatropha oil

Property	Experimental Result	Unit
Density at 15ºC	910	Kg/m^3
Kinematic viscosity at 40ºC	39.89	mm^2/s
Acid Value	7.00	mgKOH/g oil
Free Fatty Acid Composition	3.51	%
Saponification Number	195.74	mgKOH/g oil

All of the physico-chemical properties (density, viscosity, acid value, free fatty acid composition and saponification number) of purified Jatropha oil are in agreement with ASTM specification and results in other literature referred.

4.4. Characterization of Physico-Chemical Properties of Biodiesel

Comparing the physico-chemical properties of Jatropha oil and the produced biodiesel it shows significant change. This is due to the K_2O/fly ash catalyzed transesterification reaction.

Table 4.4: Physico-chemical properties of Jatropha oil biodiesel

Property	Experimental Result	Unit
Density at 20ºC	878.8	Kg/m^3
Kinematic viscosity at 40ºC	3.54	mm^2/s
Acid Value	0.463	mgKOH/g oil
Free Fatty Acid Composition	0.233	%
Saponification Number	160.5	mgKOH/g oil
Higher Heating Value	40.5	MJ/kg
Flash Point	207	ºC

All of the physico-chemical properties (density, viscosity, acid value, free fatty acid composition, saponification number, flash point and higher heating value) of purified Jatropha oil biodiesel produced at the optimum conditions (molar ratio of methanol to oil at 6.5:1, reaction temperature of 60ºC and catalyst loading of 3.44 Wt.%) are in agreement with ASTM specifications and results in other literature referred.

4.4.1. Gas Chromatography-Mass Spectroscopy (GC-MS)

The determination of fatty acid methyl ester composition of biodiesel produced from Jatropha seed oil by GC-MS was performed and the major component of the biodiesel was shown in the table below.

The GC-MS identification of compounds presented in biodiesel was shown in the table below. We can observe that the fatty acid methyl esters that were identified by their time of retention. This is in order of their retention time; Palmitoleic, Palmitic, Linoleic, Oleic, stearic and Arachidic. We can also observe that the higher percentage area is registered for Oleic and Linoleic methyl esters respectively.

Table 4.5: Identification and product composition biodiesel (FAME) liquid by GC-MS

Peak	Fatty Acid	Systemic Name of compound	Retention time (min)	Area (%)
1	Palmitoleic	9-Hexadecenoic, methyl ester	46.131	0.75
2	Palmitic	Pentadecanoic acid, methyl ester	46.349	15.24
3	Linoleic	9,12-Octadecadienoic, methyl ester	48.063	35.73
4	Oleic	9-Octadecenoic, methyl ester	48.120	39.18
5	Stearic	Methyl stearate	48.323	8.98
6	Arachidic	Eicosanoic	50.100	0.11

4.5. Analysis of Biodiesel Production

The transesterification reaction was carried out using a 500 ml capacity three naked glass reactor which is equipped with a stirrer, condenser and thermostat. The statistical analysis of the biodiesel was discussed below.

4.5.1. Statistical Analysis of 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 molar ratio of methanol to oil, reaction temperature and catalyst load.

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.

Table 4.6: Analysis of variance (ANOVA) for the regression model equation and coefficients

ANOVA for Response Surface Quadratic model						
Analysis of variance table [Partial sum of squares - Type III]						
Source	Sum of Squares	DF	Mean Square	F Value	P-value Prob > F	Remark
Model	1480.38	9	164.49	644.76	< 0.0001	Significant
A	0.59	1	0.59	2.32	0.1584	
B	1235.90	1	1235.90	4844.49	< 0.0001	
C	43.67	1	43.67	171.20	< 0.0001	
AB	4.06	1	4.06	15.52	0.0026	
AC	0.36	1	0.36	1.42	0.2615	
BC	9.46	1	9.46	37.09	0.0001	
A^2	1.79	1	1.79	7.01	0.0244	
B^2	180.02	1	180.02	705.65	<0.0001	
C^2	14.60	1	14.60	57.22	<0.0001	
Residual	2.55	10	0.26			
Lack of Fit	1.96	5	0.39	3.29	0.1087	Not significant
Pure Error	0.60	5	0.12			
Cor Total	1482.93	19				

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 yield of the transesterification processes was calculated as weight of FAME produced to the weight of Jatropha oil used multiplied by 100%. The formula is given as:

$$Yield\ of\ FEME = \frac{weight\ of\ fatty\ acid\ methyl\ ester}{weight\ of\ oil\ used} * 100\% \ldots\ldots\ldots\ldots\ldots\ldots 4.1$$

Table 4.7: Experimental and predicted values of Jatropha oil biodiesel yield

Run	Molar ratio of methanol to oil, (mole/mole)	Reaction temperature, (ºC)	Catalyst loading, (Wt.%)	Experimental Biodiesel(FAME) Yield, %	Predicted Biodiesel(FAME) Yield, %	Residual
1	9	55	1.32	80.4	80.58	-0.18
2	9	55	4.68	86.3	86.60	-0.30
3	12	60	4	90.8	91.04	-0.24
4	9	55	3	86.8	86.44	0.36
5	3.95	55	3	84.8	85.09	-0.29
6	14.05	55	3	85.6	85.79	-0.19
7	9	46.59	3	60.2	60.44	-0.24
8	12	60	2	90.6	90.06	0.54
9	9	55	3	86.6	86.44	0.16
10	12	50	2	70	70.29	-0.29
11	9	55	3	86	86.44	-0.44
12	6	50	4	74	74.20	-0.20
13	9	55	3	86.8	86.44	0.36
14	9	63.41	3	92.2	92.44	-0.24
15	6	60	2	90.4	90.65	-0.25
16	12	50	4	76.2	75.61	0.59
17	6	60	4	93.1	92.47	0.63
18	6	50	2	68.6	68.02	0.58
19	9	55	3	86.1	86.44	-0.34
20	9	55	3	86.4	86.44	-0.036

4.5.1.1. Development of Regression Model Equation

The model equation that correlates the response (yield of Jatropha oil to Biodiesel) to the transesterification process variables in terms of actual value was given below. The predicted model for a percentage of biodiesel (FAME) content in terms of the coded factors is given by the equation below.

$$\text{Yield of FAME (\%)} = +86.44 + 0.21*A + 9.51 * B + 1.79 * C - 0.71 * A* B - 0.21 * A* C$$
$$-1.09 * B * C - 0.35 * A^2 - 3.53 * B^2 - 1.01 * C^2$$

Where A= molar ratio of methanol to oil

B = reaction temperature

C= weight of catalyst amount

4.5.1.2. Model Adequacy Check

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 0.9983, 0.9967, 0.9880 respectively. The quality of the model developed could be evaluated from their coefficients of correlation. The value of R-squared for the developed correlation is 0.9983. It implies that 99.83% of the total variation in the percentage yield of biodiesel (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 4.4. The results in Figure 4.4 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 reaction process variables to the percentage yield of biodiesel. The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in Table 4.6, based on a 95% confidence level, F–value is a test for comparing model variance with residual (error) variance. If the variances are close to the same, the ratio will be close to one and it is likely that any of the factors have a significant effect on the response with the P–value less than 0.05. It is calculated by model mean square divided by residual mean square.

The model F-value of 644.76 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise (personal error or disturbance).

Values of "Prob > F" (p-value) less than 0.0500 indicate model terms are significant. In this case, B, C, AB, BC, A^2, $B^{2,}$ C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. This shows that the reaction temperature, amount of catalyst loading, interaction between molar ratio of methanol to oil and reaction temperature, interaction between reaction temperature and amount of catalyst loading, square of molar ratio of methanol to oil, square of the reaction temperature and square of catalyst loading affects the percentage yield of biodiesel production from Jatropha oil significantly.

The "Lack of Fit F-value" of 3.29 implies the Lack of Fit is not significant relative to the pure error. There is a 10.87% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good because we want the model to fit.

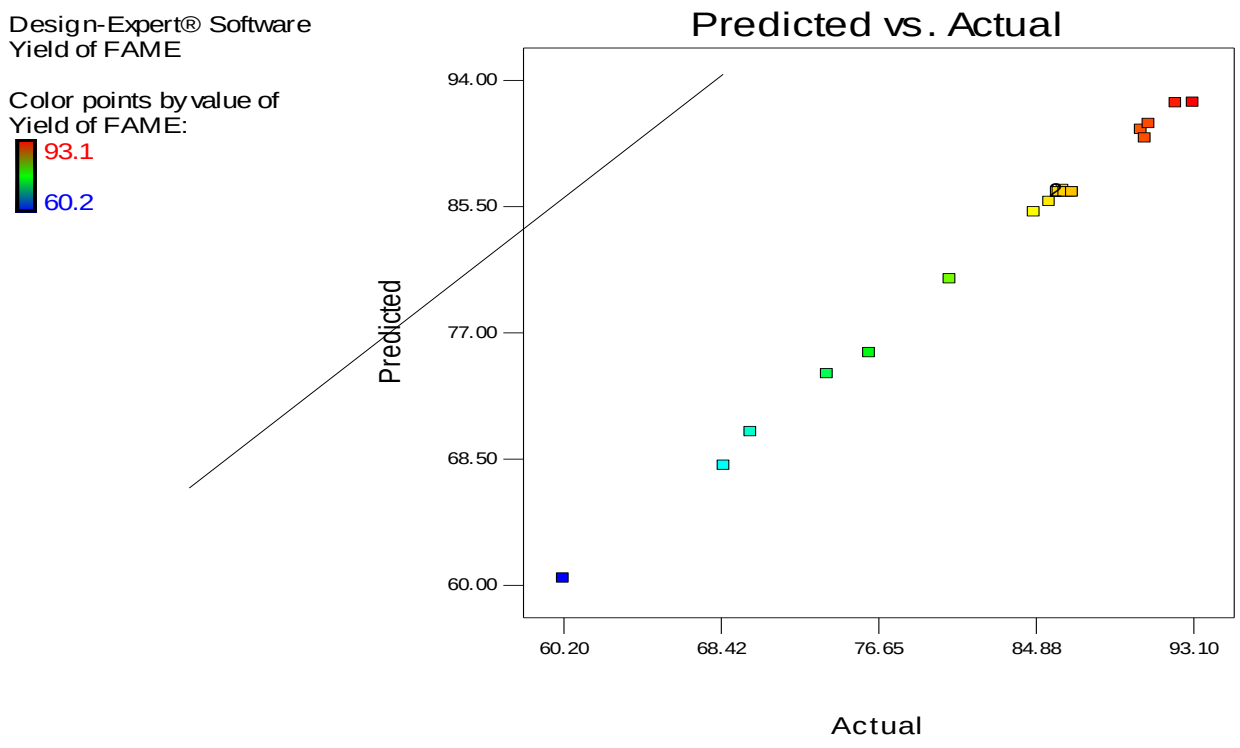


Figure 4.4: Predicted versus actual yield of FAME

4.5.2. Effect of Transesterification Reaction Process Variables

This result demonstrated that the advantage of using surface response for experimental data analysis in capturing the interaction between variables that affects the transesterification reaction. Methanol to oil molar ratio, reaction temperature, and catalyst loading was considered as input process variables. Analysis of variance on Table 4.6 has shown that main and interaction effect is significant in this model and variation of those process variables affects the product yield. Based on the analysis of variance, transesterification reaction was significantly affected by various interactions between the process variables. In addition to the interaction effect, significant individual process variables affect the transesterification reaction.

4.5.2.1. Effect of Individual Process Variables on Biodiesel Yield

A. Effect of methanol to oil molar ratio

The ratio of methanol to oil is one of the important factors that affect the conversion of triglyceride to FAME. 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.

Theoretically, one mole of triglyceride requires three moles of methanol, but in practice, higher amount is required to shift the reaction equilibrium forward and maximize the yield. Effect of methanol on the FAME yield was studied at constant temperature and catalyst load, 55ºC and 3%, respectively, as shown in Figure 4.5. It indicates that increasing of methanol to oil molar ratio from 6 to 12, doesn't have highly significant impact on the yield of FAME. Methanol to oil molar ratio of 12:1 results 86.29% FAME yield which is almost similar to methanol to oil molar ratio of 6:1 which is 85.88%. This is because, as the amount of methanol increases, it will shift the reaction equilibrium forward (i.e. since transesterification reaction is reversible) and at the same time it will result in an increase in the rate of reaction as well. However, a further increase in methanol leads to dilution of the catalyst. In addition, most probably at a higher amount of methanol, the reverse reaction which is a recombination of glycerol and ester may have started to takes place; this in turn can lead to the formation of diglyceride and monoglyceride, which ends up with the incomplete conversion.

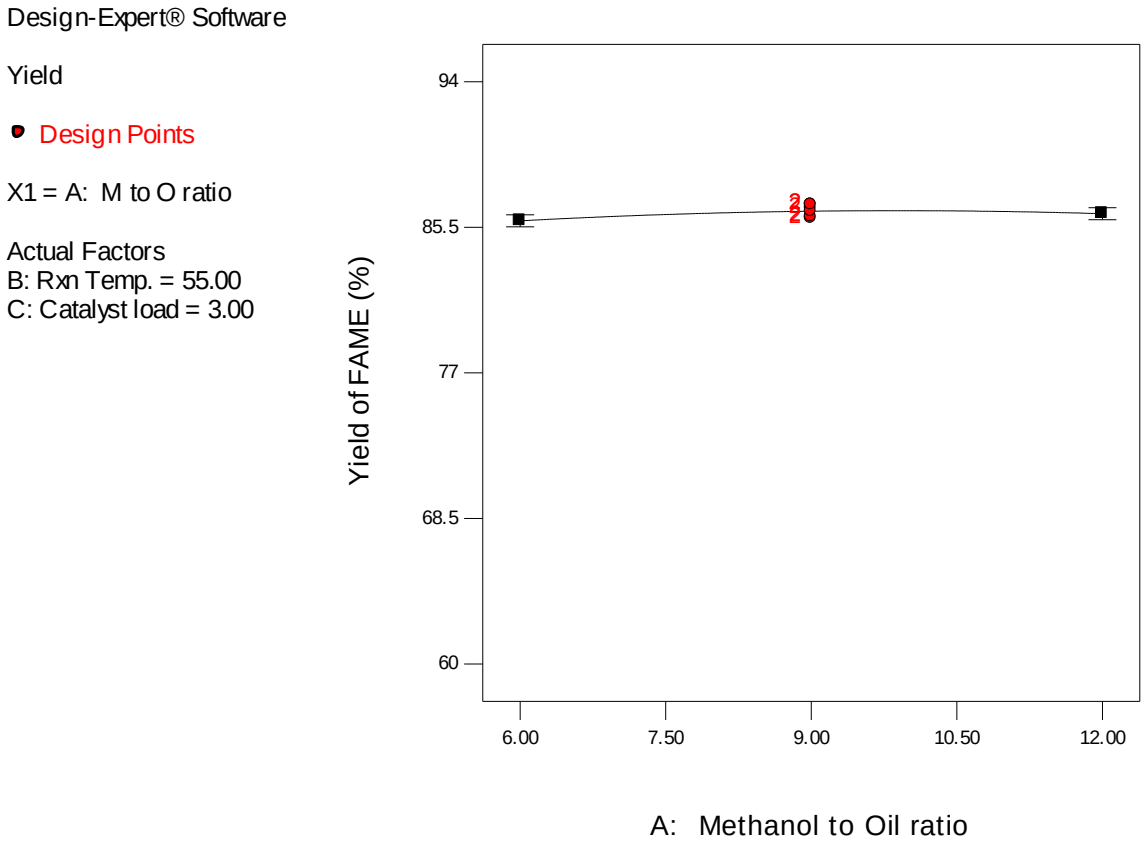


Figure 4.5: Effect of methanol to oil molar ratio on the yield of FAME at 55ºC and catalyst load 3%.

B. Effect of temperature

The effect of temperature at constant methanol to oil molar ratio (9:1) and catalyst load (3%) was studied. Figure 4.6 shows that as the temperature increases from 50ºC to 60ºC, a significant amount of increase in biodiesel (FAME) yield is observed. This 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. The increase in the yield of FAME at higher reaction temperature is due to higher rate of reaction. 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 a slower rate of reaction. However, as the temperature approaches the boiling point of methanol the percentage yield of FAME decreases.

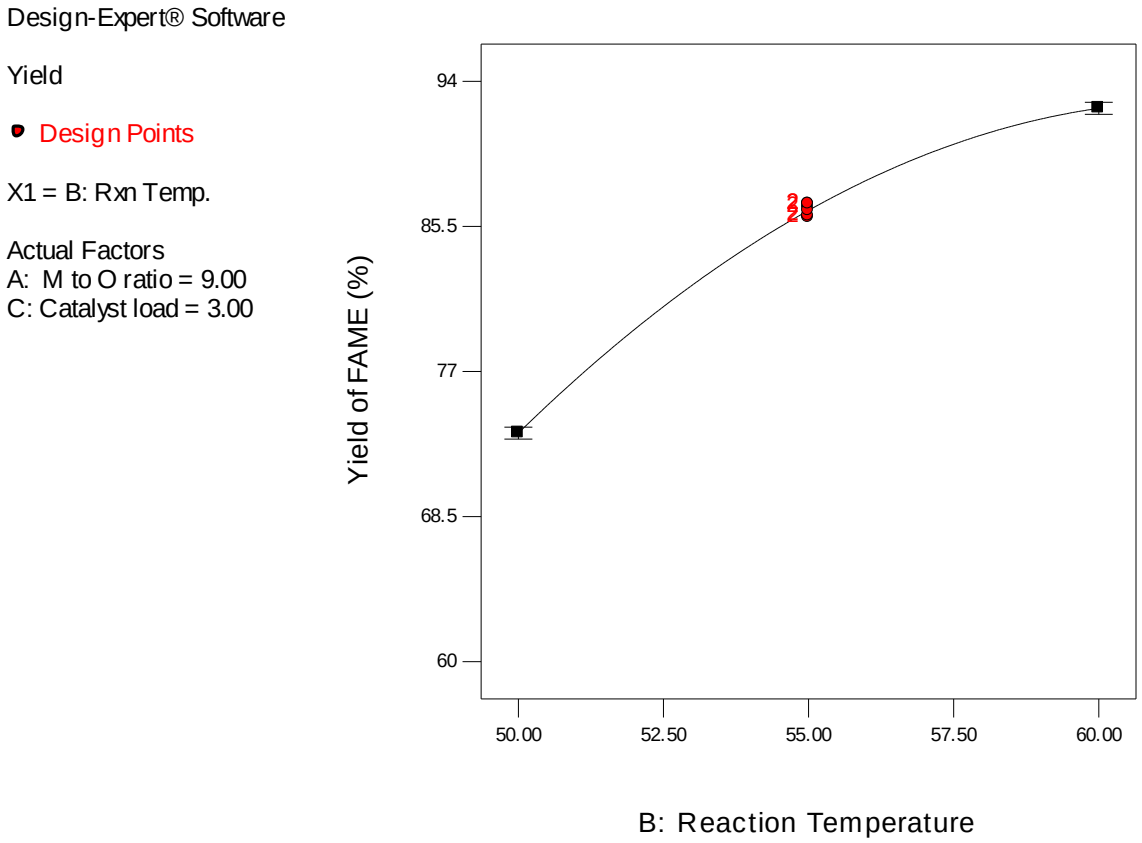


Figure 4.6: Effect of reaction temperature on yield of FAME at methanol to oil molar ratio (9:1) and catalyst load 3%.

C. Effect of catalyst load

The increase of the catalyst will increase the reaction rate so that the purity of biodiesel produced will increase. Figure 4.7 shows that increasing the catalyst amount has a significant positive effect on FAME yield. It was observed that when the catalyst load is low, incomplete transesterification occurred. However, as the amount increases, more triglyceride is changed to ester. The reason behind is increasing of the catalyst provides more active sites for the reaction of available triglyceride and methanol. In addition, the amount of available catalytic active surface is one important parameter to shift the reaction equilibrium forward in addition to the amount of methanol in the reaction mixture.

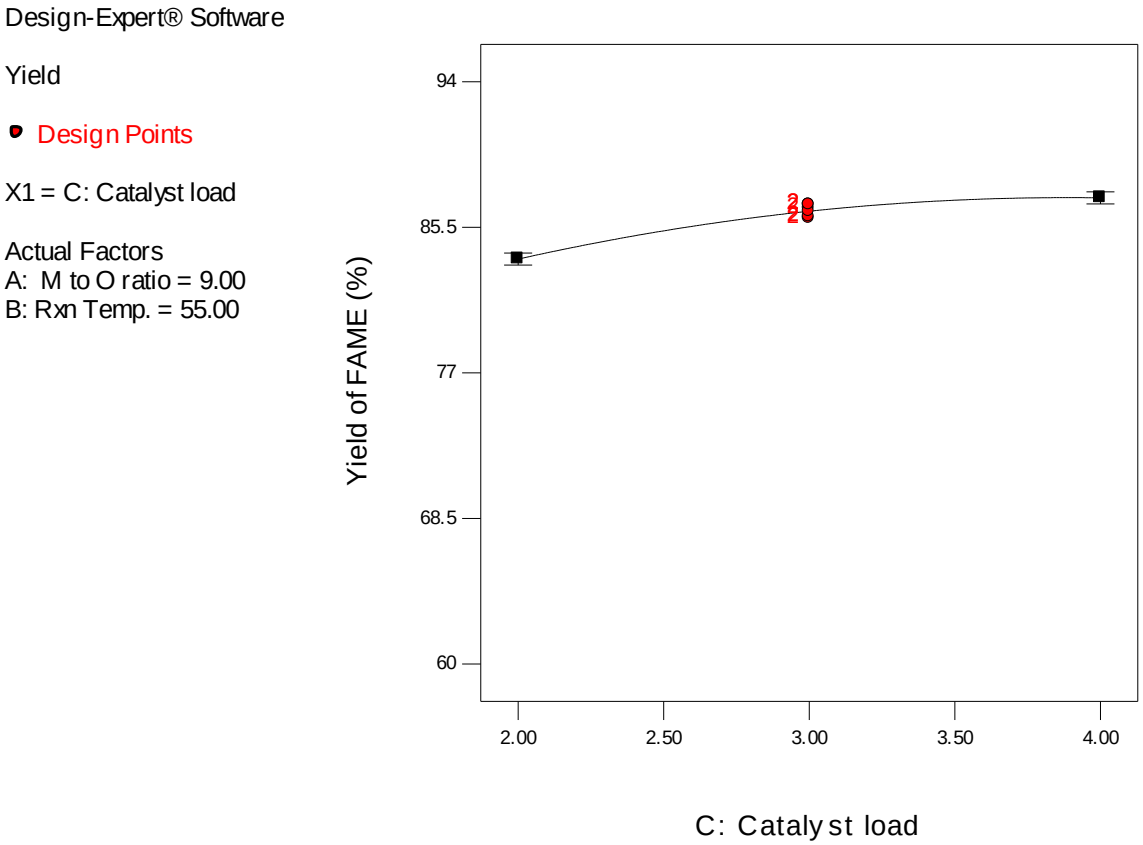


Figure 4.7: Effect of catalyst loading on the yield of FAME at methanol to oil molar ratio (9:1) and reaction temperature (55ºC).

4.5.2.2. Effects of Interaction of Process Variables on Percentage Yield FAME

The most common way to summarize the results of a central composite design experiment is in the form of a response surface plot and via response contours plot. The process variables were found to have significant interaction effects except for molar ratio of methanol to oil with catalyst load interaction.

The contour and 3-D plots of interaction effects of process variables over the FAME yield were drawn and subsequently, descriptions are given. Each contour curve represents effects of two process variables while holding the third at a constant level. Figure 4.8 and Figure 4.9 shows the interaction between molar ratio of methanol to oil and reaction temperature, reaction temperature and amount of catalyst loading on the percentage of FAME yield respectively.

The contour and 3-D plots below shows the effect of varying methanol to oil molar ratio and reaction temperature while the catalyst loading is at 3%. Initially, the effect of low level of methanol to oil molar ratio and low reaction temperature produces low percentage yield of biodiesel (FAME). Further increase of both process variables enables the optimum amount of yield. Whereas an increase in the molar ratio of methanol to oil beyond some levels decreases the yield. This might be due to catalyst deactivation. The effect of increasing temperature on the percentage yield of biodiesel in the interaction with a molar ratio of methanol to oil leads to an increase in the percentage yield.

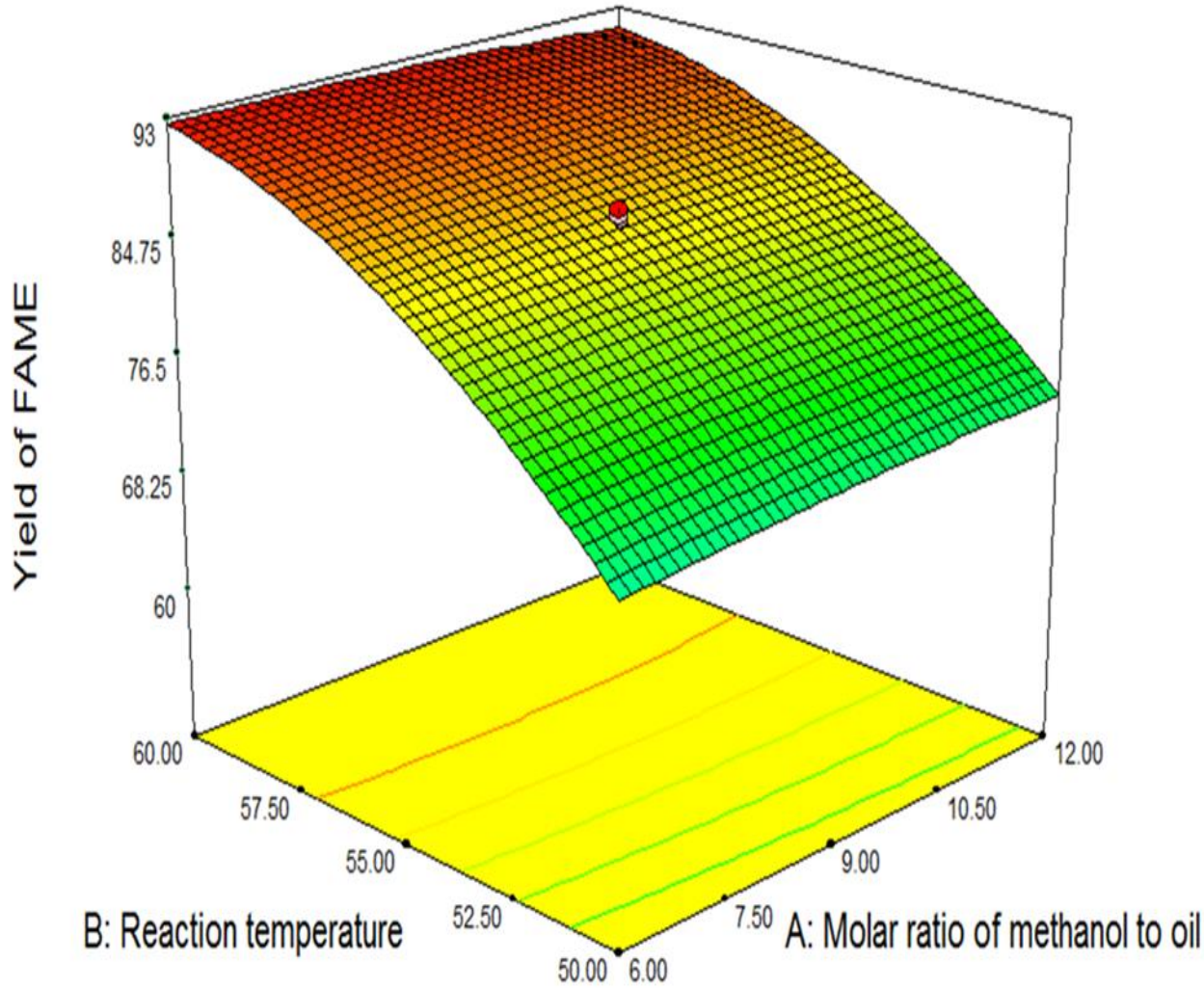


Figure 4.8a: 3-D plot of the interaction effect of molar ratio of methanol to oil and reaction temperature versus percentage yield of FAME when the catalyst loading is 3%.

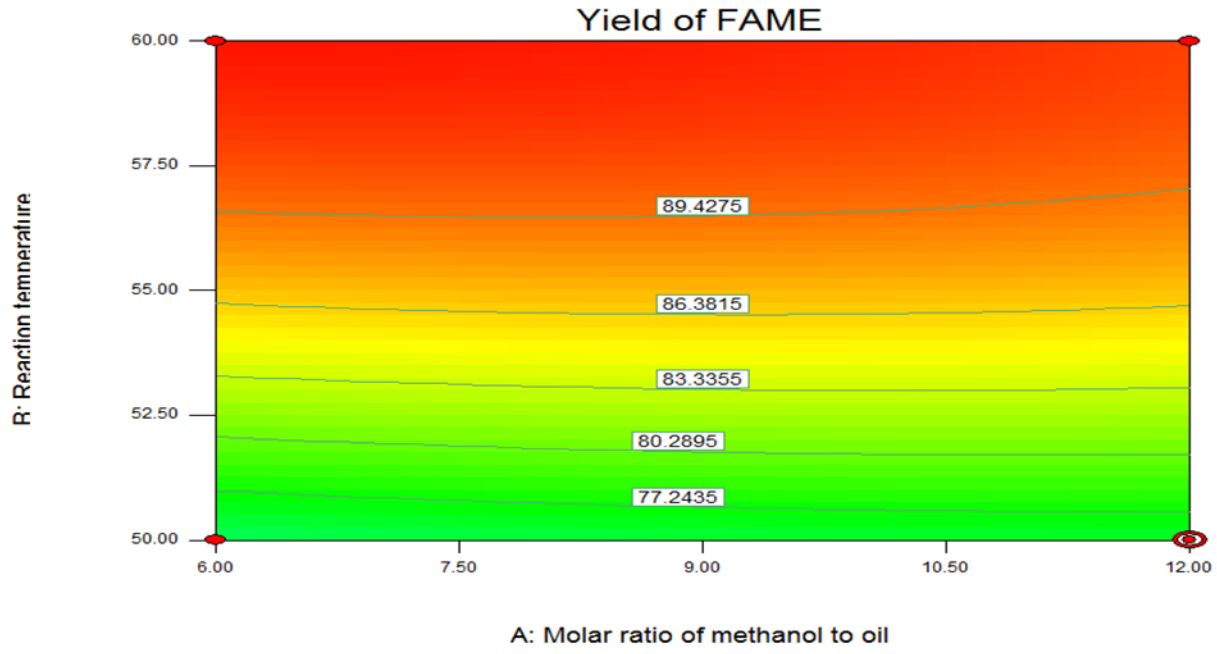


Figure 4.8b: Contour plot of the interaction effect of molar ratio of methanol to oil and reaction temperature versus percentage yield of FAME when the catalyst loading is 3%.

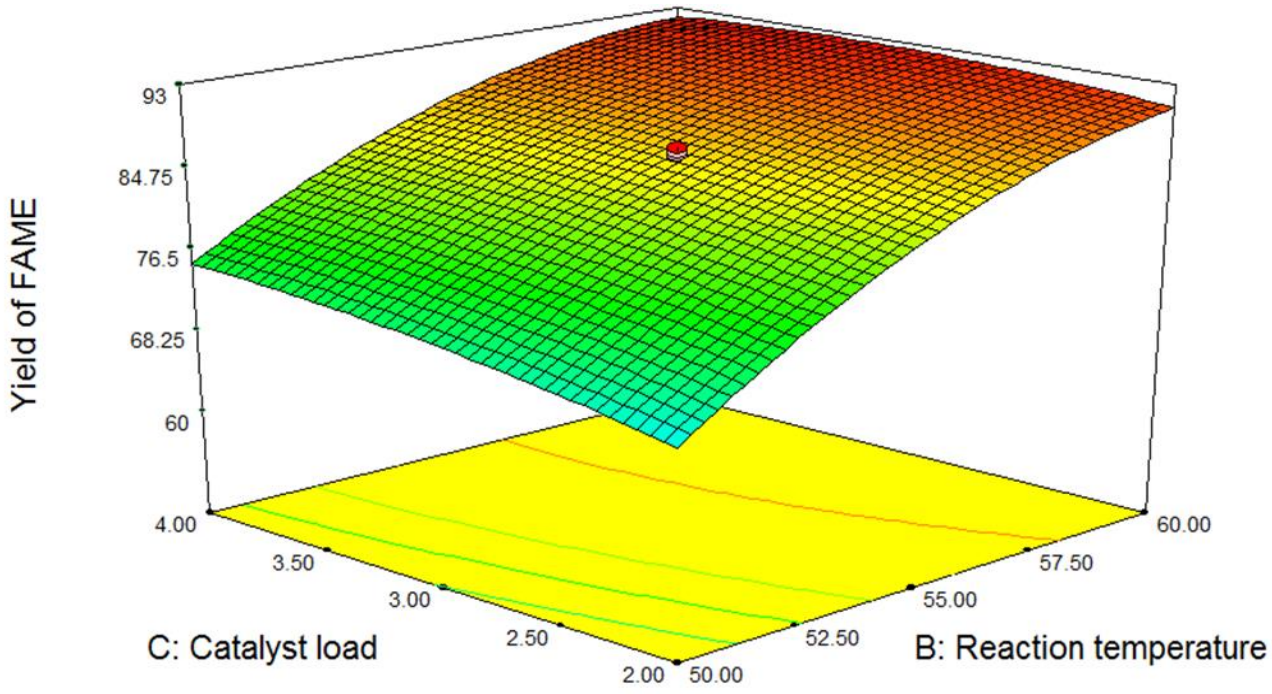


Figure 4.9a: 3-D plot of the interaction effect of reaction temperature and amount of catalyst loading versus percentage yield of FAME when the molar ratio of methanol to oil is 9:1.

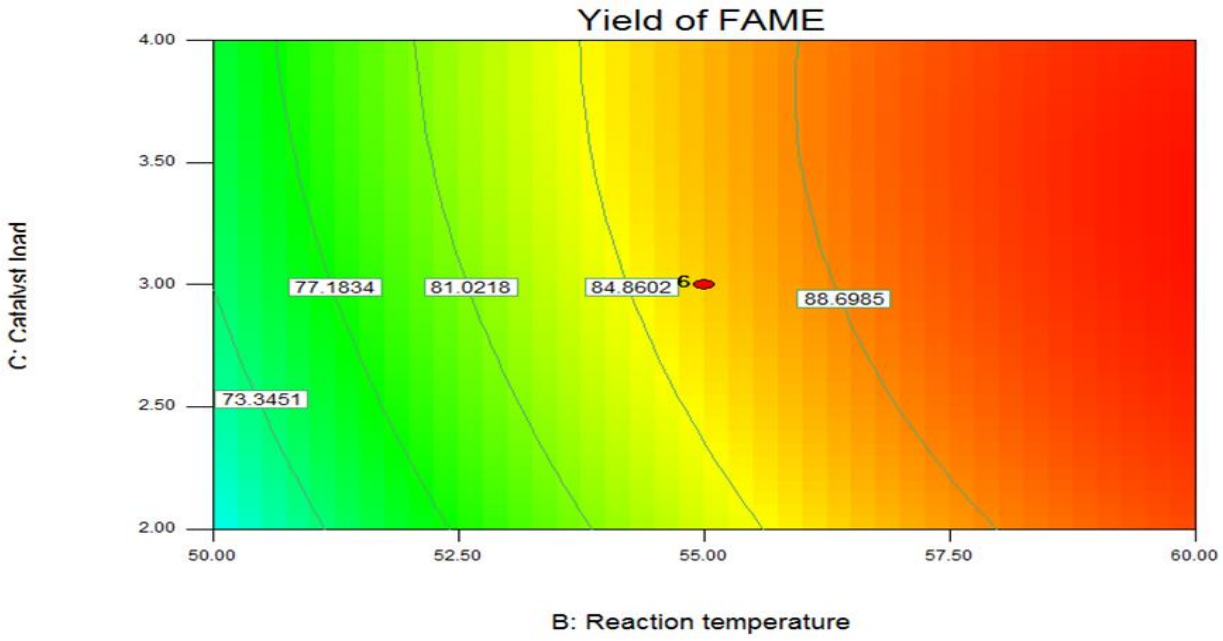


Figure 4.9b: Contour plot of the interaction effect of reaction temperature and amount of catalyst loading versus percentage yield of FAME when the molar ratio of methanol to oil is 9:1.

The 3-D and contour plots in figure 4.9a and 4.9b respectively shows that the interaction between reaction temperature and catalyst loading on biodiesel yield. As it can easily see from the two plots below, the interaction effect of the two process variables affects the yield positively at higher values. The reason behind this is as the catalyst loading increases the concentration of the catalyst increases then reaction mixture will have the possibility of accessing more active site of the catalyst to react on it and the high rate of reaction at a higher temperature will enhance the reaction to give higher yield. Similarly true if the catalyst loading is and reaction temperature decreases the catalytic active site lowers and reaction rate decreases and there is a drop in percentage yield of biodiesel produced. Generally, an increase in reaction temperature is found to increase the yield of FAME in all two cases.

This is probably because at these conditions, the higher reaction temperature is already sufficient to push the reaction forward. This phenomenon is further supported by the fact that reaction temperature is the most significant process variable that affects the yield of the FAME as indicated by the highest F-value in the ANOVA (Table 4.6).

4.5.3. Optimization of Process Variables

The optimization of process variables within the selected ranges for maximum conversion of the oil to FAME was evaluated using Design Expert 7.0.0. The optimum result predicted by the model was found to be 92.78% FAME at methanol to oil molar ratio of 6.47:1, temperature of 60ºC and catalyst loading of 3.44 Wt.% with a desirability value of 0.990. 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, the interaction between the temperature and the catalyst and the interaction between temperature and methanol to oil ratio. In order to verify this prediction, three experiments were conducted and the results were comparable with the prediction. It was found that the experimental value of 92.68% of FAME content agreed well with the predicted value. Therefore, this study shows solid fly ash impregnated with KOH and calcined at 500ºC (K_2O/fly ash) is a potential catalyst for the production of biodiesel from Jatropha oil via transesterification reaction.

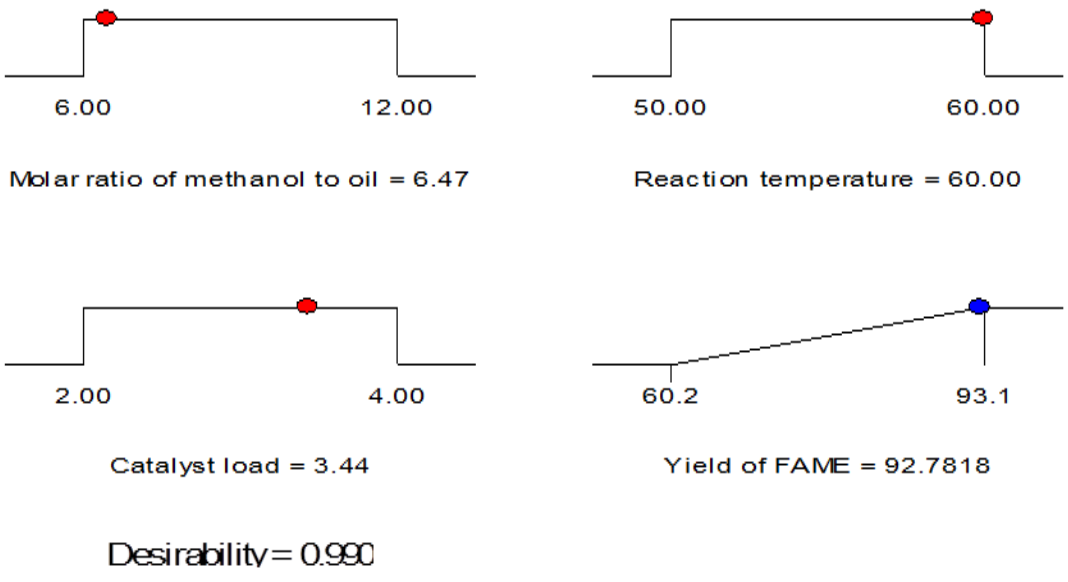


Figure 4.10: Optimum conditions predicted by the model using desirability ramp

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

In this research work, the use of K_2O/fly ash based catalysts for biodiesel production has been investigated and the produced biodiesel was characterized. Three transesterification parameters affecting the yield of biodiesel; the molar ratio of methanol to oil, reaction temperature, and catalyst load has been studied. The outputs of the experiments conducted have been analyzed by employing analysis of physico-chemical parameters. The result obtained shows that biodiesel production using solid-fly ash based catalyst, is a considerable potential in biodiesel production process, mainly because of catalyst regeneration, Simplification of the separation process 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 the design of experiment analysis in successfully capturing these effects. Of all the variables studied, reaction temperature, catalyst loading, the interaction between molar ratio of methanol to oil and reaction temperature, and the interaction between temperature and catalyst weight had more influence on the yield of the reaction. 60ºC of reaction temperature, 6.5:1 of molar ratio of methanol to Jatropha oil and 3.44wt% of catalyst loading, highest fatty acid methyl ester yield of 92.68% was obtained. The experimental results show that the prepared K_2O/FA based catalyst has excellent activity during transesterification. Since the catalyst is solid catalyst, it can decrease the wastewater treatment and the steps of purification. It has a potential for industrial application in the transesterification of Jatropha oil to biodiesel. Hence, K_2O/FA catalyst has good catalytic performance.

The K_2O/FA catalyst used for this work was selected based on the catalytic activity of the transesterification reaction performed at constant reaction variables for each prepared catalyst. So, fly ash catalyst loaded with 12 M KOH was selected for the whole research work.

Therefore, it can be concluded that K_2O/FA based is an effective catalyst for the production of biodiesel from Jatropha oil via transesterification reaction. An increase in the catalyst content caused an increase in the biodiesel yield. The drop in biodiesel yield at higher methanol to oil ratio with lower catalyst ratio could also be due to catalyst leaching and deactivation. The

percentage yield of biodiesel increased with increasing catalyst concentration at a low methanol-to oil molar ratio. The percentage yield of biodiesel increased with increasing reaction temperature at a high catalyst concentration. Physico-chemical properties determined for the oil extracted and biodiesel produced meets the ASTM specification and results in other literature referred.

5.2. Recommendations

Further investigations are recommended to understand the behavior and catalytic activity of the K_2O/fly ash-based catalysts, such as:

In this research, the selection of prepared catalyst was performed only based on catalytic activity of the prepared catalyst by conducting transesterification reaction using the same dosage for each type of catalyst but selection of the catalyst based on the surface area, pore volume and pore diameter each catalyst in the reaction are very important concepts not covered in this research which needs further investigations.

- Study the reusability and regeneration of the catalysts. In addition, the study of catalyst leaching due to the washing with solvents is also important.
- Study effect of calcination temperature, effect of calcination time and amount of potassium hydroxide loading during the preparation of catalyst on catalytic activity.
- Study strength and density of basic sites of the prepared catalyst,
- Characterization of physico-chemical properties of K_2O/fly ash-based catalysts should be done using BET and SEM.

Further study on improvement of the transesterification reaction process parameters reaction time and speed of stirrer on percentage yield of FAME is also suggested.

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APPENDICES

Appendix A: Experimental Result

Table A-1: Viscosity of Jatropha seed oil

Dynamic viscosity, mPa.sec at 40ºC			Average dynamic Viscosity, mPa.sec at 40ºC	Density, kg/m^3	Kinematic viscosity, mm^2/sec
36.1	36.4	36.5	36.3	910	39.89

Table A-2: Acid Value and FFA composition of Jatropha seed oil

Run	mass of oil, g	N_{KOH}	V_{KOH} ,ml	AV, mg KOH/g	FFA composition
1	3	0.14	2.7	7.07	3.55
2	3	0.14	2.7	7.07	3.55
3	3	0.14	2.6	6.81	3.42
			Average	7.00	3.51

Table A-3: Saponification value of Jatropha seed oil

Run	N_{HCL}	$V_{1\ HCL,}$ ml	$V_{2\ HCL,}$ ml	mass of Oil, g	SV, mgKOH/g
1	0.53	6.8	20	2	196.24
2	0.53	6.7	20	2	197.72
3	0.53	6	20	2	193.26
				Average	195.74

Table A-4: Experimental processes conditions for transesterification reaction

Run	Molar ratio of methanol to oil, mole/mole	Reaction temperature, ºC	Catalyst loading, Wt.%	Reaction time, hrs	Agitation speed, rpm
1	9	55	1.32	2	500
2	9	55	4.68	2	500
3	12	60	4	2	500
4	9	55	3	2	500
5	3.95	55	3	2	500
6	14.05	55	3	2	500
7	9	46.59	3	2	500
8	12	60	2	2	500
9	9	55	3	2	500
10	12	50	2	2	500
11	9	55	3	2	500
12	6	50	4	2	500
13	9	55	3	2	500
14	9	63.41	3	2	500
15	6	60	2	2	500
16	12	50	4	2	500
17	6	60	4	2	500
18	6	50	2	2	500
19	9	55	3	2	500
20	9	55	3	2	500

Appendix B: Composition of Jatropha Oil and Jatropha Oil Biodiesel

Table B-1: 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:	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	3.7-9.6
Oleic	Cis-9-Octadecenoic	$C_{18}H_{34}O_2$	18:1	43.3-45.8
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

Table B-2: Physico-Chemical Properties of oil from Different raw material (Alnuami W.et al. 2014)

Properties	Units	Jatropha oil	Palm oil	Soybean oil	Waste cooking oil
Kinematic viscosity at 38ºC	mm^2/s	49.93	39.6	32.6	36.4
Cetane number	-	40-45	42.0	37.9	49.0
Heating value	MJ/kg	-	-	39.6	-
Flash point	^OC	240	267	254	485
Cloud point	^OC	-	31.0	-	-
Density	g/ml	0.9186	0.9180	0.9138	0.8830
Carbon residue	Wt.%	0.10	0.23	0.25	0.46

Table B-3: Biodiesel properties from different raw materials Source (Alnuami W. et al. 2014)

Property	Jatropha	Soybean	Palm oil	WCO	Biodiesel standards		
					ASTM D 6751-02	DIN EN 14214	Diesel fuel
Density at 20ºC, kg/m^3	880	885	880	884	870-900	875-900	850
Viscosity at 40ºC, mm^2/s	2.37	4.5	5.7	4.5	1.9-6	3.5-5.0	2.60
Cloud point, ºC	-	1	13	1	-	-	4
Flashpoint, ºC	135	178	164	180	≥130	≥120	68
Acid value mgKOH/g	≤0.800					≤0.500	
Pour point	2	-7	12	-5.0	-15 to 10	-15 to 10	-20
Water, %	0.025	-	-	0.4	0.03	0.05	0.02
Sulfur, PPM	-	-	-	-	50	50	500
Carbon residue, wt.%	0.2	-	-	0.3	-	0.3	0.17
Cetane number	61	45	62	57.2	48-60	49	49
Calorific value, Mj/kg	39.2	33.5	33.5	32.9	38-42	-	42

Table B-4: Fatty acid Methyl ester Composition of Jatropha oil Biodiesel (Dhewayani 2017)

peak	Formula	Component	Composition (%)
1	$C_{17}H_{32}O_2$	Methyl Palmitoleate	0.87
2	$C_{17}H_{34}O_2$	Methyl Palmitate	16.85
3	$C_{19}H_{34}O_2$	Methyl Linoleate	2.89
4	$C_{17}H_{36}O_2$	Methyl Oleate	51.56
5	$C_{19}H_{38}O_2$	Methyl Stearate	9.59
6	$C_{15}H_{26}O_2$	Methyl Pentadec	0.25

.

Appendix C: Calculations and Formulas

C-1: Chemicals used for degumming process

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

= 3000ml*0.02

= 60 ml

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

=3000 ml*0.03

= 90 ml

C-2: Formula used for viscosity calculation

$$\mu = \frac{v}{\rho}$$

Where; μ=kinematic viscosity, mm^2/s

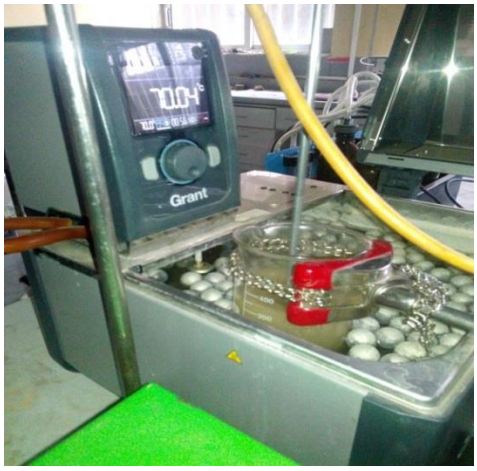
ν=dynamic viscosity, mPa.sec and

ρ=density, kg/m^3

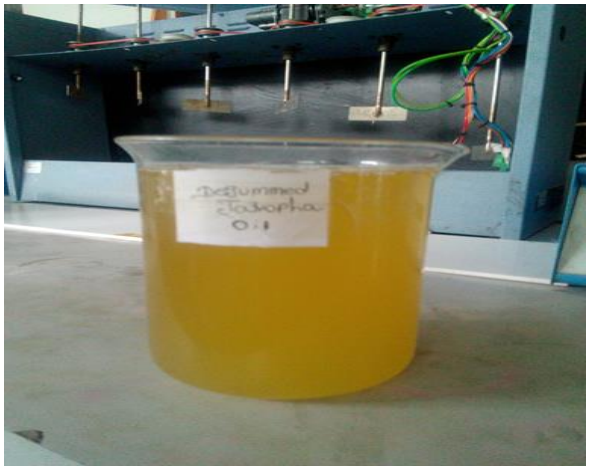
Appendix D: Photos During Laboratory Activity

a) During mechanical press extraction

b) during sieving



c) During degumming process

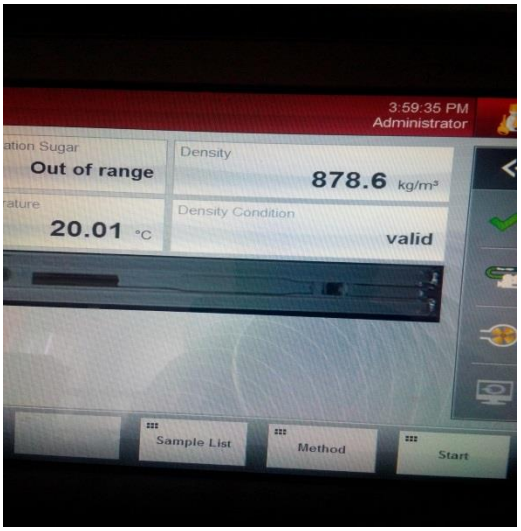


d) Degummed Jatropha oil

e) During acid value determination of Jatropha oil

f) Biodiesel

g) During catalyst preparation



h) density determination using density meter