ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
ADDIS ABABA INSTITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMEICAL ENGINEERING

BIODIESEL PRODUCTION FROM WADO SEED OIL

by

Kalay Tesfaye

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ABSTRACT

Biodiesel is a renewable, biodegradable, environmentally benign fuel for use in the diesel engines. It can be produced from renewable sources such as vegetable oils or animal fats. Although this fuel has gained worldwide recognition for many years, it is not being widely commercialized mainly because it is more expensive than petroleum diesel.

A two-step acid-base catalyzed method was successfully used in the synthesis of biodiesel from wado seed oil. The study satisfies the objective of reducing the high FFA present in the oil, followed by KOH catalyzed transesterification. The variables affecting the acid value and the methyl ester yield, such as molar ratio, catalyst concentration, reaction time and reaction temperature, were investigated to determine the best strategy for producing optimum biodiesel from the oil.

Acid value and FAME yield were used to verify the optimization of the ester conversion process. Based on the amount of WSO used, a reduction of acid value from 12.6% to 2.1 % mg KOH/g was obtained. A 94.5% FAME conversion was also obtained using a methanol/oil ratio of 6:1, 1.0% mass KOH and 55°C reaction temperature.

The important properties of the biodiesel (density, kinematic viscosity, cloud point, cetane number, iodine value, and high heating value) were compared to those of ASTM and EN standards for biodiesel. The comparison shows that the wado seed oil methyl ester could be used as an alternative to diesel.

DEDICATION

THIS WORK IS DEDICATED TO MY PARENTS: KES TESFAYE BERHE (DAD), W/RO NEGIST HAGOS (MOM), HAYMANOT, YORDANOS, & YERGALEM (SISTERS.) AND TSEGAZEAB (BRO.).

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Table of Contents

LIST OF FIGURES

ACRONOMYS

AAIT	Addis Ababa Institute of Technology
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
AV	Acid Value
CCD	Central Cubic Design
CN	Cetane Number
CP	Could Point
CSTR	Continuous Stir Tank Reactor
DOE	Design of Experiments
DV	Dynamic Velocity
EN	European Committee for Standardization
EU	European Union
FAME	Fatty Acid Methyl Ester
FFAs:	Free Fatty Acids
FP	Flash Point
GC	Gas chromatography
GHG	Green House Gases
GPNRS	Gambella Peoples' National Regional State
HHV	Higher Heating Value
HPLC	High Performance Liquid Chromatography
IV	Iodine Value
KV	Kinematic Velocity
NHP	Non-hydratable Phosphatides
PFR	Plug Flow Reactor

PLC	Private Limited Company
SNNP	Southern Nations and Nationalities People
Subsp.	Sub species
SV	Saponification Value
WSO	Wado Seed Oil

CHAPTER ONE

1. INTRODUCTION

1.1 Background

Throughout human history, the development of societies has been accompanied by an increase in growing energy needs, particularly after the Industrial Revolution. These energy requirements have been achieved mostly through the combustion of various materials such as oil, coal and natural gas. These materials are considered natural sources or fossil fuels and therefore non-renewable. High emissions of, CO_2, NO_x, SO_2, particulate matter, poly-aromatic hydrocarbons and hydrocarbons are produced during fossil fuel use, creating environmental problems. These facts have converged in the search for renewable energy sources, such as biofuels- *bioethanol* and *biodiesel*; a non-toxic biodegradable fuel, with a high heating value and high energy oxygen content (Demirbas, 2003).

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

Biodiesel is an alternative fuel from agricultural products that can be used directly in any existing unmodified diesel engine. It can be produced easily from common feed stocks (lipid sources such as: vegetable oils, animal fats and recyclable cooking oils) by transesterification in which oil or fat is reacted with a monohydric alcohol in the presence of a catalyst. Furthermore it can be blended with diesel fuel at any proportion without major changes in infrastructure and many other potential benefits (Roth Kopf, 2007). Unlike fossil diesel, pure biodiesel is biodegradable, nontoxic and essentially free of sulfur and aromatics.

Among the most promising sources, vegetable oils and animal fats have attracted much attention as a potential resource for production of biodiesel which is quite similar to conventional diesel in its main characteristics and can be blended in any proportion with petroleum diesel to create a stable biodiesel blend (Agarwal and Das, 2001).

The production and use of biodiesel has increased significantly in many countries around the world using numerous feedstock sources. Unfortunately, it is in nascent status in many African countries. Over the past decade, consumption of transport fuels in Sub-Saharan Africa has increased at a rate of about 7% per year in line with increased economic activity (Mulugetta, 2008). This has had a great economic impact on about thirty-five crude oil-importing countries in Africa. With large landmass for farming and abundance of edible and non-edible oils, some of which grow in the wild, Sub-Saharan Africa is a region with a fairly high potential for biodiesel production. One of the promising sources of biodiesel production is the wado tree (*Vitellaria paradoxa F.Gaertn ssp nilotica*), a deciduous tree 12-20 meter high, which grows naturally in the wild, especially in the savannah belt of Africa. Wado tree produces the wado seed which is processed into wado oil/butter. The wado seed contains 37-55% of fats (Enweremadu and Alamu, 2009).

Wado seed oil (WSO) is classified as oleaginous product; it is composed mainly of two fatty acids, stearic and oleic, which together account for 85-90%of the total fatty acids (Maranz et al., 2004). Soft wado seed oil has high oleic content (Badifu, 1989). The physicochemical properties of WSO are comparable with the properties of groundnut oil which has been used in biodiesel production (Ogbonnaya and Adgidzi, 2008).

Also, it has been observed that the properties of biodiesel are largely dependent on the physicochemical properties of the feedstock. According to some researchers (Ramadhas et al., 2005; Sahoo et al., 2007), the methyl esters of saturated fatty acids have a higher cloud point, cetane number and better biodiesel stability. WSO consists of 41.1% of saturated fatty acids, comprising palmitic and stearic acids. To ensure the quality of biodiesel as an alternative fuel, it has been proposed to limit the unsaturated fatty acid in biodiesel species, especially the content of higher unsaturated fatty acid such as linolenic acid which, on heating, polymerizes and leads to gum formation (Lang et al., 2001). Unlike many biodiesel

fuels, the biodiesel from WSO may less likely undergo oxidation since the oil contains natural antioxidants such as tocopherols and some phenolic compounds (Maranz, 2003). Hence, biodiesel from WSO will make a good alternative fuel.

Several approaches have been used in the production of biodiesel from vegetable oils and animal fats with high FFAs. However, there is a dearth of information on the production of biodiesel from WSO and where such exists, they are insufficient. Therefore, the production of biodiesel from WSO has not been fully explored.

In this research, biodiesel is produced through the reaction of the WSO with methanol in the presence of a catalyst using a two-step acid-base catalyzed transesterification. The catalysts used are H_2SO_4 and KOH for the esterification and transesterification steps, respectively.

1.2 Status of Biodiesel Production in Ethiopia

Ethiopia is among the poorest of the world's least developed countries, with over 45% of the population living below the poverty line. Significant improvements to Ethiopia's trade balance are needed to stimulate the required economic development. One main issue is that around 65% of Ethiopian export earnings are needed to pay for the import of petroleum products.

Despite the availability of huge energy resources in Ethiopia, the current level of harnessing this energy is very low. This, to a certain extent, depicts the poor socio-economic situation in the country on the one side, and a low level of awareness about the potential and value of energy by most stakeholders on the other side. Amongst the identified alternative renewable energy sources, biofuels and in particular energy crops received attention as a promising and sustainable energy sources, of which, biodiesel has arisen as a potential candidate for a petro-diesel substitute.

Ethiopia, being large country of diverse ecology, may harness the potential benefits from economic opportunities that may arise from biofuel production and also minimize the escalating budgetary pressure from a rise in international oil price. From international

experiences, it has been shown that the production of biofuels, particularly at a large scale, may incur negative impacts on land and food security of the poorer part of the society. Of course, positive impacts are also cited including response to price signals by smaller farmers and alleviating the environmental problems associated to the use of fossil fuels (Woldegiorgis W., 2009).

The development of biodiesel is a recent and at its initial stage in Ethiopia. So far there is no observable market use of biodiesel products. However, within a short period of time a significant number of foreign, local and joint companies have invested in the biodiesel industry. Currently more than 50 projects are in progress from which 14 companies are involved in the biodiesel industry and some of them have already started feedstock plantation for biodiesel production in five different regions (Benshangl Gumuz, Amhara, Oromia, SNNP and GPNRS), while others are at the pre-implementation stage (Kinfu, 2008). For example, in Benshangul Gumuz there is a major ongoing project of large scale jatropha plantation of more than 80,000 hectares. This project can 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 helping to alleviate rural poverty. The search for feedstock other than jatropha is still at its ground level.

1.3 Problem Statement

The depletion of world petroleum reserves and increased environmental concerns has stimulated the search for alternative renewable fuels that are capable of fulfilling an increasing energy demand (Demirbas, 2003). Some of the concerns are fluctuation of oil price, natural fossil fuel depletion, instability of world political condition, and high demand of energy over the world.

In recent decades, research concerning and knowledge about the benefits of renewable raw materials have intensified the efforts for sustainable energy sources. Assessing sustainable

renewable energy source is crucial at present, due not only to combat the fuel supply uncertainty and price fluctuations, but also becoming global concern. It's each country's responsibility to seek for environmentally benign energy sources that are supporter to the global deeds to reduce GHG and air pollutions.

A number of countries have successfully applied the use of biodiesel made from plant seed oils or animal fats, purely or by blending with petroleum diesel, and developed appropriate technologies to exploit the resources specific to their agro-climatic conditions. Ethiopia, endowed with diverse ecological varieties that have an ample potential for biofuel-production (both alcohols and biodiesel), is not benefited from its wealth. Jatropha, castor oil, palm oil, neem and others are among the known non-edible naturally occurring biodiesel feedstocks in the region. Most of the indigenous plants are not yet exploited or even not identified, hence, abandoned and left in vain. Therefore, identifying the most feasible and reliable oil bearing plant for biodiesel from indigenous species is essential for finding solution to the aforementioned problems.

1.4 Objectives of the Study

1.4.1 General objective

The general objective was the optimization of biodiesel production from oils extracted from the seeds of the wado *(Viterallia Paradoxa)* trees using a two-step acid - base catalyzed method and to compare the physicochemical properties of the biodiesel with standards.

1.4.2 Specific objectives

In order to address the aforementioned general objective, specific objects to follow are:

- To extract the crude oil from the nuts of the wado seeds by cold press and soxhlet method.
- To evaluate the physicochemical properties (mainly FFAs and SV) of the extracted WSO.

- To define optimum conditions/parameters (such as, reaction temperature, alcohol-to-oil molar ratio, and reaction time) for achieving maximum conversion.
- To determine the fuel physicochemical properties such as, acid value, saponification number, density, kinematic viscosity, iodine value, flash point, cetane number, heating value and cloud point by titration and empirical formula.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 General Overview of Biodiesel Fuel Production

Biodiesel, a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils, animal fats, and mixtures thereof, is produced by transesterification, with glycerol being produced as a co-product. Overall, the energy ratio for biodiesel production is in the range of 3.2 to 3.6 (Sheehan *et al.,* 1998). Blending biodiesel with diesel fuel offers improved lubricity and reduced emissions. Worldwide, one billion tons of diesel fuels are consumed annually (Hanna *et al.,* 2005). The total feed stocks produced that can be used, competitively, for food, feed, and industrial applications are approximately 115 million tons. Assuming a 1:1conversion on a weight basis, this represents a maximum of 12% of diesel fuel use (Hanna *et al.,* 2005). The opportunities for the future for biodiesel include improvements in the conversion technology, expanding the amount of available feedstock, and adding value to the glycerol by-product.

2.1.1 Diesel fuel markets

Diesel fuel use worldwide is estimated to be 1.14 billion tons (330 billion gallons) per year. The United States uses an estimated 18% of that or 205 million tons (60billion gallons) (USEIA, 2004). Because diesel (compression ignition) engines are more efficient than gasoline (spark ignition) engines (45% versus 30%), there is the possibility that the use of diesel engines in vehicles will increase, thereby increasing the demand for diesel fuel (DOE, 2003).

2.1.2 Biodiesel standards

If biodiesel is to be accepted as a fuel for diesel engines, it will have to be produced and handled in such a way that the variations in its properties and its performance characteristics will be less than, or equal to, what the consumer is used to with (petroleum-based) diesel fuel. A single, widely accepted standard for biodiesel is not available. Instead, the standard ASTM D6751 was developed for the United States, the CEN EN14214 Standard

was developed for the European Union (EU), and other regions also have established alternative standards. One effort being made to ensure biodiesel fuel quality is the National Biodiesel Board's BQ 9000 certification program. Numerous producers and marketers have been certified.

2.1.3 Biodiesel feed stocks

The annual production of biodiesel is increasing rapidly worldwide, from 10 thousand tons (4 million gallons) in 2000 to 3.5 million tons (1 billion gallons) in 2005 (Gubler, 2006; EBB, 2006). There are two steps that need to be taken to produce biodiesel on a large scale. They are: 1) growing the feedstocks, and 2) processing them into biodiesel. The main issue that is always debated is whether or not enough crops could be grown to provide the vegetable oil for producing the amount of biodiesel that would be required to completely replace petroleum as a transportation. In the United States, most new production assumes that soybean oil will be the oil of choice, with animal fats coming in as a distant second choice.

Although soybean oil currently is the feedstock of choice in the United States and Brazil, it is not an obvious feedstock for biodiesel production from a global perspective. Other materials (oil palm in Southeast Asia, jatropha in India, rapeseed in Eastern Europe, and crops such as sunflowers, camelina, and hazelnuts in the United States) have greater potential on an oil yield basis (Kurki *et al*., 2006). Of course, various oilseed varieties have preferred growing conditions and in most cases are not widely adaptable.

Animal fats are a viable feedstock for biodiesel production but are available on a very limited basis. Total fat production is estimated at 15 million tons per year worldwide (Rossell, 2001). Again, assuming a 1:1 conversion on a weight basis, all of the animal fat worldwide could replace less than 2% of the diesel fuel used on an annual basis.

The demand for vegetable oils and animal fats for biodiesel production will quickly deplete any surpluses. The demands represented by competing uses, primarily food, will result in increased feedstock prices, which are known to be the single largest cost in biodiesel production.

The forecasts for worldwide biodiesel demand and the production capacity vary greatly, reflecting the rapid development associated with this industry. SRI Consulting's Marketing Research Report on biodiesel (Gubler, 2006) forecasts the worldwide demand will surpass 40 million tons and the production capacity will surpass 80 million tons by 2010. Another study, Biofuel Market Worldwide (2006), estimated that worldwide biodiesel production would continue to grow rapidly and would reach 11 million tons (3.17 billion gallons) by 2010. Considering the variance in these forecasts, it is difficult to estimate a specific rate of growth. However, it is clear that extreme pressure will be exerted on the available feedstock. The feedstock supplies will need to expand beyond the estimated 115 million tons currently produced, or biodiesel production costs will rise, thus reducing its competitiveness with petroleum diesel and increasing its dependence on government incentives.

2.1.4 Opportunities

The feedstock accounts for 70% to 80% of the cost of biodiesel production, and clearly is the key factor to evaluate when considering the competitiveness of biodiesel with petroleum-based diesel fuel. However, within the biodiesel industry, the processing technologies will play a key role in determining industry leaders and maximizing profitability. By-product utilization will be another key factor as the rapid expansion of the biodiesel industry has greatly outpaced glycerin markets at both the crude- and pharmaceutical- grade levels.

Additional sources include expanded oilseed production, higher oil content varieties, and higher oil content crops. In the United States, it is estimated that expanding oilseed production by releasing 4 million hectares of productive land from government set-aside programs and switching another 8 million hectares from export grains could produce additional vegetable oil feed stocks of 2.1 million and 4.2 million tons, respectively. If the average soybean oil yield could be increased to 20%, versus the current 18%, which has been proven possible with several improved varieties, an additional 800 thousand tons of vegetable oil would be available. Or if future improvements could increase oil yields to an average of 22% oil, an additional 1.6 million tons would be available. If the oil demand

outpaces the protein demand, the soybean production could be replaced with higher yielding oil crops such as sunflower and canola, which produce as much as 500 l/ha more oil than soybeans.

New processing technologies are anticipated to improve operating efficiencies. The most significant improvement is expected to come from the use of heterogeneous catalysts systems. Such catalysts have the potential to eliminate the need for water washing to remove the excess catalysts, thus, reducing both capital and operating costs. It also is perceived that the free fatty acids present in feed stocks can be converted concurrently to alcohol esters rather than being separated out and used for the lower value purposes. Yet another potential advantage is that a higher quality glycerol will be obtained.

Glycerol, a co-product of biodiesel production, has many commercial uses. The current oversupply of glycerin may make it a burden to the industry in the near term until new markets are developed for crude glycerin, or alternative markets are developed for refined glycerin. If cost-effective markets are not available, the disposal costs could be significant. In the long run, the most profitable facilities will identify the markets to capture the significant value from the glycerin by-product. Currently, the opportunity most often cited is that of using the glycerol to produce 1, 4-propanediol, a commodity chemical and a precursor for many products.

Adding value to other co-products of biodiesel production, or at least maintaining their current values, will enhance the economic viability of the biodiesel industry.

The oilseed meals/press cakes are used predominately as animal feeds. Their values as feeds, or feed supplements, are functions of their protein content and quality and the need for additional processing to inactivate or remove the anti-growth factors such as trypsin inhibitors and glucosinolates. Opportunities for adding value to the meals include industrial uses for the proteins, such as adhesives, and the extraction of higher value materials, such as policosanols.

To summarize, the opportunities for expanded biodiesel production are great considering the high demand for petroleum-based products in both the industrialized and the

developing regions of the world. The increased awareness of the negative environmental factors associated with petroleum fuels and a desire to move to renewable fuels has caused significant growth in the biodiesel industry. However, it represents only a small fraction of the current diesel fuel demands. Even as biodiesel production and available feed stocks expand, that growth will be challenged to keep pace with the growing demand for fuel. Biodiesel feedstock availability, the price, and the resulting by-products, combined with government incentives for economic or environmental issues, ultimately will determine the competitiveness of biodiesel as a direct substitute for petroleum diesel. It is anticipated that biodiesel will drive the industrial applications for vegetable oils and animal fats but will not displace the food applications which will continue to determine the vegetable oil price for the most desirable oils, while the lower grade oils will become the industrial feed stocks. The conversion technologies will continue to improve and will allow government incentives to be phased out as the biodiesel feedstock supplies and the prices balance out compared to petroleum diesel prices and supplies. The trend toward the development of larger production facilities and consolidation of ownership is expected to continue as the competition for the feedstock supplies and fuel markets increase.

2.2 Current Technologies in Biodiesel Production

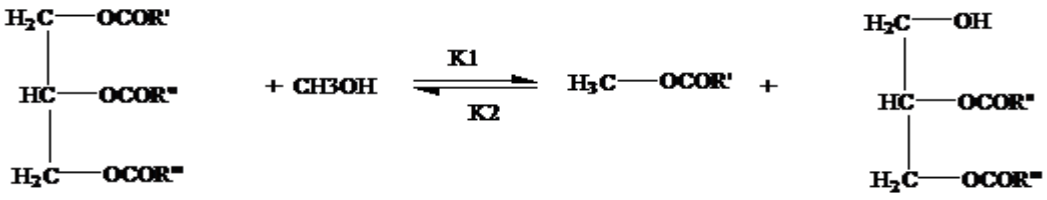
There are three basic chemical processes used to produce biodiesel from oils and fats industrially. These processes can either be batch or continuous and are the following:

- Base catalyzed transesterification of the oil with alcohol (methanol).
- Direct acid catalyzed esterification of the oil with methanol.
- Conversion of the oil to fatty acids (acid pretreatment) and then to alkyl esters with acid catalysis.

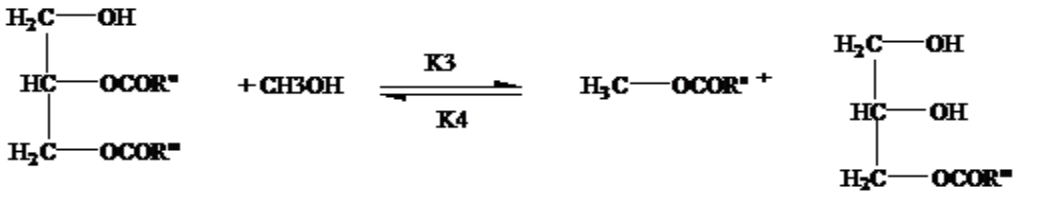
Of the pro-mentioned methods available for producing biodiesel, transesterification of natural oils and fats is currently the method of choice. The purpose of the process is to lower the viscosity of the oil or fat. Transesterification is basically a sequential reaction (Figure 2.1). Triglycerides are first reduced to diglycerides, which are subsequently reduced to monoglycerides, which are finally reduced to fatty acid esters.

The order of the reaction changes with the reaction conditions. The main factors affecting transesterification are the molar ratio of glycerides to alcohol, catalysts, reaction temperature and time, and free fatty acid and water content in oils and fats. Biodiesel as it is defined today is obtained by transesterifying triglycerides with methanol. Methanol is the preferred alcohol for obtaining biodiesel because it is the cheapest alcohol (Demirbas A., 2008).

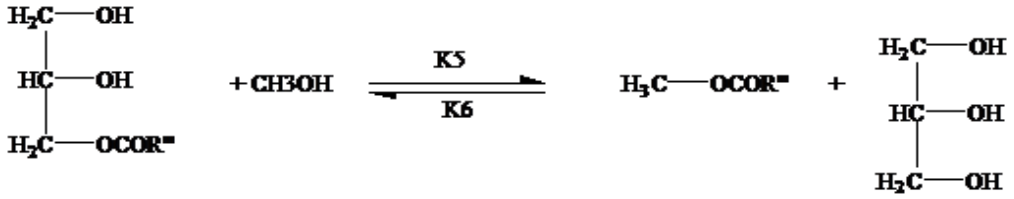
Base catalysts are more effective than acid catalysts and enzymes in relation to reaction time (Ma and Hanna, 1999). Methanol is made to react with triglycerides to produce methyl esters (biodiesel) and glycerol (figure 2.1).



Triglyceride Methanol methyl ester Diglyceride



Diglyceride Methanol Methyl Ester Monoglyceride



Monoglyceride Methanol Methyl Ester Glycerol

Fig. 2.1 A sequential transesterification reaction of triglyceride to methyl esters

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

2.2.1 Batch processes

A batch reactor is basically a discontinuous process reactor in which all reactants are loaded at once. Straight batch systems usually consist of a series of tanks in which each phase of production is completed before being pumped to the next phase. This implies that batch systems require more space for the extra processing vessels.

The biodiesel manufacturing processes are batch wise. The oil is submitted to transesterification in a batch reactor in the presence of a large amount of ethanol, and catalyst. An excess of methanol is necessary chiefly to ensure full solubility of triglyceride and keep the viscosity of the reaction mixture low, but also for shifting the chemical equilibrium. The transesterification reaction may be considered finished when maximum conversion is achieved.

The batch process allows high flexibility with respect to the composition of the feedstock. In turn, the economic indices are on the lower side because of lower equipment productivity and higher operation costs, such as manpower and automation. High labor cost per batch and also difficulty of large scale production are the main drawbacks of the batch process (Demirbas A., 2008).

2.2.2 Catalytic continuous process

The Catalytic continuous process technology of biodiesel production is a conceptual scheme of a continuous process working at low pressure that is capable of processing a feedstock with a larger amount of free fatty acids, such as unrefined non-edible vegetable oils, tallow fat and used cooking oil. Continuous flow systems are highly efficient and quick at processing high quality feedstock with a low level of FFA (less than 0.5%)(Che Franklin N., 2008). For this reason in the first reactor the esterification of free fatty acids with methanol is carried out. Then the transesterification reaction follows in the

second reactor. A homogeneous catalyst is currently used, either as alkaline hydroxide or alkaline methoxide (Demirbas A., 2008).

2.2.3 Supercritical processes

Performing the esterification in supercritical conditions has been studied initially as a method to solve the problem of miscibility of oil and methanol that hinders the kinetics in normal conditions. Since the critical coordinates of methanol are T_c = 239 ° C and P_c = 80 bar, raising the temperature and pressures at sufficiently high values is necessary. The reaction involves no catalyst .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 (Demirbas A., 2008).

The addition of co-solvent in combination with supercritical conditions seems to be an efficient means to reduce significantly the operating temperature. 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.

2.2.4 Hydrolysis and esterification

A simpler manufacturing procedure would consist in first performing the hydrolysis of triglycerides and isolating the fatty acids followed by esterification. Significant advantages would be the possibility of extracting high value fatty acids from the lipid material, as well as obtaining high purity glycerol. The hydrolysis reaction can be carried out without a catalyst working in milder conditions compared to full esterification. A temperature close to 270 ^{0}C and pressures from 70 to 200 bar have 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 A., 2008).

2.2.5 Enzymatic process

The transesterification reaction can be catalyzed by enzymes, the most common being the lipase. The reaction takes place at normal pressure and temperatures 50 to 55°C with low energy consumption. The yield of methanolysis depends on several factors such as temperature, pH, type of microorganism producing the enzyme, the use of co-solvents, *etc.* However, low yields in methyl esters and very long reaction times make the enzymatic processes not competitive enough at this time (Demirbas A., 2008).

2.3 Types of Transesterification Reaction

Transesterification is the chemical conversion of the oil into its corresponding fatty ester. It's one of the most common methods used to reduce oil viscosity in the biodiesel industry. 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 (Demibas, 2008).

2.3.1 Homogeneous base and acid catalyzed transesterification

The base catalyzed transesterification reaction commonly uses alkali catalysts such as NaOH, CH_3ONa, CH_3OK and KOH. In the alkali catalytic methanol transesterification method, the catalyst is dissolved into methanol by vigorous stirring in a small reactor. The oil is transferred into a biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil. A successful transesterification reaction produces two liquid phases: ester and crude glycerol (Vyas et al., 2009). It is reported to be very sensitive to the purity of the reactant. Free fatty acid (FFA) content should not exceed beyond a certain limit. It has been found that the alkaline-catalyzed transesterification process is not suitable to produce esters from unrefined oils. In order to prevent saponification during the reaction, FFA and water content of the feed must be below 2 wt. % and 0.05 wt. %, respectively. Because of these limitations, only pure vegetable oil feeds are appropriate for alkali-catalyzed transesterification without extensive pre-treatment.

The liquid acid-catalyzed transesterification process (also known as Esterification process) is not much popular as the base-catalyzed process. It uses strong acids as catalysts to convert a high FFA content feedstock reacted with alcohols to its corresponding esters. Homogeneous acid catalyzed reaction is slower than the homogeneous base-catalyzed reaction. However, the performance of the acid catalyst is not strongly affected by the presence of FFAs in the feedstock. In fact, acid catalysts can simultaneously catalyze both esterification and transesterification. Thus, a great advantage with acid catalysts is that they can directly produce biodiesel from low-cost lipid feed stocks. For acid-catalyzed systems, sulfuric acid, HCl, BF_3, H_3PO_4, and organic sulfonic acids, have been used by different researchers (Demibas, 2008).

2.3.2 Heterogeneous acid and base catalyzed transesterification

Homogeneous catalysts showed greater performance toward transesterification to obtain biodiesel. The use of heterogeneous catalysts could be an attractive solution. Heterogeneous catalysts can be separated more easily from reaction products. Undesired saponification reactions can be avoided by using heterogeneous catalysts. They enable the transesterification of vegetable oils or animal fats with high contents of FFAs, such as deep-frying oils from restaurants and food processing. 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 (Demibas, 2008).

2.3.3 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. 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 (Demibas, 2008).

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.

2.3.4 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).

2.3.5 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).

2.3.6 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 FFAs 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 draw backs of the esterification process -requires longer time reaction to come to completion and transesterification- problem of soap formation process (Wang Y. *et al*., 2007). Figure 2.2 depicts the schematic description of a two-step catalyzed biodiesel production from WSO.

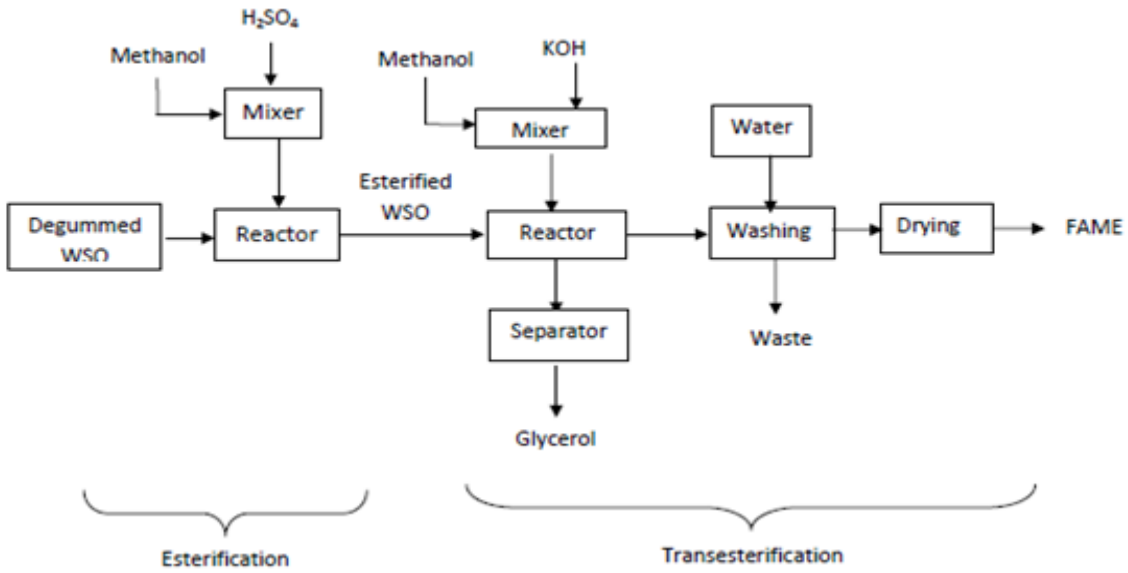


Figure 2.2 Scheme for the two-step acid- alkali catalyzed method of WSO biodiesel production.

2.4 Biodiesel Production Processes

2.4.1 Process flow chart

Today, most of the biodiesel is produced by the alkali-catalyzed process. Figure 2.1 shows a simplified flow chart of the alkali-catalyst process. As described earlier, feed stocks with high free fatty acid will react undesirably with the alkali catalyst thereby forming soap. The maximum amount of free fatty acids acceptable in an alkali-catalyzed system is below 2.5 wt. % FFA. If the oil or fat feedstock has FFA content over 2.5 wt. %, a pretreatment step is necessary before the transesterification process.

2.4.2. Raw materials treatment

The raw materials, which can be vegetable oils, animal fats, or recycled greases, used in the production of biodiesel contain triglycerides, free fatty acids, water, and other contaminants in various proportions. Some crude vegetable oils contain phospholipids that need to be removed in a degumming step. Phospholipids can produce lecithin, a commercial emulsifier (Van Gerpen and Dvorak, 2002).

Liu et al. compared the different degumming methods, such as membrane filtration, hydration, acid micelles degumming, supercritical extraction, etc. The characteristics of the raw oils should be investigated before choosing the suitable degumming method because different degumming methods have their advantages and disadvantages (Liu *et al.,* 2008). The oil can be separated through membrane filtration according to the average molecular weight or the particle size of phospholipids. Although degumming method can solve the problem, its process involves two steps with the use of an organic solvent. Therefore, this method has no superiority on cost because of its complicated processing (Carvalho *et al*., 2006; Souza, 2008).

In the hydration process, because of phospholipids hydrophilicity, hot water can be added into the oil with stirring. The phospholipids solubility will be significantly reduced, so it could be separated from the oil by natural settlement. The hydration method features a simple process, easy operation, and high yields refining, but non-hydratable phospholipids

cannot be removed by this method, as reported by Verleyen et al (Verleyen *et al*., 2002). For removing non-hydratable phospholipids (NHP), critic acid or phosphoric acid can be added into the oil which is heated to 70 ^{0}C, this is called the special micelles degumming method.

Moreover, by refining with supercritical CO_2 extraction, it can effectively remove the free fatty acids and the per oxidation products that are in the crude oil. However, the high pressure required in this process will be the biggest challenge in its industrial application (Eisenmenger and Dunford, 2008; Chen *et al.,* 2007)

The free fatty acids are removed in a refining step and excess free fatty acids can be removed as soaps in a later pretreatment step. In addition, deodorization is another important step in the raw material treatment (Demirbas and Kara, 2006).

Next, in order to determine the percentage of FFA in the oils or fats, titration is performed. As described above, if the percentage of FFA is over 2.5 wt. %, pretreatment is necessary to reduce the content of FFA. This step also determines the amount of catalyst required in the neutralization step.

2.4.3 Pretreatment of acidic feed stocks

Many pretreatment methods have been proposed for reducing the high free fatty acid content of the oils, including steam distillation, extraction by alcohol (Turkay & Civelekoglu,1991), and esterification by acid catalysis (Zhang et al., 2008). However, steam distillation for reducing high free fatty acids requires a high temperature and has low efficiency. Because of the limited solubility of free fatty acids in alcohol, extraction by alcohol method needs a large amount of solvent and the process is complicated.

Compared with the two former methods, esterification by acid-catalysis makes the best use of the free fatty acids in the oil and transforms it into biodiesel. The catalysts can be homogeneous acid-catalysts or solid acid-catalysts. Compared with the former one, solid acid-catalysts offer some advantages for eliminating separation, corrosion, toxicity, and

environmental problems, but the reaction rate is slower (Zhang et al., 2008; Serio *et al*.,2005).

An alternative approach to reduce the FFA is to use iodine as a catalyst to convert free fatty acids into biodiesel. An obvious advantage of this approach is that the catalyst (iodine) can be recycled after the esterification reaction. Li *et al*. (2008) found through orthogonal tests, under the optimal conditions (i.e. iodine amount: 1.3 wt. % of oils; reaction temperature: 80 ^{0}C; ratio of methanol to oils: 1.75:1; reaction time: 3 h) that the FFA content can be reduced to < 2%.

Another new method of pretreatment is to add glycerol into the acidic feedstock and heat it to a high temperature of about 200 ^{0}C, normally with a catalyst such as zinc chloride. The glycerol will react with the FFA to form monoglycerides and diglycerides. Then the FFA level will become low and biodiesel can be produced using the traditional alkali-catalyzed transesterification method. The advantage of this approach is that no alcohol is needed during the pretreatment and the water formed from the reaction can be immediately vaporized and vented from the mixture. However, the drawbacks of this method are its high temperature requirement and relatively slow reaction rate (Van Gerpen, 2004).

2.4.4. Catalyst and alcohol

In general, there are three categories of catalysts used for biodiesel production: alkalis, acids, and enzymes.

Enzyme catalysts have become more attractive recently since it can avoid soap formation and the purification process is simple to accomplish. However, they are less often used commercially because of the longer reaction times and higher cost. To reduce the cost, some researchers developed new biocatalysts in recent years. An example is so called whole cell biocatalysts which are immobilized within biomass support particles. An advantage is that no purification is necessary for using these biocatalysts.

Compared with enzyme catalysts, the alkali and acid catalysts are more commonly used in biodiesel production. The alkali and acid catalysts include homogeneous and

heterogeneous catalysts. Due to the low cost of raw materials, sodium hydroxide and potassium hydroxide are usually commercially used as alkali homogeneous catalysts. These materials are the most economic because the alkali-catalyzed transesterification process is carried out under a low temperature and pressure environment, and the conversion rate is high with no intermediate steps. However, the alkali homogeneous catalysts are highly hygroscopic and absorb water from air during storage. They also form water when dissolved in the alcohol reactant and affect the yield. Therefore, they should be properly handled.

On the other hand, some heterogeneous catalysts are solid and it could be rapidly separated from the product by filtration, which reduces the washing requirement (Dennis *et al.,* 2010). In addition, solid heterogeneous catalysts can stimulatingly catalyze the transesterification and esterification reaction that can avoid the pre-esterification step, thus these catalysts are particularly useful for those feed stocks with high free fatty acid content. However, using a solid catalyst, the reaction proceeds at a slower rate because the reaction mixture constitutes a three-phase system, which, due to diffusion reasons, inhibits the reaction.

The alcohol materials that can be used in the transesterification process include methanol, ethanol, propanol, butanol, and amyl alcohol. Among these alcohols, methanol and ethanol are used most frequently. Methanol is especially used because of its lower cost and its physical and chemical advantages. Ma and Hanna (1999) reported that methanol can react with triglycerides quickly and the alkali catalyst is easily dissolved in it. However, due to its low boiling point, there is a large explosion risk associated with methanol vapors which are colorless and odorless. Both methanol and methoxide are extremely hazardous materials that should be handled carefully. It should be ensured that one is not exposed to these chemicals during biodiesel production (Qian *et al.,* 2008).

2.4.5. Mixing and neutralization

The purpose of mixing methanol with the catalyst is to produce methoxide which reacts with the base oils. Most of the catalysts (e.g. NaOH, KOH) are in solid form and do not

readily dissolve into methanol, it is best to start agitating the methanol in a mixer and add the catalyst slowly and carefully (ISTC, 2006). Once the catalyst completely dissolves in the methanol, the methoxide is ready to be added to the oil. Once the methoxide is added into the oil, a neutralization reaction will immediately start. Some alkali catalysts will react with rudimental acids during the pretreatment step or will react with the free fatty acids from the oil. Therefore, more catalyst needs to be added to complete the reaction.

2.4.6. Transesterification and separation

When the catalyst, alcohol, and oil are mixed and agitated in a reaction vessel, a transesterification reaction will start. A stirred reactor is usually used as the reaction vessel for continuous alkali-catalyzed biodiesel production. Recently, there is an increased interest in new technologies related to mass transfer enhancement.

As previously mentioned, if the free fatty acid level or water level is too high, it may cause problems downstream with the saponification and the separation of the glycerol by-product.

Therefore, the amount of water and free fatty acids in the feedstock oil should be monitored during the reaction. Once the transesterification reaction is completed, two major products exist: esters (biodiesel) and glycerol.

The glycerol phase is much denser than the biodiesel phase and settles at the bottom of the reaction vessel, allowing it to be separated from the biodiesel phase. Phase separation can be observed within 10 min and can be completed within several hours of settling. The reaction mixture is allowed to settle in the reaction vessel in order to allow the initial separation of biodiesel and glycerol, or the mixture is pumped into a settling vessel. In some cases, a centrifuge may be used to separate the two phases (Van Gerpen, 2004). Both the biodiesel and glycerol are contaminated with an unreacted catalyst, alcohol, and oil during the transesterification step.

Soap that may be generated during the process also contaminates the biodiesel and glycerol phase. Schumacher (2007) suggested that although the glycerol phase tends to

contain a higher percentage of contaminants than the biodiesel, a significant amount of contaminants is also present in the biodiesel. Therefore, crude biodiesel needs to be purified before use.

2.4.7. Refining crude glycerol

Although biodiesel is the desired product from the reactions, the refining of glycerol is also important due to its numerous applications in different industrial products such as moisturizers, soaps, cosmetics, medicines, and other glycerol products. It is one of the few products that has a good reactivity on sump oil, and is extremely effective for washing shearing shed floor, so it can be used as a heavy duty detergent and degreaser. Whittington (2006) reported that glycerol can even be fermented to produce ethanol, which means more biofuel can be produced.

According to the statements of Van Gerpen *et al.* (2004), typically produced glycerol is about 50% glycerol or less in composition and mainly contains water, salts, unreacted alcohol, and unused catalyst (Dennis *et al*., 2010).

The unused alkali catalyst is usually neutralized by an acid. In some cases, hydrochloric or sulphuric acids are added into the glycerol phase during the re-neutralization step and produce salts such as sodium chloride or potassium sulphate, the latter can be recovered for use as a fertilizer. Generally, water and alcohol are removed to produce 80–88% pure glycerol that can be sold as crude glycerol. In more sophisticated operations, the glycerol is distilled to 99% or higher purity and sold in different markets.

After the re-neutralization step, the alcohol in the glycerol phase can be removed through a vacuum flash process or by other types of evaporators. Usually, the alcohol vapor is condensed back into liquid and reused in the process. However, the alcohol may contain water that should be removed in a distillation column before the alcohol is returned to the process. The alcohol recovery step is more difficult when the alcohol that is used, such as ethanol or isopropanol, forms an azeotrope with the water. Gerpen (2005) proposed the use of a molecular sieve to remove the water generated.

2.4.8. Purification of crude biodiesel

After separation from the glycerol phase, crude biodiesel is mainly contaminated with residual catalyst, water, unreacted alcohol, free glycerol, and soaps that were generated during the transesterification reaction. Normally, crude biodiesel enters a neutralization step and then passes through an alcohol stripper before the washing step. In some cases, acid is added to crude biodiesel to neutralize any remaining catalyst and to split any soap. Soaps react with the acid to form water soluble salts and free fatty acids. Gerpen (2005) stated that neutralization before the washing step reduces the materials required for the washing step and minimizes the potential for emulsions being formed during the washing step. Unreacted alcohol should be removed with distillation equipment before the washing step to prevent excess alcohol from entering the wastewater effluent. The primary purpose of this step is to wash out the remnants of the catalyst, soaps, salts, residual alcohol, and free glycerol from the crude biodiesel. Generally, three main approaches are adopted for purifying biodiesel: water washing, dry washing, and membrane extraction (Dennis *et al*., 2010).

2.4.8.1. Water washing

Since both glycerol and alcohol are highly soluble in water, water washing is very effective for removing both contaminants. It also can remove any residual sodium salts and soaps. The primary material for water washing is distilled warm water or softened water (slightly acidic) (Chen et al., 2007; Demirbas & Kara, 2006). Warm water prevents the precipitation of saturated fatty acid esters and retards the formation of emulsions with the use of a gentle washing action. Softened water (slightly acidic) eliminates calcium and magnesium contamination and neutralizes any remaining alkali catalysts.

After washing several times, the water phase becomes clear, meaning that the contaminants have been completely removed. Then, the biodiesel and water phases are separated by a separation funnel or centrifuge. Moreover, because of the immiscibility of water and biodiesel, molecular sieves and silica gels, etc., can also be used to remove water from the biodiesel. The remaining water can be removed from the biodiesel by passing the product over heated Na_2SO_4 (25 wt. % of the amount of the ester product) overnight and

then be removed by filtration. However, there are many disadvantages to this method, including an increased cost and production time, polluting liquid effluent, product loss, etc. Moreover, emulsions can form when washing the biodiesel made from waste cooking oils or acidic feed stocks because of the soap formation (Dennis *et al*., 2010).

2.4.8.2. Dry washing

Dennis *et al.* (2010) used dry washing by replacing the water with an ion exchange resin or a magnesium silicate powder in order to remove impurities. These two dry washing methods can bring the free glycerol level down and is reasonably effective for removing soaps. Both the ion exchange process and the magnesol process have the advantage of being waterless and thus eliminate many of the problems outlined above. Although the magnesol process has a better effect on the removal of methanol than the ion resins, none of the products from this process fulfill the limits specified in the EN Standard.

2.4.8.3. Membrane extraction

Gabelman and Hwang (1999) proved that the contaminants can be removed by using a hollow fiber membrane extraction, such as polysulfone. In this method, a hollow fiber membrane (1 m long, 1 mm diameter) filled with distilled water is immersed into the reactor (20 ^{0}C). The crude biodiesel is pumped into the hollow fiber membrane (flow rate: 0.5 ml/min; operating pressure: 0.1 M Pa). Following this step, biodiesel is passed over heated Na_2SO_4 and then filtered to remove any remaining water (He *et al*., 2006). This approach effectively avoids emulsification during the washing step and decreases the loss during the refining process. The purity of the biodiesel obtained is about 90% and the other properties conform to the ASTM standards. It is a very promising method for purifying biodiesel.

2.4.9. Characterization of biodiesel fuels

For commercial fuel, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure it meets inter-national standards. A few specifications have been set but the ASTM D6751 and EN14214 standards are the most commonly used standards

(Table 2.1). Some properties in the standard, such as the cetane number or density, can reflect the properties of the chemical compounds that make up the biodiesel, and other properties provide an indication of the quality of the production process. Generally, biodiesel standards identify the parameters that pure biodiesel must meet before being used as a pure fuel or being blended with distillate fuels (Dennis *et al*., 2010).

To ensure safe operation in diesel engines, the most important aspects of the biodiesel product are the completion of the reaction, the removal of the free glycerol, residual catalyst and alcohol, and the absence of free fatty acids (Zheng *et al.,* 2008). As mentioned before, if the transesterification reaction is not complete then triglycerides, diglycerides, or monoglycerides may be left in the final product. Chemically, each of these compounds contains a glycerol molecule. Fuel with excessive free glycerol may plug the fuel filter sand cause combustion problems in the diesel engine. Therefore, the ASTM standard requires the total glycerol to be <0.24% of the final biodiesel product. On the other hand, since residual methanol, even as little as 1%, can lower the flashpoint of the final biodiesel product from 170 ^{0}C to <40 ^{0}C, the EN 14214 standard limits the amount of alcohol to a very low level (Van Gerpen *et al*., 2004). Finally, although a specific value for the residual catalyst is not included in the ASTM standard, it is limited by the specification on levels of sulfated ash, which may lead to engine deposits and high abrasive wear levels.

Because the European specification for sulfur content (i.e. EN14214) is much tighter than the US requirement, Ali et al. (1995) reported that a number of producers in Europe are resorting to the use of vacuum distillation for the removal of sulfur compounds from the final biodiesel product. In addition, some vegetable oils, yellow greases, and brown greases leave an objectionable color in the biodiesel. Although there is no color specification in the ASTM standard, in some cases, an activated carbon bed, which is an effective method for the removal of excessive color, is used to produce a colorless biodiesel (National Biodiesel Board, 2007).

Table 2.1 Specifications and test methods of ASTM D6751 and EN 14214 standards

Property	Unit	Limits		Test Method	
		ASTM D6751	EN 14214	ASTM D6751	EN 14214
Flash point	^{0}C	130.0 min	101.0 min	D93	ISO CD3679e
Kinematic viscosity at 40 ^{0}C	mm^2/s	1.9–6.0	3.5–5.0	D445	EN ISO 3104
Cetane number	–	47 min	51 min	D613	EN ISO 5165
Sulphated ash content	% (m/m)	0.020 max		D874	ISO 3987
Copper strip corrosion	–	No. 3 max	Class 1	D130	EN ISO 2160
Acid value	mg KOH/g	0.80 max	0.5 max	D664	pr EN 14104
Free glycerol	% (m/m)	0.020 max		D6584	pr EN 14105m
Total glycerol	% (m/m)	0.240 max	0.25 max	D6584	pr EN 14106
Phosphorous content	% (m/m)	0.001 max	0.01 max	D4951	pr EN 141101
Carbon residue					
ASTM D6751 (100% sample)	% (m/m)	0.050 max	–	D4530	EN ISO 10370
EN 14214 (10% bottoms)	–	–	0.3 max	–	–
Cloud point	^{0}C	Report customer	–	D2500	EN SIO 3675
Density at 15 ^{0}C	kg/m^3	–	860–900	–	EN SIO 12185
Distillation T90 AET ^{0}C	^{0}C	360 max	–	D1160	–
Sulfur (S 15 Grade)	ppm	0.0015 max	–	D5453	–
Sulfur (S 500 Grade)	ppm	0.05 max	–	D5453	–
Sulfur content	mg/kg	–	10 max	–	–
Water and sediment	%vol.	0.050 max	–	D2709	–
Water content	mg/kg	–	500 max	–	EN ISO 12937
Total contamination	mg/kg	–	24 max	–	EN 12662

Oxidation stability at 110 ^{0}C	h	–	6 min	–	pr EN 14112
Iodine value	–	–	120 max	–	pr EN 14111
Linolenic acid methyl ester	% (m/m)	–	12 max	–	pr EN 14103d
Polyunsaturated (P4 double bonds) methyl esters	% (m/m)	–	1 max	–	pr EN 14103
Ester content	% (m/m)				pr EN 14103d
Methanol content		–	96.5 min	–	pr EN 141101
Monoglyceride content	% (m/m)	–	0.2 max	–	pr EN 14105m
Diglyceride content	% (m/m)	–	0.8 max	–	pr EN 14105m
Triglyceride content	% (m/m)	–	0.2 max	–	pr EN 14105m
Alkaline metals (Na + K)	% (m/m)	–	0.2 max	–	pr EN 14108
	mg/kg	–	5 max	–	pr EN 14109

2.5 Storage of Biodiesel Product

Biodiesel is safe to store and the properties of biodiesel should conform to respective standards after it has been stored for a longtime. There are several key factors that need to be considered for the storage of biodiesel, including exposure temperature, oxidative stability, fuel solvency, and material compatibility (Leung *et al*., 2006).

Lee *et al.* (1995) stated that the temperature of stored biodiesel should be controlled so as to avoid the formation of crystals which can plug fuel lines and fuel filters. For this reason, the storage temperature of most pure biodiesel is generally kept between 7 and 10 ^{0}C. Even in extremely cold climates, underground storage of pure biodiesel usually provides the storage temperature necessary for preventing crystal formation (Van Gerpen *et al.,* 2004).

Bondioli *et al.* (1995) noted that the stability of biodiesel is an important property when it is to be stored for a prolonged period. Poor stability can lead to an increased acid value and fuel viscosity and to the formation of gums and sediments. Therefore, if the duration of storing biodiesel or biodiesel blends is more than 6 months, it should be treated with an antioxidant additive (Van Gerpen *et al.,* 2004). Moreover, because water contamination will lead to biological growth in the fuel, it should be minimized in the stored fuel by using

biocides. Biodiesel storage tanks made of aluminum, steel, Teflon, and fluorinated polyethylene or polypropylene should be selected. The tanks should minimize the possibility of water contamination and should be cleaned prior to use for biodiesel storage (Mittelbach and Gangl, 2001).

2.6 Main Factors Affecting the Yield of Biodiesel

2.6.1. Alcohol quantity

Many researchers recognized that one of the main factors affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride. Theoretically, the ratio for transesterification reaction requires 3 mol of alcohol for 1 mol of triglyceride to produce 3 mol of fatty acid ester and 1 mol of glycerol. An excess of alcohol is used in biodiesel production to ensure that the oils or fats will be completely converted to esters and a higher alcohol triglyceride ratio can result in a greater ester conversion in a shorter time. The yield of biodiesel is increased when the alcohol to triglyceride ratio is raised beyond 3 and reaches a maximum. Further increasing the alcohol amount beyond the optimal ratio will not increase the yield but will increase cost for alcohol recovery. In addition, the molar ratio is associated with the type of catalyst used and the molar ratio of alcohol to triglycerides in most investigations is 6:1, with the use of an alkali catalyst. When the percentage of free fatty acids in the oils or fats is high, such as in the case of waste cooking oil, a molar ratio as high as 15:1 is needed when using acid-catalyzed transesterification (Dennis *et al*., 2010).

2.6.2. Reaction time

Freedman *et al*. (1984) found that the conversion rate of fatty acid esters increases with reaction time. At the beginning, the reaction is slow due to the mixing and dispersion of alcohol into the oil. After a while, the reaction proceeds very fast. Normally, the yield reaches a maximum at a reaction time of less than 90 min, and then remains relatively constant with a further increase in the reaction time (Alamu, 2007). Moreover, excess reaction time will lead to a reduction in the product yield due to the backward reaction of transesterification, resulting in a loss of esters as well as causing more fatty acids to form soaps (Eevera *et al*., 2009; Ma *et al.,* 1998).

2.6.3. Reaction temperature

Temperature clearly influences the reaction and yield of the biodiesel product. A higher reaction temperature can decrease the viscosities of oils and result in an increased reaction rate, and a shortened reaction time. However, Leung and Guo (2006) and Eevera *et al.* (2009) found that when the reaction temperature increases beyond the optimal level, the yield of the biodiesel product decreases because a higher reaction temperature accelerates the saponification reaction of triglycerides. The reaction temperature must be less than the boiling point of alcohol in order to ensure that the alcohol will not leak out through vaporization (Dennis *et al*., 2010).

2.6.4. Catalyst

Catalyst type and concentration can affect the yield of the biodiesel product. As mentioned before, the most commonly used catalyst for the reaction is sodium hydroxide. However, Freedman *et al*. (1984) found that sodium methoxide was more effective than sodium hydroxide because upon mixing sodium hydroxide with methanol a small amount of water will be produced, which will affect the product yield because of the hydrolysis reaction (Guo, 2005). This is the reason why the catalyst should be added into the methanol first and then mixed with the oil.

As the catalyst concentration increases the conversion of triglyceride and the yield of biodiesel increase. This is because an insufficient amount of catalysts result in an incomplete conversion of the triglycerides into the fatty acid esters. Usually, the yield reaches an optimal value when the catalyst (NaOH) concentration reaches 1.5 wt. % and then decreases a little with a further increase in catalyst concentration. The reduction of the yield of the biodiesel is due to the addition of excessive alkali catalyst causing more triglycerides to react with the alkali catalyst and form more soap (Leung and Guo, 2006; Guo, 2005).

2.6.5 Mixing intensity

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

2.6.6 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.

2.7 Basic Plant Equipment Used in Biodiesel Production

The basic plant equipments used in biodiesel production are reactors, pumps, settling tanks, centrifuges, distillation columns, and storage tanks. The reactor is the only place in the process where chemical conversion occurs. Reactors can be grouped into two broad categories, batch reactors and continuous reactors. In the batch reactor, the reactants are fed into the reactor at the determined amount. The reactor is then closed, and the desired reaction conditions are set. The chemical composition within the reactor changes with time. The construction materials are an important consideration for the reactor and storage tanks. For the base-catalyzed transesterification reaction, stainless steel is the preferred material for the reactor (Van Gerpen *et al.*, 2004).

Key reactor variables that dictate conversion and selectivity are temperature, pressure, reaction time (residence time), and degree of mixing. In general, increasing the reaction temperature increases the reaction rate and, hence, the conversion for a given reaction time. Increasing the temperature in the transesterification reaction does impact the operating pressure.

Two reactors within the continuous reactor category are continuous stirred tank reactors (CSTRs) and plug flow reactors (PFRs). For CSTRs, the reactants are fed into a well-mixed

reactor. The composition of the product stream is identical to the composition within the reactor. Hold-up time in a CSTR is given by a residence time distribution. For PFRs, the reactants are fed into one side of the reactor. The chemical composition changes as the material moves in plug flow through the reactor (Van Gerpen *et al.*, 2004).

The pumps play the key role in moving chemicals through the manufacturing plant. The most common type of pump in the chemical industry is a centrifugal pump. The primary components of a centrifugal pump are (1) a shaft, (2) a coupling attaching the shaft to a motor, (3) bearings to support the shaft, (4) a seal around the shaft to prevent leakage, (5) an impeller, and (6) a volute, which converts the kinetic energy imparted by the impeller into the feet or head. The gear pumps are generally used in biodiesel plants. There are a number of different types of positive displacement pumps including gear pumps (external and internal) and lobe pumps. External gear pumps generally have two gears with an equal number of teeth located on the outside of the gears, whereas internal gear pumps have one larger gear with internal teeth and a smaller gear with external teeth (Van Gerpen *et al.*, 2004).

The separation of biodiesel and glycerine can be achieved using a settling tank. While a settling tank may be cheaper, a centrifuge can be used to increase the rate of separation relative to a settling tank. Centrifuges are most typically used to separate solids and liquids, but they can also be used to separate immiscible liquids of different densities. In a centrifuge separation is accomplished by exposing the mixture to a centrifugal force. The denser phase will be preferentially separated to the outer surface of the centrifuge. The choice of appropriate centrifuge type and size are predicated on the degree of separation needed in a specific system.

An important separation device for miscible fluids with similar boiling points (*e.g.*, methanol and water) is the distillation column. Separation in a distillation column is predicated on the difference in volatilities (boiling points) between chemicals in a liquid mixture. In a distillation column the concentrations of the more volatile species are enriched above the feed point and the less volatile species are enriched below the feed point.

2.8 Environmental Impacts of Biodiesels

In contrast to conventional diesel, biodiesel creates substantial reduction in emission; hence, these properties make Biodiesel a good alternative fuel to petroleum-based diesel oil.

Biodiesel has many other environmental benefits, such as it is biodegradable, non-toxic, and has a low emission profile (including potential carcinogens). Moreover since the primary feedstock for Biodiesel is a biologically-based material that can be grown season after season, it is renewable.

2.9 Description of the Wado Tree

2.9.1 Taxonomy and nomenclature

Family: Sapotaceae

*Sub species***:** Two subspecies are recognized, *paradoxa* and *nilotica*

*Vernacular/common names***:** Wado/Wedo (Anyuwaa-Ethiopia), Shea-butter tree (English), karité (France), Lulu (Arabic), etc.

2.9.2 Distribution and habitat

The tree is widespread in the savannah regions across Africa from Senegal to Ethiopia. Subspecies paradoxa occurs in a wide latitudinal belt between 5° and 15°N from Senegal to the Central African Republic. Subspecies nilotica is found in Sudan, Uganda, Ethiopia and western Zaire. The species is rarely found outside its natural distribution range (Booth and Wickens, 1988**)**.

The two subspecies differ in altitudinal range. Subsp. nilotica occurs at higher altitudes (650-1600 m) than subsp. paradoxa which is mainly found at 100-600 m altitude, occasionally up to 1300 m. Mean annual rainfall in the area of distribution is 600-1400 mm and with 3-7 dry months (less than 50 mm rain). Subsp. paradoxa is generally more drought resistant than nilotica. Like other wide-ranging African tree species it can grow on a variety of soil types.

Characteristically, Vitellaria paradoxa C. F. Gaertner subsp. *nilotica* (VPN) is a medium-sized, 12-20 meters high tree, which is deciduous in the dry seasons, and with poor stems form. Its branches develop into a number of large, knotted, wide-spreading limbs that form a dense crown with the lower branches dropping to the ground. The bark has a dark grey to almost black colour and is deeply fissured and cross-cut to form very thick, four to six centimeters wide, square or rectangular scales (Teketay *et al*., 2003).

2.9.3 Ecology and botany of wado tree

Wado is native to tropical Africa, reaching upwards of 12 to 20m high (Fig.2.1), its branches are short and thick, with a grayish bark, red inside, deeply sprung and the cork of which divides into small irregular quadrangular prisms, very resistant to bush fires. The branches, more or less spreading, are short, thick, with ring-shaped rolls, bearing leaves at the end only. The leaves are large isolated, membranous, covered with a brownish down when young, tough and glabrous when adult (DeMos, S., 2001). The fruit is a greenish-yellow ellipsoidal or spherical berry, harvested when fully mature, between June and September. It is estimated to live between 200 to 300 years, with 15 to 20 years of growth required before fruiting.

Figure 2.3 The Wado tree from GPRS (*Photo by Author*, *May 2010*)

The oil-rich kernels are the most valuable part of the wado tee, and when fresh represent 30-45% of the whole fruit weight. The fat content varies widely among individual trees and within and among populations and years. The quality of fat produced also varies, some kernels yielding solid fat, others oil. Despite this inherent fluctuation, there is some indication that kernels of VPN produce oil of a lower melting point, which contains less un-saponifiable matter. On average, fat content accounts for 40%-60% of dry kernel weight.

2.9.4 General use

The main product is butter/oil which is extracted from the seeds (40-60% by weight of the seeds). It is one of the most affordable and widely used vegetable fats in the Sahel and plays

an important role in the economy of the region. It is especially important in areas with less than 1000 mm rain/year that are not suitable for growing oil palms. Shea nut cake is increasingly used for livestock and poultry feed, and leaves and young sprouts serve as forage. The trees are traditionally favored and protected by farmers and have played an important role in soil and water conservation in semi-arid Wes Africa. The husks can be used in heavy metal treatments of industrial waste waters. The oil /butter have nutritional, medicinal, and industrial value.

2.10 Design of Experiments

2.10.1 Central composite design

A central composite design (CCD) of experiments, originally developed by Box and Wilson (1951), is one the most efficient class of designs capable of generating a response surface. Several factors at several levels can generate a response surface. The minimum number of levels and factors is three for a second order model. CCD are useful for sequential experimentation in which the cube portion is used to allow estimation of the first order effects and the later addition of the star points permits second order terms to be added to the model and estimated. Systematic errors were avoided by randomized order of experimental runs. For each categorical variable, a 20 factorial CCD for the three variables, consisting of 8 factorial points, 6 axial points and 6 replicates at the center points were employed, indicating that altogether 20 experiments were required, as calculated from the following equation:

$$N = 2^3 + 2n + n_c \qquad 2.1$$

where, N= the total number of experiments required

n= the number of factors

c=center points

The experimental plan was made using the CCD and the responses measured were the acid value and the yield of fatty acid methyl esters (FAME) for the esterification and

transesterification processes respectively. A five-level-three-factor CCD was employed in the optimization study, requiring 20 experiments. The methanol-to-oil molar ratio, catalyst concentration, reaction duration, and reaction temperature were the independent variables selected to optimize the conditions for Acid value determination and FAME production of the two step catalyzed biodiesel production from wado seed oil. The experiments were carried out in randomized order and data was statistically analyzed by the Design Expert software version 7.0.0 (STAT-EASE Inc., Minneapolis, USA).

The center points are used to determine the experimental error and the reproducibility of the data. The independent variables are coded to the (−1, 1) interval where the low and high levels are coded as −1 and +1, respectively. The axial points are located at (±α, 0, 0), (0, ±α, 0) and (0, 0, ±α) where α is the distance of the axial point from center and makes the design rotatable. In this study, α value was fixed at 1.682 (rotatable). The independent variables chosen in this study were coded according to the equation given below.

$$x_i = \frac{X_i - X_0}{\Delta X} \qquad 2.2$$

where, x_i= the dimensionless coded value of the i^{th} independent variable,

X_i = is the natural value of the ith variable

X_0 = the central value of X_i in the investigated area

ΔX = the step change value (size)

2.10.2 Model fitting and statistical analysis

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). The experimental data obtained by following the above procedures were analyzed by the response surface regression procedure using the following second-order polynomial equation generated by Design-Expert 7.0.0 software (Stat-Ease Inc., USA). Second-order coefficients were generated via regression. The response was initially fitted to the factors via multiple regressions. The quality of the fit of the model was evaluated using the coefficients of determination and analysis of variance. The quadratic response surface model was fitted to the following equation:

$$Y = \beta_o + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} {x_i}^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} x_i x_j \qquad 2.3$$

in which, Y is the response factor (acid value or percentage conversion), x_i and x_j are the uncoded independent variables,$\beta_o, \beta_i, \beta_{ii}, and\ \beta_j$ are intercept, linear, quadratic and interaction constant coefficients, respectively.

2.11 Summary

Biodiesel is a clean-burning diesel fuel with a chemical structure of fatty acid alkyl esters. Of the various methods available for producing biodiesel, the alkali-catalyzed transesterification of vegetable oils and animal fats is currently the most commonly adopted method. Transesterification is basically a sequential reaction. However, when the raw materials (oils or fats) contain a high percentage of free fatty acids or water, the alkali catalyst will react with the free fatty acids to form soaps and the water can hydrolyze the triglycerides into diglycerides and form more free fatty acids. These are undesirable reactions which reduce the yield of the biodiesel product. Therefore, after refining the raw materials, the acidic feed stocks should be pre-treated to inhibit the saponification reaction.

There are three primary approaches for reducing the amount of free fatty acids: esterification of free fatty acids with methanol, in the presence of acidic catalysts; using iodine as a catalyst; adding glycerol into the acidic feedstock with a catalyst like zinc chloride and heated to a high temperature. The first approach can eliminate the separation, corrosion, toxicity, and environmental problems, but the reaction rate is slower while the advantage of the last approach is that no alcohol is needed and the water (formed from the reaction) can be immediately vaporized and vented from the mixture. The transesterification reaction requires an alcohol as a reactant and a catalyst. The most commonly used alcohol is methanol while sodium hydroxide and potassium hydroxide are the most commonly used catalysts. During the reaction, glycerol will be produced as a by-product. Because of its numerous industrial applications, the crude glycerol should be

refined with purity higher than 99% to make it usable. For refining the crude biodiesel produced, the product should first be neutralized and then put through an alcohol stripper before cleaning by either one of the following approaches: water washing, membrane extraction, and dry washing. A very promising method for washing biodiesel is the hollow fiber membrane extraction, which effectively avoids emulsification during the washing step and decreases the refining loss. As a commercial fuel, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure that it meets international standards even if it has been stored for a long time.

There are four primary factors affecting the yield of biodiesel, i.e. alcohol quantity, reaction time, reaction temperature, and catalyst concentration. To ensure a complete transesterification reaction, the molar ratio of alcohol to triglycerides should be increased to 6:1 with the use of an alkali catalyst. For oils with a high percentage of free fatty acids, a higher molar ratio is needed. Because the conversion rate of fatty acid esters increases with reaction time but the yield of the biodiesel product reaches a maximum at an optimal reaction time. Higher reaction temperature can decrease the viscosity of oils, enhancing the reaction rate. The optimal temperature ranged between 50 ^{0}C and 60 ^{0}C, depending on the oil used.

The central composite design method is the most widely used optimization tool. It gives more relevant values than the frequently used types of optimization.

CHAPTER THREE

3. MATERIALS AND METHODS

The experimental work has been done in the laboratory of Department of Chemical Engineering, Addis Ababa Institute of Technology; Addis Ababa University, Addis Ababa, Ethiopia.

3.1 Materials

The major raw materials used during the experiment are WSO, analytical grade (AG) methanol and H_2SO_4 and KOH as a homogeneous catalyst. The oil was obtained from two different sources. The roasted WSO, processed using a screw press, was procured from a local association located at Punyiwdo province. The other was the oil extracted by soxhlet apparatus set using hexane as a solvent. The chemicals were purchased and obtained from *Neway* PLC, *Micron Laboratories* PLC, and the Chemical Engineering Department of Addis Ababa Institute of Technology (AAIT), Addis Ababa, Ethiopia (Table 3.1).

3.1.1 Wado seed collection

Fresh wado fruits were collected from Eliya, Abobo, and Gog vicinities of the GPNRS (the South-Western administrative region of Ethiopia) (Figure 3.1). The pulps were removed from the fruit by hand to release the nuts. The de-pulped nuts were sun dried on the open floor for 14 days to remove the water from the seeds and to ease the detachment of the seeds from the nuts.

Samples were randomly selected to determine moisture content in the nuts according to AOAC Standard (AOAC, 1980). 100 g of each sample was oven-dried at 105^0C for 7h at the GPNRS Soil Testing Laboratory. The dried samples were then cooled in a desiccator and re-weighed to determine the weight loss. The test was replicated three times and the average moisture content of the wado nut is found to be 35%. The dry nuts were then bagged in plastic container and stored for subsequent use.

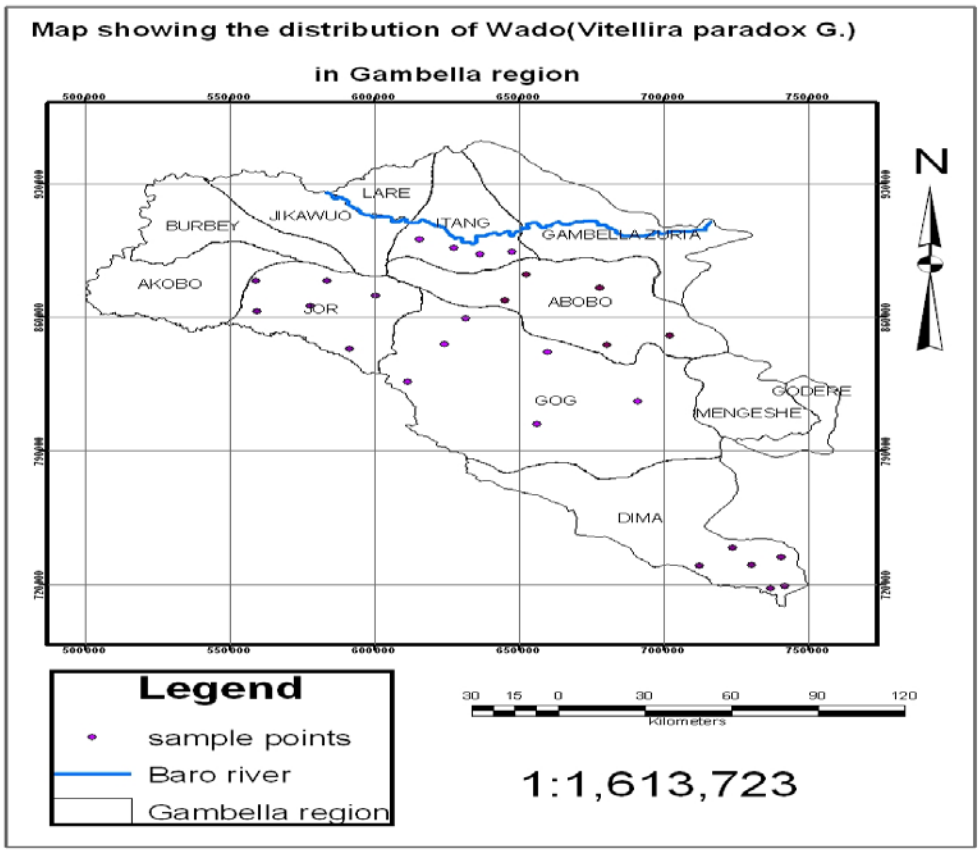


Figure 3.1 Distribution map of wado tree in Gambella Region (*Map generated using ArcGIS 9.2 software by the Author*).

Table 3.1 Lists of chemicals and reagents used

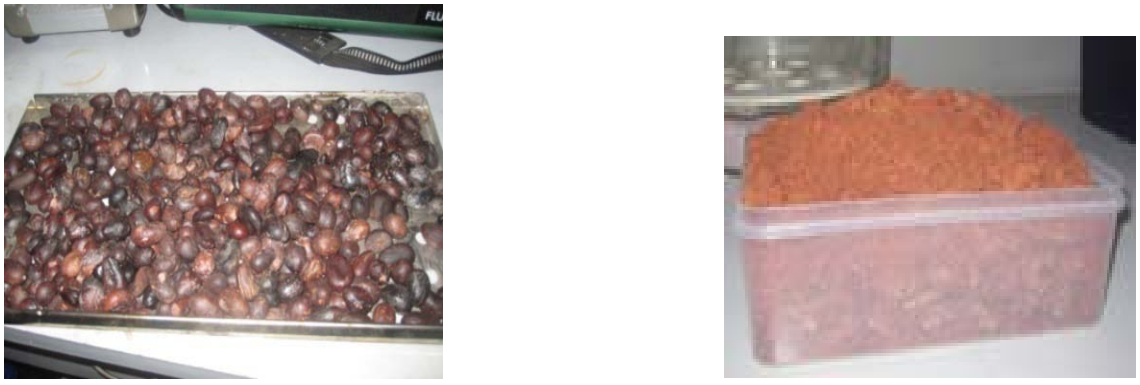
Chemicals	
Methyl orange	Hexane
Phenolphthalein (95-97%)	Methanol (99.5%)
Sodium thiosulfate	Sulfuric acid (98%)
Hydrochloric acid	diethyl ether
Potassium hydroxide(pure)	Phosphoric acid (95%)
Sodium hydroxide (min 99%)	Sodium sulphate
Ethanol (96%)	

3.2 Experimental Method

3.2.1 Wado seed preparation

Nuts were dried at 50^{0}C for 6 h to remove some moisture. Afterward all the seeds were de-hulled using Beco disk mill cracker. The seeds/kernels were separated from the husk by sifting and stored in a plastic bag until the next process. Then, the kernels were further dried at 105^{0}C for 24hr in the oven to determine the moisture content of the seeds. The nuts were further dried for another 5 days at 50^{0}C. Finally, the clean kernels were grounded in to powder (about 2.0mm in order ease the extraction) using an electric coffee grinder machine to increase surface area for extraction (Figure 3.2 **a** and **b**).

(a) Wado seed to the left, Beco disk mill in the middle and coffee grinder to the right



(b) WSO kernel and grounded kernel

Figure 3.2 Wado seed preparation

3.2.2 Determination of moisture content of wado kernel

The wado kernels were cut into smaller chips to ease moisture removal. The crucible was weighed with and without the amount of kernels. The crucible with kernels was dried in an oven at 105°C for 8h. The sample was removed each 2h from the oven and placed in the desiccator for 30 minutes to cool and re-weighed till constant weight is obtained. Finally, the weight was taken and compared with the initially recorded weight.

The percentage moisture content was then calculated using the formula in equation 4.2.

3.2.3 Oil extraction

The grounded seed was used for oil extraction. The extraction method used was known as soxhlet extraction. About 20 g of milled seed was loaded in to soxhlet apparatus.

The extraction was carried out at 68 ^{0}C (boiling temperature of hexane) for 9 h in a water bath heated by a thermostat (set-up is shown in Figure 3.3).

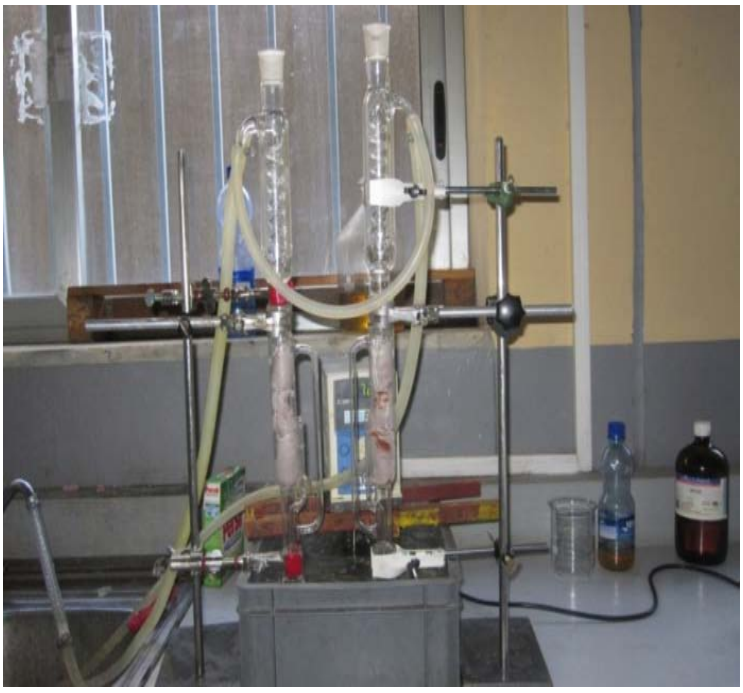


Figure 3.3 Experimental set-up for Soxhlet Extraction

Supernatant solution was collected which was the mixture of the extracted oil and the hexane. Since some amount of suspension was available within the supernatant solution, filtration was employed to remove all the suspension from the extracted oil. After filtration, the hexane was distilled off in a rotary evaporator (Eyela, N-N Series, Rikakikai Co. Ltd. Tokyo, Japan) at 70^0C *(Figure 3.4).* The samples were transferred into brown glass bottles and stored in a refrigerator until all analyses were completed.

Figure 3.4 Rota vapor used to separate the hexane from the extracted wado seed oil

3.2.4 Determination of the percentage of seed oil extracted

20 g of the sample was placed in the thimble and about 150 ml of hexane was poured into round bottom flask. The apparatus was heated at 68^0C and allowed for 9 h of continuous extraction using soxhlet apparatus. The experiment was repeated in triplicate. At the end the solvent was distilled off using rotary evaporator.

The percentage of oil extracted was determined using equation 4.4.

3.2.5 Purification of crude oil

3.2.5.1 Degumming

The oil was heated to 70^{0}C under stirring at 1000 rpm in a jacketed glass vessel connected to a circulation thermostat, 3% of distilled water (which first was heated to approximately 80^{0}C) and 2% of phosphoric acid (85%) was added. The mixture was stirred for 60 minutes and removed. Then, it was allowed to settle for 20 minutes.

The precipitated matter was separated by centrifugation for 50 minutes at 3500 rpm. The experimental set-up is shown in Figure 3.5.

Figure 3.5 Experimental set-up for degumming of crude oil.

3.2.5.2 Washing

About 20% hot distilled water was added to the degummed oil and stirred vigorously for 3-5 minutes. The mixture was poured in to a separatory funnel and the water was drained off. This process continued till the pH of the oil reached almost neutral. Finally, the oil was dried in oven at 100 ^{0}C for 2h to remove the water present.

3.2.6 Physicochemical properties purified oil

The oils (pressed and solvent extracted) were mixed after purification and, then analyzed for physicochemical properties such as density, viscosity, acid value, free fatty acid value, and saponification value.

3.2.6.1 Determination of density

Heated sample at 40^0C was filled into graduated cylinder ***(50 ml)*** and its temperature was recorded until a reading of 25^0C was reached. Densimeter was used to measure the Specific Gravity (SG) of the oil at 25 ^{0}C. The density of the sample was calculated from equation 4.5.

3.2.6.2 Determination of kinematic viscosity

Vibro viscometer was used to determine a viscosity of the oil. The sample was kept in the water bath heated by thermostat until it reaches the 40^0C (equilibrium temperature)**.** After maintaining the equilibrium temperature**,** the vibro viscometer tip was inserted in 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 (μ) of the oil was calculated from equation 4.6.

3.2.6.3 Determination of acid value

Acid value (AV) of the oil was determined using the method described by IUPAC (1979) and modified by Egan *et al*. (1981) as outlined below:

Standard alcoholic potassium hydroxide solution (0.1 N) was prepared by dissolving KOH (pellet) with 95 %ethanol. The solution was filtered and stored in brown bottle for five days. A phenolphthalein 10 g per liter of 95% v/v ethanol was used us an indicator. Furthermore, a mixture of 1 to 1 ratio (v/v) 95% ethanol and diethyl ether was prepared by mixing 500 ml diethyl ether and 500 ml of ethanol.

25 ml of diethyl ether was mixed with 25 ml of hot ethanol and 1 ml of phenolphthalein solution (1 %). Next, the mixture was carefully neutralized with 0.1N KOH. About 5g of the

melted oil was dissolved in the mixed neutral solvent and titrated with aqueous 0.1N ethanolic KOH, shaking constantly until a pink colour which persisted for 15 seconds was obtained. The volume of 0.1 N ethanolic KOH (V) for the titration was noted.

The total acidity (acid number) in mgKOH/g oil was calculated using equation 4.9(**a**).

The free fatty acid, FFA, of the oil was calculated from the acid value using equation 4.9(**b**).

3.2.6.4 Saponification Value Determination

Saponification value of the oil was determined using method described by Egan et al. (1985) with slight modification as outlined below:

Potassium hydroxide solution of 0.5M, in 95 %(v/v ethanol) was prepared. 35 g of KOH pellet was dissolved in 20 ml water, and the solution was mixed with 1000 ml of 95% ethanol. The solution was allowed to stand for 12 hours at room temperature and a clear supernatant solution decanted off. The filtered solution was then kept in the dark for storage. Hydrochloric acid of 0.5M was standardized and a 2% phenolphthalein as indicator was prepared.

2 g of the oil sample was introduced into a 250 ml conical flask connected to a reflux condenser and 25 ml of alcoholic KOH solution was added into it. The flask was heated at 78^0C (boiling temperature of ethanol) for 1hr, swirling intermittently using magnetic stirrer until complete saponification. The flask was removed from the heat mantel, and then 5 drops of phenolphthalein indicator was added, and the hot soap solution obtained was slowly titrated against the 0.5N HCl. The end point was reached when pinkish coloration changed to colorless (volume V_a was recorded). Blank determination was also conducted along with that of sample, using the same reagents minus sample (and volume V_b was recorded).

The saponification value (SV) (expressed as the number of milligram of KOH required to saponify 1g fat) was calculated using equation 4.8.

3.2.6.5 Determination of high 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 g 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 2000g 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. The determination of the oils calorific value was conducted following the same procedure as that for standardization, except that the sample was solid fat.

Including the corrections for heat transfer between the surrounding and the apparatus, heat liberated by the glowing wire etc, the heat value of the oil was calculated according to equation 4.10(**a**).

3.2.6.6 Determination of melting point

A melting point of the oil was determined using $BU\ddot{C}HI$ Melting Point B-540 Apparatus. The melted oil was poured into a small heat resistant glass capillary and then let to solidify. After this, the solidified glass capillary was inserted into the $BU\ddot{C}HI$ apparatus. The melting temperature set point was assigned on the apparatus. When the first melting was observed on the watching screen, the corresponding temperature was recorded.

3.3 Experimental Design for Two-step Acid-base Catalyzed Biodiesel Preparation

The application of two-step acid-base catalyzed biodiesel production was introduced. The process consisted of two-steps: esterification and transesterification. In the first step, the FFA value of the oil was reduced to about 1% using H_2SO_4 catalyzed esterification. In the second step all triglycerides were converted into methyl esters (biodiesel) using KOH

catalyzed transesterification (flow chart is shown in Figure 2.2*)*. Experimental design was analyzed and done by the Design-Expert 7.0.0 program.

The experimental design selected for this study was Central Composite Design (CCD). The responses measured were the acid value and the yield of fatty acid methyl esters (FAME) for the esterification and transesterification reactions, respectively. Furthermore, the physicochemical analysis of the biodiesel was carried out.

3.3.1 Acid - catalyzed esterification

The three esterification process variables studied are reaction time, methanol to oil molar ratio and weight percentage of catalyst. The reaction temperature and mixing speed was set at optimum point where the maximum reduction could be achieved.

Table 3.2 lists the range and levels of the three independent variables studied. The levels of the variables investigated are chosen by considering the operating limits of the reaction. The experiments were carried out in randomized order.

Table 3.2 Independent variables and levels used for CCD for acid-catalyzed esterification process

Variables	Symbols	Levels[a]				
		-1.68 $(-\alpha)$	-1	0	+1	+1.68 $(+\alpha)$
Methanol- to -oil ratio (v/v)	M	0.17	0.2	0.25	0.3	0.33
Amount of Catalyst (v/v)	C	0.16	0.5	1	1.5	1.84
Reaction time (h)	t	0.32	1	2	3	3.68

[a] Transformation of variable levels from coded (X) to uncoded could be obtained as:

$M = 6 + 1X$; $C = 0.5 + 0.2X$ and $T = 55 + 5X$

A five-level-three-factor central CCD was employed in this optimization study, requiring 20 experiments. The 20 experiments were carried out and data was statistically analyzed by the Design-Expert program to find the suitable model for the acid value reduction as a function of the above three variables. The value of α for this CCD was 1 .68.

Table 3.3 shows the complete experimental design matrix of CCD for the factorial design (n- factors, each at two-level). The order in which the runs were made was randomized to avoid systematic errors. The test was made following combinations given in the table.

Table3.3 Central composite design arrangement for the esterification step

	Coded Factor			Actual Factors		
Run	X1	X2	X3	Methanol to oil ratio	Catalyst to oil ratio	Reaction time
1	-1	-1	-1	0.2	0.5	1
2	-1	-1	1	0.2	0.5	3
3	-1	1	-1	0.2	1.5	1
4	-1	1	1	0.2	1.5	3
5	1	-1	-1	0.3	0.5	1
6	1	-1	1	0.3	0.5	3
7	1	1	-1	0.3	1.5	1
8	1	1	1	0.3	1.5	3
9	-1.68	0	0	0.17	1	2
10	1.68	0	0	0.33	1	2
11	0	-1.68	0	0.25	0.16	2
12	0	1.68	0	0.25	1.84	2
13	0	0	-1.68	0.25	1	0.32
14	0	0	1.68	0.25	1	3.68
15	0	0	0	0.25	1	2
16	0	0	0	0.25	1	2
17	0	0	0	0.25	1	2
18	0	0	0	0.25	1	2
19	0	0	0	0.25	1	2
20	0	0	0	0.25	1	2

3.3.2 Base - catalyzed transesterification

A five-level-three-factor CCD was also used. Methanol-to-oil ratio (M), catalyst concentration (C) and reaction time (T) were the independent variables selected to optimize response (% FAME). The coded and uncoded levels of the independent variables in this step are given in Table 3.4.

Table 3.5 shows the complete experimental design matrix of CCD for the factorial design (n- factors, each at two-level) of the base transesterification reaction. The order in which the runs were made was randomized to avoid systematic errors. The central values (zero level) chosen for experimental design were the methanol-to-oil molar ratio of 6:1, catalyst concentration of 1% (w/v), and temperature 55°C.

Table 3.4: Independent variables and levels used for CCD for base-catalyzed transesterification of two–step catalyzed process

Variables	Symbols	Levels[a]				
		-1.68 ($-\alpha$)	-1	0	+1	+1.68 ($+\alpha$)
Methanol- to -oil ratio (mol/mol)	M	0.96	3	6	9	11.04
Amount of Catalyst (%wt.)	C	0.16	0.5	1	1.5	1.84
Reaction Temperature (^{0}C)	T	46.59	50	55	60	63.41

[a] Transformation of variable levels from coded (X) to uncoded could be obtained as:

$M = 6 + 3X$; $C = 1 + 0.5X$ and $T = 55 + 5X$

Table 3.5 Central composite design matrix for the transesterification step

	Coded Factor			Actual Factors		
Run	X1	X2	X3	Methanol to oil ratio	Catalyst to oil ratio	Reaction Temperature
1	-1	-1	-1	3	0.5	50
2	-1	-1	1	3	0.5	60
3	-1	1	-1	3	1.5	50
4	-1	1	1	3	1.5	60
5	1	-1	-1	9	0.5	50
6	1	-1	1	9	0.5	60
7	1	1	-1	9	1.5	50
8	1	1	1	9	1.5	60
9	-1.68	0	0	0.96	1	55
10	1.68	0	0	11.05	1	55
11	0	-1.68	0	6	0.16	55
12	0	1.68	0	6	1.84	55
13	0	0	-1.68	6	1	46.59
14	0	0	1.68	6	1	63.41
15	0	0	0	6	1	55
16	0	0	0	6	1	55
17	0	0	0	6	1	55
18	0	0	0	6	1	55
19	0	0	0	6	1	55
20	0	0	0	6	1	55

3.3.3 Laboratory Reactor Setup

The batch transesterification reaction system employed in this work is shown in Figure3.4 below. A 250ml glass reactor equipped with magnetic stirrer, eclectic thermostat, and condenser was used in all experiments. The reactor was connected to a water bath heated with thermostat, which was capable of controlling the temperature within deviation of 1^0C. The magnetic stirrer provided the mixing requirement.

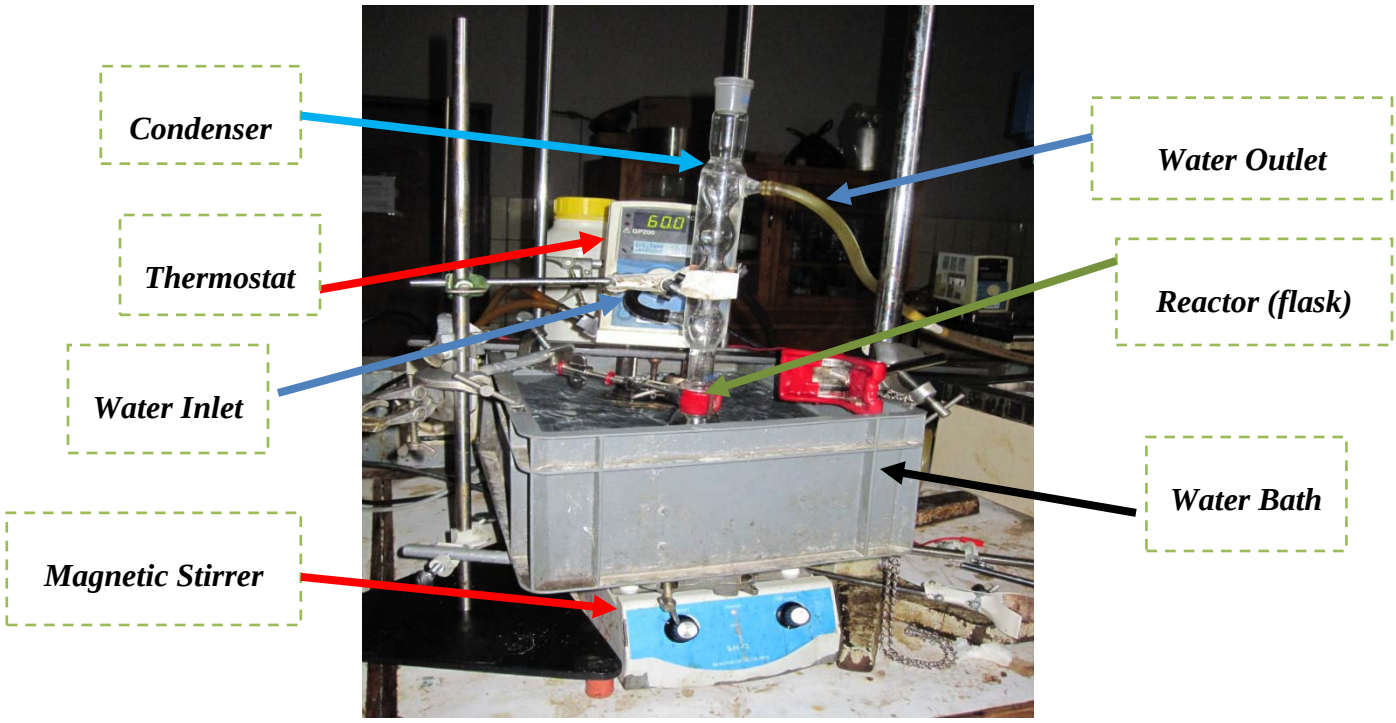


Figure3.4 The experimental setup for the biodiesel production using two-step catalyzed method.

3.4 Biodiesel Production Procedures

3.4.1 Acid catalyzed esterification

The oil is solid at room temperature and hence, requires a heating energy for the reaction to proceed. 100 ml of the melted oil was poured into the reaction flask and heated to 55^0C. The methanol-to-oil ratio (M), duration of the reaction (t), and weight percentage of catalyst (%Wt) were used as described in Table 3.2. The reaction temperature and mixing speed of the reactor were fixed at 55^0C and 550 r.p.m, respectively.

After completion of the reaction, the mixture was, then centrifuged at 1000 rpm for 50 minutes to drain off the excess methanol and the water formed as a by-product. The acid value of the mixture was measured by titration. The sample that presented the lowest acid value (hence lowest) FFA content in the shortest reaction time and lowest methanol to oil

ratio was chosen as the optimum condition and was used for the next step (base-catalyzed transesterification reaction).

3.4.2 Base-catalyzed transesterification

The product from the esterification reaction, which was obtained at the optimum reaction conditions, was converted to methyl esters using KOH as homogeneous catalyst. Same experimental setup was used that of the esterification process.

100ml of oil sample was used all time. The oil was heated to the required reaction temperature. The reaction was carried out according to the reaction parameters shown in Table 3.4. The reaction time (1h) and stirring speed (550 rpm) were fixed all time. After completion, the product was poured in separatory funnel and allowed to form biodiesel and glycerol layers over night.

The glycerol was drained off using gravity and the biodiesel was centrifuged for further separation. After separation, the product was washed with 20% hot distilled water (v/v) and neutralized with a 2 % phosphoric acid (v/v). The water was removed from the biodiesel first by mixing with anhydrous sodium sulphate and passing it in vacuum filter covered with fine silica gel. The remained biodiesel was heated in an oven at 100^0C for 1h and stored in a glass bottle for further analysis.

3.5 Physicochemical Properties of Biodiesel

The biodiesels from the transesterification reaction were characterized for their physical and chemical properties. The extensively characterized physical properties were specific gravity, kinematic viscosity, higher heating value, and cloud point.

The biodiesels were, also characterized for their chemical properties such as acid value, iodine value, saponification value, cetane index, and flash point.

Standard methods applied for the ester characterization are presented in Table 3.6.

Table 3.6: Standard methods for biodiesel Characterization

Property of biodiesel	Test method
Acid value	IUPAC 1979
FFA	Egan et al., 1985
Saponification value	Egan et al., 1985
Heating value	Parr, 1987
Cloud point	ASTM D2500

The details on equipment and procedures are presented as follows:

3.5.1 Specific gravity

The same procedure was used to determine the specific gravity of the biodiesel as discussed on characterization of purified wado seed oil.

3.5.2 Kinematic viscosity

The same procedure was used to determine the kinetic viscosity of the biodiesel as discussed on characterization of purified wado oil.

3.5.3 Acid Value

The same procedure was used to determine the acid value of the biodiesel as discussed on characterization of wado seed oil.

3.5.4 Saponification value

The same procedure was used to determine the saponification value of the biodiesel as discussed on characterization of wado seed oil.

3.5.5 Determination of heating value

The same procedure was used to determine the heating value of the biodiesel as discussed on characterization of wado seed oil.

3.5.6 Determination of iodine value

The Iodine value (IV) of the biodiesel was determined using the empirical formula suggested by Dembirbes (1998) for determination of higher heating value (HHV). After rearrangement the iodine value (IV) was calculated from equation 4.12.

3.5.7 Determination of cetane number

The cetane number of the biodiesel was determined using the empirical formula suggested by Kalayasiri *et al*., (1996). The formula was obtained by relating saponification value (SV) and iodine value (IV) of the biodiesel. The CN was calculated using equation 4.18].

3.5.8 Determination of flash point

A flash point of the biodiesel was determined using an open cup method. A cup was filled with the biodiesel up to a mark (about 75 ml) and was heated by a Bunsen burner. A hand thermometer was inserted into the cup to read the temperature. A small open flame was maintained from an external supply of natural gas. Periodically, the flame was passed over the surface of the oil. When the flash temperature was reached, the surface of the biodiesel caught with fire. The temperature at this moment was noted and reported as flash point temperature.

3.5.9 Determination of cloud point

The cloud point of biodiesel was determined using ASTM D5773. A glass beaker was filled with biodiesel. The sample cooled at a 2^0C rate using a chiller, and continuously monitored until haze (wax-like solids) formation appeared. The temperature at which the haze observed was recorded and reported as cloud point temperature of the biodiesel. The cloud point is a measure of the temperature at which components in the biodiesel begin to solidify out of the solution.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1 Seed Preparation, Oil Extraction, Oil Purification and Oil Characterization

4.1.1 Seed preparation

The ratio of kernel weight to the raw seed weight was calculated using equation 4.1.

$$W = \frac{\text{mass of kernel}}{\text{total amss of nut}} \qquad 4.1$$

But mass of kernel was 14 Kg and the total weight of the seed was 22 Kg. The weight of the kernel, W was calculated by substituting these values in to equation 4.1. The result was: $W = 0.6364$

Therefore, the kernel weight was 63.64 % of raw seed (nut) weight.

The moisture content test of the kernel was triplicated and the results are summarized in table 4.1 based on equation 4.2

$$moisture\ content = 100 * \left[\frac{W_1 - W_2}{W_2}\right]\% \qquad 4.2$$

Where, W_1 = Original weight of the sample before drying

W_2 = Weight of the sample after drying

Table 4.1 Moisture content of wado seed kernel

Run	Sample weight (g)			Moisture content (% w/w)	
	w_1	w_2	w_1-w_2	Seed	
1	10	9.28	0.72	7.2	7.33
2	10	9.17	0.83	8.3	
3	10	9.35	0.65	6.5	

4.1.2 Oil extraction

14 Kg seeds were grounded in to almost 2mm particle size. 9Kg of the powdered seed was used for oil extraction using soxhlet apparatus. After separation, about 4.5 litre of crude oil was obtained. Then, the density (ρ) of the crude oil was measured and the result was 980 kg/m^3.

The mass, m, of the oil extracted was calculated from the basic mass-density relationship given below in equation 4.3.

$$m = \rho_{oil} * V_{oil} \qquad 4.3$$

Substituting values,

m = 4.41 kg oil was extracted.

The oil content (oil yield) of the powdered seed was calculated by:

$$\text{Oil Yield} = \frac{\text{mass of crude oil extracted}}{\text{mass of total seedl used}} * 100\% \qquad 4.4$$

Substituting values,

$$= \frac{4.41\ kg}{9\ kg} * 100\% = 49.0\%$$

The oil content of the seed was calculated to be 49.0%. This value was found to be in agreement with previous findings (Nkouam *et al.*, 2007).

4.1.3 Oil purification

Degumming

Based on the method discussed in previous chapter; 3% (v/v) hot distilled water and 2% (v/v) phosphoric acid is required for degumming 5.5 l crude wado oil.

Hence, the amount distilled water required = amount of oil*0.03

= 0.165 liters

Amount of phosphoric acid require = amount of oil* 2%

= 5.5 litre * 0.02

= 0.11 liters

4.1.4 Physicochemical properties of wado seed oil

Wado seed oil was characterized prior to biodiesel prepare. Table 4.3 summarizes the physicochemical properties. The details of the properties are discussed below as follows

Table 4.2: Physico-chemical properties of wado seed oil

Physicochemical properties	Unit	Value
Acid value	mgKOH/g	12.6
FFA	%	6.28
Density	Kg/m^3	980
HHV	MJ/kg	39.56
Iodine value	$I_2g/100g$	94.6
Melting Point	^0C	38.2
Oil yield	%	49
Saponification value	mgKOH/g	204
Viscosity (40^0C)	mm^2s^{-1}	42. 2

4.1.4.1 Specific gravity

Melted oil sample was brought to 25°C and a test portion was transferred to the measuring cylinder. Densimeter was inserted in to the cylinder. Then, the reading was taken. The specific gravity observed was 0.98.

Hence, the density of the oil is determined using the specific gravity.

$$SG = \frac{\rho_{oil}}{\rho_w} = \rho_{oil} \qquad 4.5$$

where, ρ_{oil} = Density of wado oil used

ρ_w = Density of equal volume water =1g/ml

Therefore, the density of the oil was 0.98g/ml or $980kg/m^3$.

4.1.4.2 Kinematic viscosity

The viscosity of oil was measured using Vibro viscometer. The device detects the dynamic viscosity, which is resistance to flow with vibration. The observed kinematic viscosity was 42.02mm^2/sec which is in agreement with literature data.

$$\mu = \frac{v}{\rho} \qquad 4.6$$

Where, μ=kinematic viscosity, mm^2/s

ν=dynamic viscosity, mpa.sec

ρ=density, Kg/m^3

4.1.4.3 Saponification value

The saponification number was determined by using titration. Solutions were prepared with the required concentration. In order to know the exact concentration, the solution was standardized. Hence, primary and secondary standardization was used.

Mass of KOH =N*equivalent weight*Volume of solution in liter

= 0.5mol/l *56.11g/mol*1l

= 28.055g

Mass of HCl = N*equivalent weight*Volume of solution in liter

=0.5*36.5*1l

=18.25g

V_{HCl}=m/ρ=18.25/1.16 =15.73ml

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

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

$$V_1\, N_1 = V_2 N_2 \qquad 4.7$$

Solving for N_2,

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

Similarly the experiment was repeated and validated concentrations were:

$N_3 = 25*0.1/5.5 = 0.4545$

$N_4 = 25*0.1/5.4 = 0.46$

The average concentration was taken and is

$N_{HCl} = 0.46$

Similarly, HCl is used to standardize the ethanolic alcohol solution. 25ml of ethanolic KOH was titrated against HCl using 3 drops of methyl orange as indicator. The volume of HCl was noted.

$N_{31} = (V_2N_2)/V_3 = 34.7*0.46/25 = 0.634$

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

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

$N_{KOH} = 0.625$

2g of oil was dissolved in ethanolic KOH and titrated with HCl. Similarly blank titration was done. In both cases, the volume of HCl was recorded. The saponification value was then calculated using equation 4.6.

$$SV = \frac{56.1 * N * (V_b - V_a)}{w} \qquad 4.8$$

where, w= weight of oil used, 2g

N= normality of HCL solution, 0.46N

V_a= volume of HCl solution used in the test, 29.4 ml

V_b= volume of HCl solution used in blank, 45.2 ml

Values for unknowns in equation 4.8 were substituted; hence the SV was calculated. The observed value was 204 mg of KOH/g of oil, which is in agreement with literature data. The experimental result was attached in Appendix C.

4.1.4.4 Acid value

The titrant volume was observed to be 11.2ml. The acid value of the oil was calculated from equation 4.9.The total experimental result was given at Appendix C.

$$AV = \frac{56.1 * N * V}{m} \qquad 4.9(\boldsymbol{a})$$

where, V= the volume of 0.1N solution of ethanolic KOH, 11.2ml

N= concentration (exact normality) of ethanolic KOH, 0.1N

m = mass in gram of the test portion, 5g

Substituting the values in to equation 4.9,

AV= (11.2*0.1*56.1)/5 = 12.6 mg KOH/g of oil

The % FFA value was calculated from the acid value using the relation:

$$AV = FFA * 2 \qquad 4.9(\boldsymbol{b})$$

Therefore,

% FFA = AV/2= 12.6/2

= 6.3 %

The %FFA value was far beyond the required limit for biodiesel transesterification.

4.1.4.5 Higher heating value

It was determined by using bomb calorimeter. 1g of benzoic acid was used as a calibrating substance. The amount of water used to fill the calorimetric container was 2000g. Equation 4.10 was used to calculate the HHV of the oil.

$$HHV = \frac{[m_w * C_w + (m_c)_{app}](t_m + c - t_o) - \sum b}{m} \qquad 4.10\ (a)$$

Where: HHV= Higher heating value, cal/g

m =Mass of the fuel, g

m_w = Mass of the calorimeter water, g

C_w = Specific heat of the calorimeter water, C_w = 1cal/g^{o}C

t_o = First temperature reading of main test, ^{0}C

t_m = Last temperature reading of main test, ^{0}C

c = Correction for heat exchange between calorimeter and the surrounding, min*^{0}C

$\sum b$ =Correction for heat exchange between calorimeter and the surrounding, cal

The correction, c was calculated from the formula in equation 4.10 (b) .

$$c = \mathrm{m}'\Delta\mathrm{n} - (\Delta\mathrm{n} + \Delta\nu)\mathrm{F} \qquad 4.10\ (b)$$

where, m'= duration of main test, min

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

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

The factor F can be approximated to

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

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

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

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

The HHV of benzoic acid was known with a guaranteed heat of combustion of 6324 Cal/g. The recorded higher heating value of the oil is 39.56MJ/kg. The result is in agreement with literature data. See Appendix C for more experimental calculations.

4.1.4.6 Iodine Value

Iodine value is the measure of the degree of unsaturation of a particular oil or fat. It was determined using empirical equations given in equation 4.11.

$$\text{HHV} = 49.43 - [0.041(\text{SV}) + 0.015(\text{IV})] \qquad 4.11(\mathbf{a})$$

$$\text{IV} = \frac{-\text{HHV} + 49.43 - 0.041(\text{SV})}{0.015} \qquad 4.11(\mathbf{b})$$

The iodine value of the oil was calculated equal to 94.3 g I_2/100g.

4.1.4.7 Melting point

The melting point of the solidified oil was determined by BUCHI Melting Point B-540 Apparatus. 0.3 g of solid WSO was introduced into the capillary tube. Then the temperature set of the apparatus was adjusted to heat to 45 ^{0}C. The first melting was observed on the watching screen and the temperature was recorded, and it was 38.2 ^{0}C.

4.2 Optimization of Reaction Conditions by Response Surface Methodology

The reaction parameters were optimized using DOE software. In contrast with the classical optimization process, which may lack to account the effectiveness of different combination of parameters, RSM provides elaborate vision over various combinations of parameters.

4.2.1 Acid catalyzed esterification

Experiments were conducted with CCD to visualize the effects of independent factors on response (acid value reduction) and the results were evaluated. Important parameters considered during the study were the methanol to oil ratio (M), the acid to oil ratio (C), and reaction time (t).

The complete design matrixes together with both the experimental as well as predicted values obtained for acid-catalyzed esterification process are shown in Table 4.3. All the three variables are shown in both coded and uncoded (actual) form. The predicted values of acid value (AV) from the model were reasonably close to the experimental values. Runs 15–20 at the center point were used to determine the experimental error. Acid value obtained ranged from 2.10 to 17.1%.

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). ANOVA was further carried out to justify the adequacy of the model (Equation 12). Using the coefficients determined, the predicted model in terms of uncoded (actual) factors for acid value is given:

$$\begin{aligned} AV = {} & +69.83686 - 388.97327 * M + 1.73084 * C - 12.96648 * t \\ & -44.50000 * M * C + 14.70000 * M * t + 1.01000 * C * t \\ & +708.71367 * M^2 + 5.23452 * C^2 + 1.63213 * t^2 \end{aligned} \qquad 4.12$$

where, M = molar ratio of methanol to oil, v/v

C = H_2SO_4 (catalyst) amount, v/v

t = reaction time, h

Table 4.3: CCD arrangement and response for acid catalyzed esterification

Run	Coded factors			Actual factors			Acid value (mg KOH/g)	
	X1	X2	X3	Methanol to oil ratio	Catalyst to oil ratio	Reaction Temperature	Actual value	Predicted value
1	-1	-1	-1	0.2	0.5	1	11.4	10.22546
2	-1	-1	1	0.2	0.5	3	5.74	4.239548
3	-1	1	-1	0.2	1.5	1	12.1	14.53533
4	-1	1	1	0.2	1.5	3	13.4	10.56942
5	1	-1	-1	0.3	0.5	1	5.88	6.008812
6	1	-1	1	0.3	0.5	3	3.1	2.962905
7	1	1	-1	0.3	1.5	1	7.07	5.868687
8	1	1	1	0.3	1.5	3	6.37	5.868687
9	-1.68	0	0	0.17	1	2	8.39	4.84278
10	1.68	0	0	0.33	1	2	3.2	11.88607
11	0	-1.68	0	0.25	0.16	2	3.5	3.524799
12	0	1.68	0	0.25	1.84	2	5,47	3.792966
13	0	0	-1.68	0.25	1	0.32	8.7	8.997906
14	0	0	1.68	0.25	1	3.68	2.1	2.05854
15	0	0	0	0.25	1	2	2.84	4.362331
16	0	0	0	0.25	1	2	2.71	2.694074
17	0	0	0	0.25	1	2	3.11	2.694074
18	0	0	0	0.25	1	2	2.61	2.694074
19	0	0	0	0.25	1	2	2.63	2.694074
20	0	0	0	0.25	1	2	2.92	2.694074

ANOVA for the quadratic model for acid value is listed in Table 4.4. From the ANOVA for response surface quadratic model for acid value, the Model F-value of 5.41 and Prob > F of 0.0072 implied that the model was significant.

For the model terms, values of Prob>F less than 0.05 indicated that the model terms were significant. In this case M, C, t, M^2, and t^2 are significant model terms, but C^2 with Prob > F less than 0.005 (i.e. 0.0596) was noticed insignificant due to less value for Model F-Value (4.51). However, the interaction terms were found to be insignificant. Because values greater than 0.1000 indicate the model terms were, therefore, insignificant.

Table 4.4 Analysis of variance (ANOVA) for the quadratic polynomial model for esterification

Source	Sum of Squares	df	Mean Square	F Value	P-value Prob > F
Model	266.13	9	29.57	5.41	0.0072
M	84.39	1	84.39	15.43	0.0028
C	32.70	1	32.70	5.98	0.0345
t	41.97	1	41.97	7.67	0.0198
MC	9.90	1	9.90	1.81	0.2082
Mt	4.32	1	4.32	0.79	0.3949
Ct	2.04	1	2.04	0.37	0.5550
M^2	45.24	1	45.24	8.27	0.0165
C^2	24.68	1	24.68	4.51	0.0596
t^2	38.39	1	38.39	7.02	0.0243
Residual	54.70	10	5.47		
Lack of Fit	54.51	5	10.90	294.44	< 0.0001
Pure Error	0.19	5	0.037		
Cor Total	320.83	19			

Multiple regression coefficients as indicated in Table 4.5 were obtained by employing a least square technique to predict quadratic polynomial model for the acid value.

Table 4.5: Regression coefficients and significance of response surface quadratic model for acid catalyzed esterification.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	2.69	1	0.95	0.57	4.82	
M	-2.49	1	0.63	-3.9	-1.08	1.00
C	1.55	1	0.63	0.14	2.96	1.00
t	-1.75	1	0.63	-3.16	-0.34	1.00
MC	-1.11	1	0.83	-2.95	0.73	1.00
Mt	0.74	1	0.83	-1.11	2.58	1.00
Ct	0.51	1	0.83	-1.34	2.35	1.00
M2	1.77	1	0.62	0.4	3.14	1.02
C2	1.31	1	0.62	-0.064	2.68	1.02
t2	1.63	1	0.62	0.26	3	1.02

Sequential Model Sum of Squares and Model Summary Statistics of the response quadratic model for acid catalyzed esterification were given in Table 4.6.

Table 4.6 Sequential model sum of squares and model summary statistics of the response quadratic model for acid catalyzed esterification

Source	Sum of squares	df	Mean square	Std. Dev.	R^2	Adj. R^2	Pred. R^2	F value	P-value	press	VIF
Linear	159.06	3	53.02	3.18	0.4958	0.4012	0.1966	5.24	0.0104	257.74	1.00
2FI	16.26	3	5.42	3.35	0.6465	0.3371	-1.0689	0.48	0.6989	63.77	1.00
Quadratic	90.81	3	30.27	2.34	0.9295	0.6761	-0.2859	5.53	0.0168	412.54	1.00
Cubic	17.94	4	4.49	2.48	0.9854	0.6372	-24.1268	0.73	0.6020	8061.40	1.00
Residual	36.75	6	6.13								1.00
Total	1019.86	20	50.99								

The tables show that linear and quadratic terms of M, linear and quadratic term of C, linear and quadratic term of term of t, were found to be significant model terms in reducing the acid value.

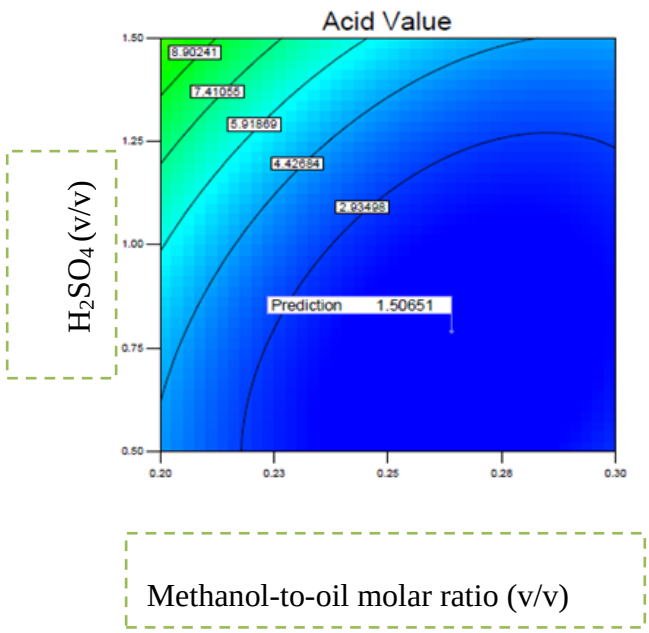
The significance of each coefficient in the model equation was evaluated by the P-value as shown in Table 4.4.The smaller magnitude of the P-value, the more significant is the corresponding coefficient. Considering the linear effect, all the three operating parameters were found to be significant terms in decreasing the acid value in the treated product. Effect of *M*, *C* and *t* on acid value reduction is shown in Figure 4.1a–c. The optimized critical values were found to be 0.25 v/v M, 1% v/v C and 2h t, locating the stationary point in the experimental region. Verification experiments showed reasonably close value of 2.1mg KOH/g to the predicted value 2.05854for the stationary point and thus confirmed the adequacy of the predicted model.

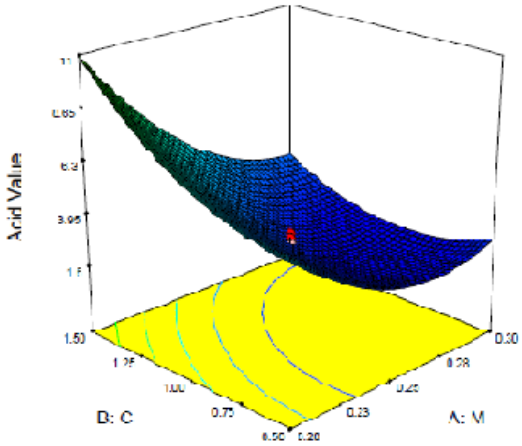
In table 4.6, the value of the determination coefficient (R^2) and Adj.R2 was found to be 92.95% and 67.61%, respectively. These high values of the coefficients indicated the significance of the model. This implies that the full quadratic regression model can be used to explain acid catalyzed esterification.

The relationship between independent and dependent variables of the developed model is shown in Fig.4.1a–c in the form of contour plots.

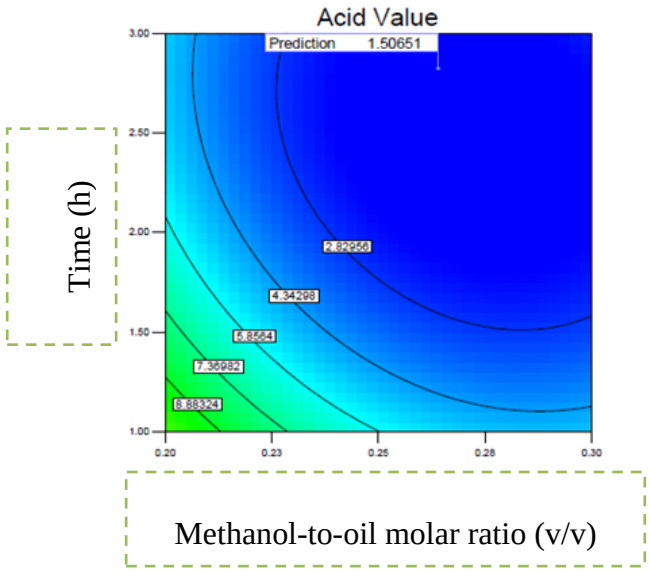
4.2.1.1Effects of parameters

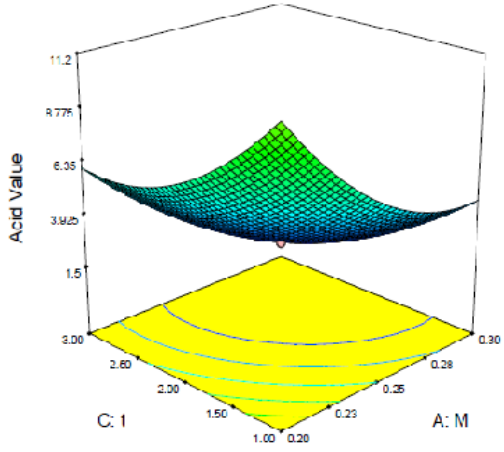
Contours and Surface plots (Figure 4.1 a–c) were drawn at constant value of 0.25 v/v Methanol-to-oil ratio M, 1% v/v H_2SO_4 concentration and 2h of reaction time (t), respectively.





(a)





(b)

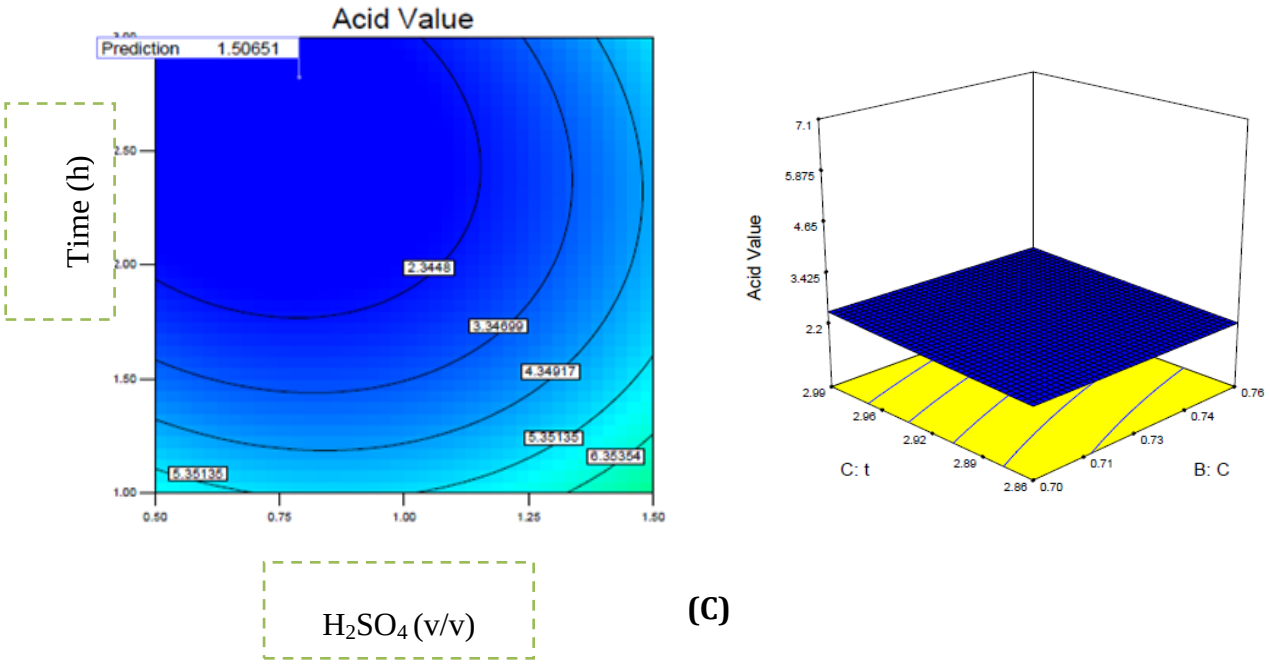


Figure 4.1 Contour plots of acid value (mg KOH/g) predicted from the quadratic model

The responses corresponding to the contour plots of second order predicted model indicated that, for low methanol-to-oil ratio, acid value reduces with increasing catalyst concentration (Figure 4.1-a) and reaction time (Figure 4.1-b), reaction time being less effective as the contours are almost parallel to y-axis. However, at higher methanol-to-oil ratio, there seemed to be less effect of increase in catalyst concentration (Figure 4.1-b) but there was increase in acid value with increase in reaction time (Figure 4.1-a). This could be due to greater positive coefficients of methanol–time (M*t) interaction than methanol–catalyst (M*C) interaction.

At low catalyst concentrations, there was slight decrease in acid value with increase in reaction time, since the time effect was little positive (Figure 4.1-b). For higher catalyst concentrations, the decrease of acid value with increase in methanol-to-oil ratio became smaller (as a result of the negative interaction term M*C).

It was also observed that increasing reaction time beyond 2hr min does not have much effect on reducing the acid value (Figure.4.1-b and c). This might be due to the effect of water produced during the esterification of FFAs, which prevented the reaction in forward direction.

Generally, maximum reduction in acid value was obtained at design points 0.25 %(v/v) Molar ratio, 1 %(v/v) H_2SO_4 and 2h reaction time. These three factors have shown a positive reduction effect to the acid value within the range.

4.1.2.2 Characterization of the esterified oil

The optimal product of esterification was analyzed prior to prepare biodiesel for physicochemical properties.

The major property of interest to analyze was acid value (AV). The acid values for each 20 experiment was shown in Table 4.3. The properties of the sample with optimal reduction in acid value are summarized in Table 4.7.

Table 4.7 Physico-chemical properties of the treated (Esterified) WSO

Physico-chemical properties	Unit	Value
Density	Kg/m^3	910
Viscosity (40°C)	mm^2s^{-1}	38.97
Acid value	mgKOH/g	2.1
FFA	%	1.05
HHV	MJ/kg	39.05
Melting Point	°C	37.6

4.2.2 Base- catalyzed transesterification

The transesterification was carried out at using the previously shown set-up at Figure3.4.

The reaction was carried out using the treated oil sample with lower acid value from the esterification step.

4.2.2.1 Feed material requirement

100ml of treated oil was used for each run. The amount of methanol and catalyst required for the process parameters at central point was calculated as follows.

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

$$\frac{n_{MeOH}}{n_{oil}} = 6 \qquad 4.13$$

$$\frac{\frac{\rho_{MeOH} * V_{MeOH}}{M_{MeOH}}}{\frac{\rho_{0il} * V_{oil}}{M_{oil}}} = 6$$

Substituting the values in to the formula:

$$\frac{\frac{0.791\,g/ml * V_{MeOH}}{32.04\,g/mol}}{\frac{0.91\,g/ml * 100\,ml}{880\,g/mol}} = 6$$

Solving for V_{MeOH} ,

$$V_{MeOH} = 25.23 \text{ ml of methanol}$$

The amount of catalyst required when the ratio of catalyst weight to oil is 1%;

$$m_{oil} = \rho_{oil} * V_{oil} \qquad 4.14$$

$$m_{oil} = \frac{0.91g}{ml} * 100ml$$

$$m_{oil} = 90g \text{ oil}$$

From the catalyst to oil ratio (% wt.),

$$\frac{m_{KOH}}{m_{oil}} = 1\%$$

$$m_{KOH} = 1\% * m_{oil} = 0.9\ g$$

Similarly, the amount of methanol and KOH calculated for all experiments. The calculated values of the process parameters are given in Appendix C.

4.2.2.2 Statistical analysis

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.

Experimental as well as predicted values of percentage conversion of the oil to biodiesel at the design points are shown in Table 4.8. All 20 of the designed experiments were conducted. The actual yield of biodiesel produced at different process parameters was calculated. The yield of the transesterification processes were calculated as sum of weight of FAME produced to weight of oil used, multiplied by 100.The formula is given as:

$$\text{Yield of FAME} = \frac{\text{weight ofFAME}}{\text{weight of oil used}} * 100 \qquad 4.15$$

The results are given in Appendix C. FAME obtained ranged from 33.4 to 94.5%.

Table 4.8 CCD arrangement and response for alkali transesterification

Run	Codeded Factors			Actual Factors			% FAME	
	X_1	X_2	X_3	M	C	T	Actual value	Predicted value
1	-1	-1	-1	3	0.5	50	48.50	50.70
2	-1	-1	1	3	0.5	60	54.74	58.16
3	-1	1	-1	3	1.5	50	60.32	64.89
4	-1	1	1	3	1.5	60	70.60	69.11
5	1	-1	-1	9	0.5	50	77.03	80.92
6	1	-1	1	9	0.5	60	90.35	88.18
7	1	1	-1	9	1.5	50	90.40	89.38
8	1	1	1	9	1.5	60	93.18	93.38
9	-1.68	0	0	0.954622	1	55	33.40	29.39
10	1.68	0	0	11.04538	1	55	74.60	75.22
11	0	-1.68	0	6	0.159104	55	77.50	75.20
12	0	1.68	0	6	1.840896	55	94.00	93.81
13	0	0	-1.68	6	1	46.59104	88.24	83.66
14	0	0	1.68	6	1	63.40896	92.12	93.10
15	0	0	0	6	1	55	94.01	94.31
16	0	0	0	6	1	55	94.20	94.31
17	0	0	0	6	1	55	94.12	94.31
18	0	0	0	6	1	55	94.42	94.31
19	0	0	0	6	1	55	94.04	94.31
20	0	0	0	6	1	55	94.50	94.31

The model equation that correlates the response (yield of the oil to FAME) to the transesterification process variables in terms of actual value after excluding the insignificant terms was given below. The predicted model for percentage of FAME content (FAME %) in terms of the coded factors is shown in Equation 4.16 below:

$$\begin{aligned} \text{FAME}(\%) = {} & -319.89143 + 25.49371 * M + 57.80377 * C + 9.98467 * T \\ & -0.95667 * M * C - 3.50000E-003 * M * T - 0.32500 * C * T \\ & -1.65021 * M^2 - 12.24350 * C^2 - 0.082413 * T^2 \end{aligned} \quad 4.16$$

where, M = molar ratio of methanol to oil

C = weight of catalyst amount

T = reaction temperature

The statistical analysis of the ANOVA is given in Tables 4.9. The multiple regression coefficients were obtained by employing a least square technique to predict quadratic polynomial model for the fatty acid methyl ester content (Table 4.10). Hence, the best fitting model was determined. The model was selected based on the highest order polynomial where the additional terms were significant and the model was not aliased as suggested by the DOE software.

The coefficients of the response surface model, as provided by the above quadratic model equation, were also evaluated. From the ANOVA of response surface quadratic model for FAME conversion, the Model F-value of 62.72 and Prob > F of <0.0001 implied that the model was significant. For the model terms, values of Prob>F less than 0.05 indicated that the model terms were significant. In this case M, C, T, M^2, C^2, and $T^2$are significant model terms (all have Prob > F less than 0.050). This tells us that the methanol ratio, catalyst, temperature, and the quadratic terms affect the yield much significantly. However, the interaction terms were found to be insignificant. Because values greater than 0.1000 indicate the model terms were, therefore, insignificant (Table 4.9).

Table 4.9 Analysis of variance (ANOVA) for response surface quadratic model for alkali transesterification

Sum of			**Mean**	**F**	**p-value**	
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	6209.33	9	689.93	62.72	< 0.0001	significant
M	*2535.68*	*1*	*2535.68*	*230.53*	*< 0.0001*	
C	*321.36*	*1*	*321.36*	*29.22*	*0.0003*	
T	*112.20*	*1*	*112.20*	*10.20*	*0.0096*	
MC	*16.47*	*1*	*16.47*	*1.50*	*0.2491*	
MT	*0.022*	*1*	*0.022*	*2.005E-003*	*0.9652*	
CT	*5.28*	*1*	*5.28*	*0.48*	*0.5041*	
M^2	*3178.82*	*1*	*3178.82*	*288.99*	*< 0.0001*	
C^2	*135.02*	*1*	*135.02*	*12.27*	*0.0057*	
T^2	*61.17*	*1*	*61.17*	*5.56*	*0.0401*	
Residual	110.00	10	11.00			
Lack of Fit	*109.79*	*3*	*21.96*	*535.17*	*< 0.0001*	
Pure Error	*0.21*	*3*	*0.041*			
Cor Total	6319.33	15				

As can be seen from p-values of the model coefficients, the value of the methanol to oil molar ratio in both linear and quadratic is much less than 0.0001. This indicated that molar ratio is the most significant in determining the model than rest. Similarly, the quadratic temperature term is less significant when compared to its linear term. However, in order to minimize error, all of the coefficients were considered in the design. The low lack of fit from the ANOVA analysis indicated that the model does indeed represent the actual relationships of reaction parameters, which are well within the selected ranges (Table 4.9*).* The Lack of Fit F-value of 3 implies its insignificance relative to the pure error. Non-significant lack of fit is good because we want the model to fit.

Table 4.10 Regression coefficients and significance of response surface quadratic model for the base catalyzed transesterification

Factor	Coefficient Estimate		Standard Error	95% CI		
		df		Low	High	VIF
Intercept	94.31	1	1.35	91.30	97.33	
M	13.63	1	0.90	11.63	15.63	1.00
C	4.85	1	0.90	2.85	6.85	1.00
T	2.87	1	0.90	0.87	4.87	1.00
MC	-1.43	1	1.17	-4.05	1.18	1.00
MT	-0.052	1	1.17	-2.67	2.56	1.00
CT	-0.81	1	1.17	-3.43	1.80	1.00
M^2	-14.85	1	0.87	-16.80	-12.91	1.02
C^2	-3.06	1	0.87	-5.01	-1.11	1.02
T^2	-2.06	1	0.87	-4.01	-0.11	1.02

Table 4.11 Sequential Model Sum of Squares and Model Summary Statistics of the response quadratic model for alkli catalyzed transesterification

Source	Sum of squares	df	Mean square	Std. Dev.	R^2	Adj. R^2	Pred. R^2	F value	P-value Prob>F	press
Mean	1.302E+005	1	1.302E+005							
Linear	2969.25	3	989.75	14.47	0.4699	0.3705	0.1568	4.73	0.0151	5328.58
2FI	21.78	3	7.26	16.00	0.4733	0.2302	-0.3181	0.028	0.9932	8329.42
Quadratic	3218.31	3	1072.77	3.32	**0.9826**	**0.9669**	0.8616	97.53	<0.0001	874.71
Cubic	80.99	4	20.25	2.20	0.9954	0.9855	-0.0048	4.19	0.0489	6349.56
Residual	29.01	6	4.83							
Total	1.65E+005	20	6824.18							

The quality of the model developed was evaluated based on the correlation coefficient value, R^2. The $\mathbf{R^2}$ value for Equation 4.16 was **0.9826**. This indicated that 98.26% of the total variation in the biodiesel yield was attributed to the experimental variables studied. The closer the $\mathbf{R^2}$ value to unity, the better the model will be as it will give predicted values which are closer to the actual values for the response. From the ANOVA and regression analysis on Table 4.9 and Table 4.10, respectively it can be seen that the linear terms of M,

C and T, the quadratic term M^2, C^2,and T^2 were significant (because Prob > F less than 0.05), but the the interactions (cross products) MC, MT, and BC were insignificant.

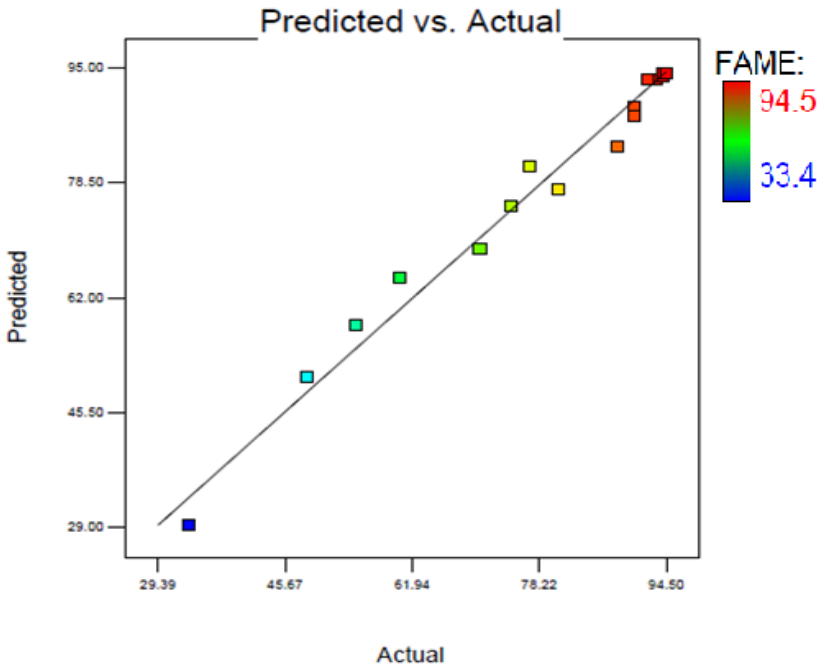


Figure 4.2 Yield Plot for the observed and predicted of FAME yield

The graph of the predicted values obtained using the developed correlation versus actual values is shown in Figure 4.2. The plot contains a line of unit slope (i.e. the line of perfect fit) with points corresponding to zero error between predicted values and actual. This plot therefore clarifies the performance of the correlation in an evident way. Hence, the regression model equation granted a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit. This outcome indicates that it was successful in creating the correlation between the three process variables to the FAME.

4.2.2.3 Effect of process parameters

Based on the analysis of variance, the transesterification reaction was significantly affected by various interactions between the process variables. This result demonstrated the advantage of using design of experiments in capturing the interaction between variables that affects the transesterification reaction. The effect could be due to the independent

variable alone or due to their interaction. The individual and interaction effects of the variables are well discussed below:

Effect of individual parameter on biodiesel yield

Figure 4.3 shows the effect of individual reaction parameters on the FAME yield.

Effect of methanol-to-oil molar ratio

The methanol-to-oil ratio is one of the important factors that affect the conversion of triglyceride to FAME. Stoichiometrically, three moles of methanol are required for each mole of triglyceride, but in practice, a higher molar ratio is required in order to drive the reaction towards completion and produce more FAME as products. The results obtained in this study are in agreement with this. As shown in Figure 4.3-a, the methanol-to-oil ratio showed positive influence to the yield of methyl ester, but the yield started to decrease as the ratio much increased. The increase is due to the positive sign in the experimental model. The decrease in the yield contrary to increase in molar ratio may be due to the separation problem resulted from excessive methanol. Higher ratio of methanol used could also minimize the contact of access triglyceride molecules on the catalyst's active sites which could decrease the catalyst activity.

Effect of catalyst concentration

From Figure 4.3- b, it was observed that the catalyst concentration influenced the biodiesel yield in a positive manner up to a certain concentration. Beyond this concentration, the biodiesel yield decreased with increase in potassium hydroxide concentration. When the catalyst mount was improved, the interactive (active) site of the catalyst was increased; thus, the transesterification reaction was accelerated and biodiesel yield was increased.

Effect of temperature

Temperature increase clearly influences the reaction rate and biodiesel yield in a positive manner. The temperature increase affected the biodiesel yield in a positive manner till 60°C and after that it decreased (Figure 4.3-c). The increase in the yield of FAME at higher reaction temperature is due to higher rate of reaction. From the experimental model

analysis the p-value of the temperature term was nearer to the p-value limit. Hence, its effect on the biodiesel is almost constant.

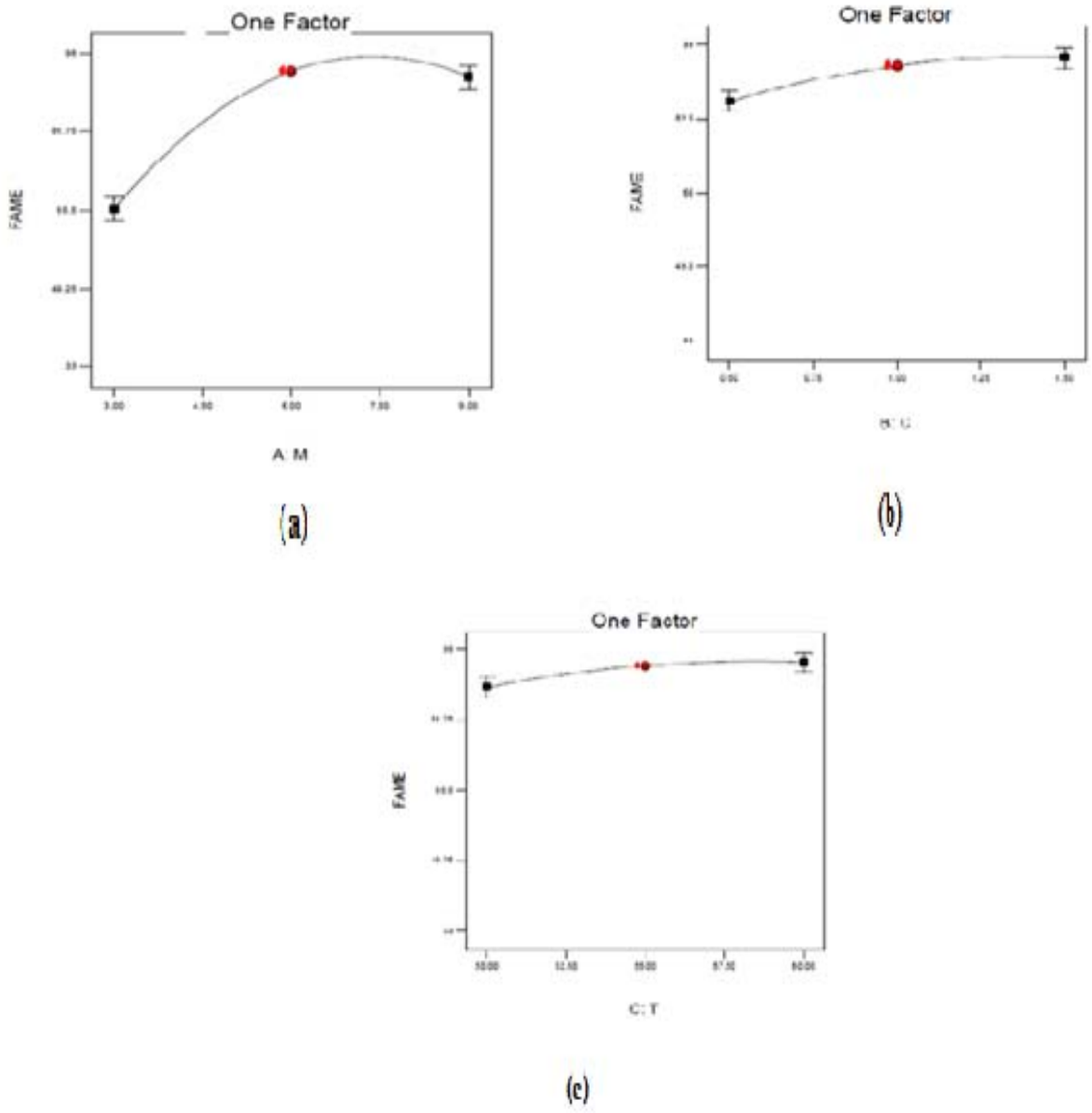
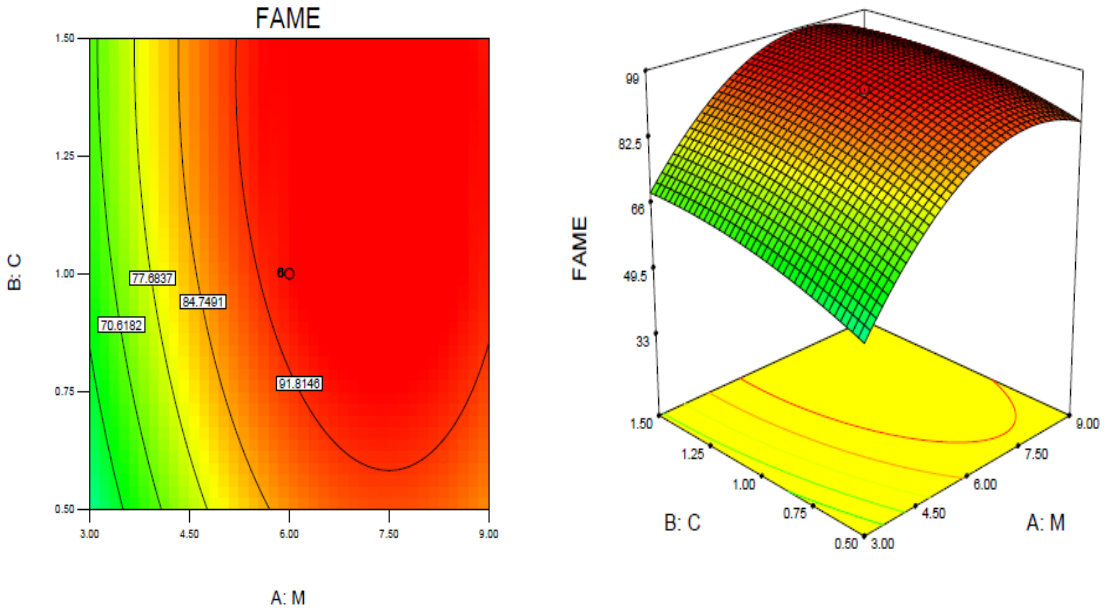


Figure 4.3 The individual effect of (a) ratio methanol to oil, (b) weight of catalyst, and (c) reaction temperature towards methyl ester yield

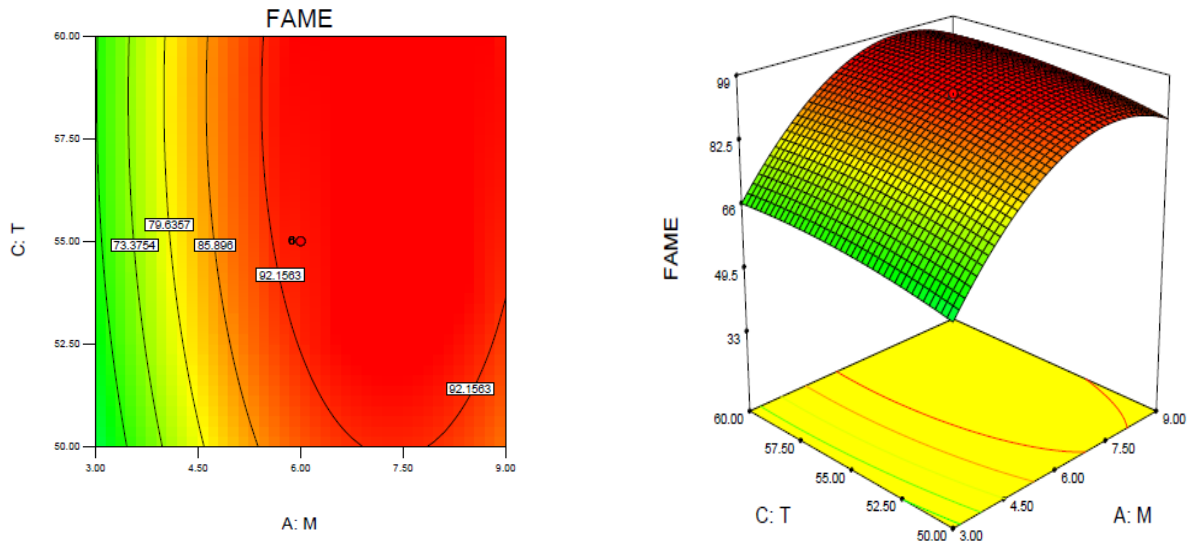
Effect of interactive parameters on biodiesel yield

Contour plots (Figure 4.4 a-c) were drawn to show the relationships between dependent and independent variables of the developed model. Each contour curve presented the effect of two variables on the methyl ester yield, holding the third variable at constant level. The third variable is held at zero level. However, the interaction factor also must be considered as the individual effect plot does not give information regarding the significant interaction involved.

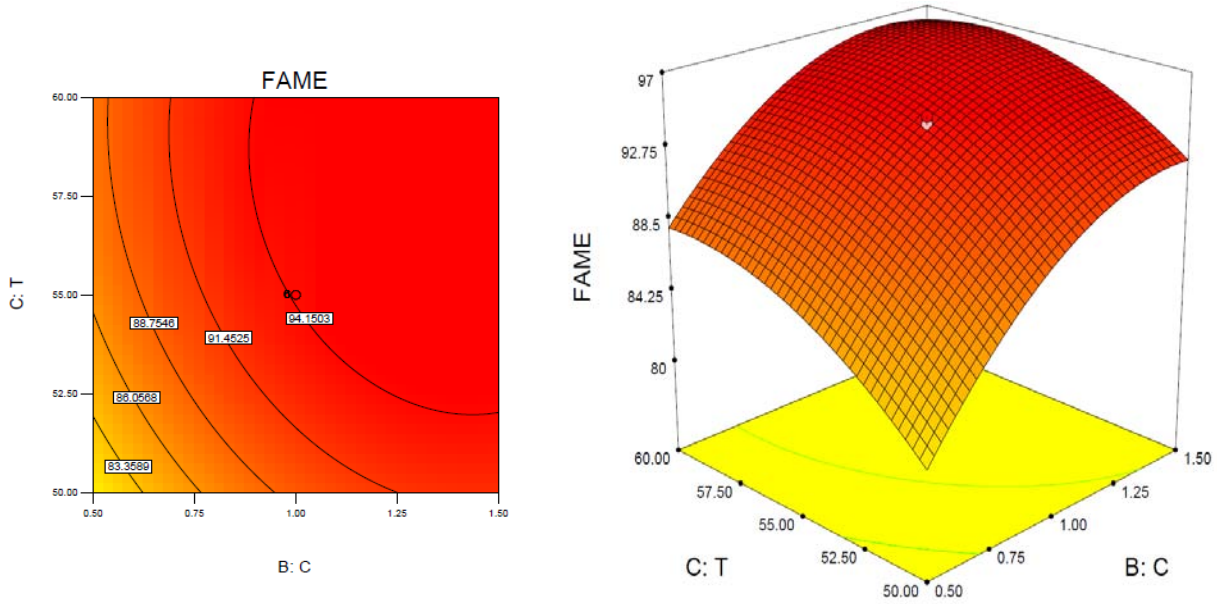
Remarkable interaction between the independent variables could be observed if the contour plots had an elliptical profile. The relationship between independent and dependent variables of the developed model in the response surface plots at the stationary value of 6:1 methaol-to-oil molar ratio, 1% catalyst concentration and 55^0C reaction temperature, is shown in Figure 4.4.



(a) Methanol to oil ratio vs catalyst amunt when reaction temperature is at 55^0C



(b) Methanol –to-oil ratio vs Reaction time when the catalyst weight is 1%.



(c) Catalyst amount vs reaction time when the molar ratio is 6:1.

Figure 4.4wws Contour and response surface Plot of FAME yield (%) in terms of coded factors: the Effect of Methanol/Oil Molar Ratio and Catalyst Concentration (a), methanol/Oil molar ratio and reaction tempertaure (b) reaction Temparature and Catalyst Concentration (c), on Methyl Ester Production

From Equation 4.16, it was clearly shown that all the linear terms had positive coefficients, whereas the quadratic terms and the interaction terms had negative coefficients. Therefore, an increase in temperature, KOH catalyst and methanol to oil molar ratio to a certain extent could result in a higher %FAME. However, a reduction in the %FAME could be obtained when using too high KOH catalyst , temperature and methanol to oil molar ratio.

Figure 4.4-a showed the strong interaction between methanol/oil molar ratio (M) , and KOH catalyst concentration (C). This can also be confirmed by the high p-values of the interaction paranaters. It could also be seen from Figure 4.4-a that the FAME yield increased with increasing catalyst concentration at first. However, when the catalyst concentration reached a certain level, the reverse trend was observed. The similar pattern was followed when increasing methanol/oil molar ratio.

This could be due to the fact that the positive coefficient for the linear paramaters (M,C, and T) played the main role when the KOH catalyst concentration and methanol/oil molar ratio were at lower level, while at higher level,the interaction terms and the quadratic terms showed more significant negative effect, leading to the decrease of the yield. This was consistent with the physical explanation.

Since the methanol and triglyceride in the oil are immiscible, addition of catalyst can facilitate the transesterification reaction, and rapidly increase the yield. However, when the catalyst concentration was too high, soap could be quickly formed which made the separation of glycerol from biodiesel more difficult, thus reducing the yield.

Similarly, the increase of the methanol amount, on one hand, will drive the reaction to the right since the transesterification reaction is an equilibrium process; on the other hand, excess methanol will help increase the solubility of glycerol resulting in the reaction driven to the left, thus decreasing the yield.

Figure 4.4-b showed the effect of methaol/oil ratio and the reaction temperture when the level of catalyst concentration was fixed. At low methanol to oil ratio, %FAME increased with reaction temprature increase. Also, the FAME yield increase with increased molr ratio certain level.

Figure 4.4-c showed the effect of reaction temperture and catalyst concentration on the methyl ester yield when the level of methanol/oil molar ratio was fixed. At a certain level of catalyst concentration, the increase in reaction temprature T increase the methyl ester yield. An explanation to this has been attributed to the fact that at a higher intial temprature helps in faster settlement of glycerol (Gupta et al., 2007). However, the temprature increase affected the FAME yield in a positive manner un til 60^0C. After that the effect was negtaive. This could be explained by the higher p-value nearly high p-value and the negative coffecint for the reactive and quadratic term in the model, indicating the non-significant effect.

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

Using the optimization function in Design Expert, it was predicted that at the following conditions; 6:1 methanol to oil molar ratio, 1% catalyst concentration and 55 ^{0}C of reaction temperature an optimum FAME yield of 94.5% can be obtained. In order to verify this prediction, experiments were conducted and the results were comparable with the prediction. It was found that the experimental value of 94.31% of FAME content agreed well with the predicted value.

From the response surface and contour plots, the optimum levels of three variables were found to be 0.26 v/v methanol-to-oil ratio, 1% H_2SO_4 concentration and 2 h reaction time. The model predicted the maximum percentage of fatty acid methyl ester content of 94.5%.

Therefore, this study shows that a two-step acid base catalyzed process is a perfect chioce of biodiesel production from wado seed oil.

4.3 Physicochemical Properties of Biodiesel

Table 4.12 Physicochemical properties of the FAME produced by base transesterification from WSO

Run	M	C	T	% FAME	Phsicochemical properties								
					ρ Kgm^{-3}	μ (mm^2s^{-1})	AV (mgKOHg-1)	SV (mgKOHg-1)	HHV (MJ/kg)	IV ($gI_2(100g)^{-1}$)	CN	FP (°C)	CP (°C)
1	3	0.5	50	48.50	888	5.55	0.602					179	8
2	3	0.5	60	54.74	888	6.0	0.552					180	7
3	3	1.5	50	60.32	860	4.6	0.4023					184	8
4	3	1.5	60	70.60	870	4.96	0.601					182	7
5	9	0.5	50	77.03	870	5.46	0.583					188	7
6	9	0.5	60	90.35	882	4.64	0.464					190	6
7	9	1.5	50	90.40	880	5.48	0.596					190	8
8	9	1.5	60	93.18	886	4.51	0.402					188	7
9	1.0	1	55	33.40	874	4.92	0.682					178	7
10	11.1	1	55	74.60	870	5.56	o.543					196	7
11	6	0.2	55	77.50	880	5.95	0.414					183	8
12	6	1.8	55	94.00	874	5.95	0.384					193	8
13	6	1	46.6	88.24	890	7.2	0.533					186	8
14	6	1	63.4	92.12	859	3.9	0.451					196	6
15	6	1	55	94.01	880	3.9	0.225	185	41.01	55.67	36.74	194	7
16	6	1	55	94.20	887	4.2	0.323	201	39.86	88.6	71.46	198	6
17	6	1	55	94.12	880	3.8	0.296	197	40.1	88.4	54.12	196	6
18	6	1	55	94.42	870	4.1	0.301	179	40.82	84.73	57.73	200	6
19	6	1	55	94.04	870	4.6	0.262	193	40.6	61.13	60.83	196	5
20	6	1	55	94.50	880	4.4	0.294	186	40.42	92.27	54.88	195	5

The procedures described in section 4.1.4.1 to section 4.1.4.6 were used to determine the specific gravity (SG), kinematic viscosity (KV), acid number (AV), Saponification value (SV), and calorific value (HHV) and Iodine value (AV) of the biodiesel, respectively. The cetane number (CN) was calculated using empirical formula which relates SV and IV to CN.

The flash point (FP) of the biodiesel was determined using open cup method as described in section 3.5.8. The cloud point (CP) of biodiesel was determined using ASTM D2500 as mentioned in section 3.5.9.

Table 4.12, lists the physico-chemical properties of the biodiesel determined by titration and empirical formulas. The details of each are discussed below.

4.3.1 Specific gravity

The SG of the biodiesel was found in the range values between 0.85-0.9. The density of the biodiesel produced, therefore, was measured and values were found to be in the range 850-900kg/m3. When average of the results are compared with the ASTM D6751, which is 870–890 kg/m3 for biodiesel, the value is acceptable.

The change in the density shows that the density of the biodiesel decreased with increasing molar ratio. This was probably due to a decrease in residual triglycerides. The density of the biodiesel decreased with increasing reaction temperature. The influence of the catalyst amount on the density of the FAME shows a decrease as the catalyst amount increased.

4.3.2 Viscosity

The viscosities of the biodiesel produced at lower temperature are higher than that of the corresponding experiments conducted with the same feed ratio but at higher temperature. This is due to effects of the operating parameters that affect the transesterification reaction. On the other hand, the viscosity of the biodiesel increased slightly with increase in reaction temperature.

The increase in molar ratio decreases the viscosity to some extent. This is probably because of the free area created for the triglycerides to convert to biodiesel as the molar ratio

increased. But, as the molar ratio increases it inhabits the contact between the triglycerides and the catalyst. Hence no change in viscosity is observed when excess molar ratio was used. Viscosity decreased up to optimal catalyst concentration then it was almost constant.

4.3.3 Acid Value

The Acid value of the biodiesel produced was found to be 0.225-0.682 mgKOH/g. The result indicates that acid value of the diesel decreased significantly after transesterification reaction. Furthermore, higher acid value resulted in low yield of biodiesel.

Acid value affects storage ability of biodiesel. Contact with air and water is the major factors affecting storage stability. Oxidation is usually accompanied by an increase in the acid value and viscosity of the fuel. In the presence of water the ester can hydrolyze to long-chain FFA, which also causes the acid value to increase.

4.3.4 Higher heating value

The heating value depends on the composition of the fuel. Since all the oils have very nearly the same carbon, hydrogen and oxygen contents the gross and net heating values of each fuel per unit mass will be close to each other. Biodiesel has lower energy content (lower heating value) than conventional diesel fuel.

4.3.5 Iodine value

All of the measured IVs fall in the En14124 standard (Table 4.13). Higher IV indicates a higher quantity of double bonds in the sample and greater potential to polymerize in engine and hence lesser stability. The process transesterification reduces the iodine value to a small extent.

4.3.6 Cetane number

The cetane number (CN) was determined using empirical formula developed by Kalayasiri et al., (1996). The empirical formula used to determine the CN was:

$$CN = 46.3 + \left(\frac{54.58}{SV}\right) - 0.225(IV) \qquad 4.18$$

CN of 6 selected samples based on their higher % FAME was determined. The results showed that most of them have increased the CN within the permissible minimum limit.

4.3.7 Flash Point

The flash point was measured as indicated in section 3.5.8. The values are ranged from 179 to 200^{0}C (Table 4.12). Hence, the flash point of the WSO biodiesel lies within the permissible range.

4.3.7 Cloud Point

The CP is determined by visually checking for a haze occurrence in the normally clear fuel, while the fuel is cooled under carefully controlled conditions. Cloud Point data obtained on Table 4.12 shows a relatively high value. This predicts the cold temperature limit at which start-up or performance problems may be expected to occur.

Table 4.13 Comparison of fuel properties with ASTMD6751 and EN14214 standards

	WSO Biodiesel		
Properties	**Values**	**ASTM D6751**	**EN14214**
Density at 25°C (kg m^{-3})	870		860-900
Kinematic viscosity at 40°C (mm^2 s^{-1})	3.8	1.9-6.00	3.5-5.0
Flash point (°C)	200	130 min	>101
Cloud point (°C)	5		
Heating value (MJ kg-1)	41.01	*	
Cetane number	71.46	47 min	51 min *
Acid value (mg KOH g-1)	0.225	0.5 max	0.5 max
Iodine value (I2 g 100 g-1)	78.47		120 max

*where, *min* = minimum; *max* = maximum

Most of the fuel properties of the WSO methyl ester tested compare well with ASTM D6751 EN14214 standards as shown in Table 4.13. Among the general parameters, kinematic viscosity and density are key fuel properties for diesel engines. According to ASTM standard, for biodiesel to be used in diesel engines the kinematic viscosity must be between 1.9 and 6.0mm^2s^{-1} and according to EN-14214 standard, the density must fall between 860 and 900 Kgm^{-3}. The comparison showed that the WSO biodiesel could be used as an alternative to diesel.

The physicochemical studies and the comparisons made with revealed that transesterification improved the important fuel properties tested. As expected, the methyl ester of WSO has relatively closer fuel properties to petroleum diesel than the WSO.

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

In this research, a two-step acid-alkali catalyzed method was used in the synthesis of biodiesel from wado seed oil. The process parameters affecting the acid value and yield of FAME conversion has been studied and the statistical and experimental design was done by using design expert 7.0.0 software. The outputs of the experiments conducted have been analyzed by employing physicochemical parameter determination.

- In the first step, the effects of the methanol-to-oil molar ratio, catalyst concentration, and reaction time were investigated to determine the best strategy for producing biodiesel from WSO. Based on the experimental results, it was found that all the process variables exhibited significant interaction effect on the reduction of acid value of the WSO. The optimized critical values were found to be 0.25 v/v methanol-to-oil molar ratio, 1% v/v H_2SO_4 concentration and 2 h reaction time. Accordingly, the acid value was able to reduce to 2.1 mg KOH/g.

- It second step, the effects of molar ratio, catalyst concentration and reaction temperature was observed. The ester yield, generally, increased with increased molar ratio, catalyst concentration and reaction temperature. Methanol to oil molar ratio and catalyst amount has played an important role in improving the FAME yield. The best result was obtained at a catalyst concentration of 1.0%, molar ratio 6:1 and reaction temperature of 55°C, respectively, while the reaction was complete at about 1hr.

- The ester yield obtained from the two-step transesterification process ranged from 33.40 to 94.5%. The yield is strongly dependent on the product of the pretreatment step (Esterification).

- The fuel properties tested are within the ASTM and EN norms and were found to be very close to those of petroleum diesel. The results showed that transesterification improved the important fuel properties tested. The calorific value of the WSO biodiesel is slightly lower than that of diesel but has a higher calculated cetane number. The density and the viscosity were indicators of the biodiesel quality against the process variables. Higher iodine value indicates a higher quantity of double bonds in the sample and greater potential to polymerize in engine and hence lesser stability. Generally, the FAME of WSO has relatively closer fuel properties to petroleum diesel than the oil.

5.2 Recommendation

The present study has enabled us to confirm that WSO may be used as a resource to obtain biodiesel, which could offer more opportunities for generation of rural employment and increasing income. However, further research and development on additional fuel property using HPLC or GC analysis, blending conditions, engine performance and emission tests and techno-economic analysis are necessary.

Moreover, in order to reduce the cost of reagents the concept of recycle is important. Therefore, the catalysts and also the excess alcohol should be reused.

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APPENDIX

Appendix A: Composition of Wado Seed Oil

Table A1: Fatty Acid Composition of wado seed oil

Fatty Acid	Systemic Name	Formula	Structure	Wt %
Palmitic acid	Hexadecanoic	$C_{16}H_{32}O_2$	16:0	6.52 -8.12
Stearic acid	Octadecanoic	$C_{18}H_{36}O_2$	18:0	28.65 -30.94
Oleic acid	Cis-9-Octadecenoic	$C_{18}H_{34}O_2$	18:1	54.99 -57.72
Linoleic acid	Cis-9,cis-12-octadecadienoic	$C_{18}H_{32}O_2$	18:2	6.18 -7.79
Linolenic acid	Cis-6,cis-9,cis-12-octadecatrienoic	$C_{18}H_{30}O_2$	18:3	0.65 -0.90

Source**:** Okullo et al., 2010

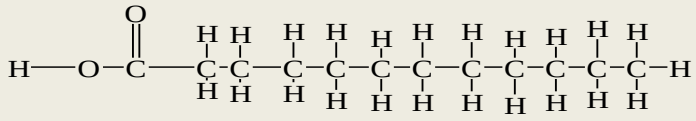
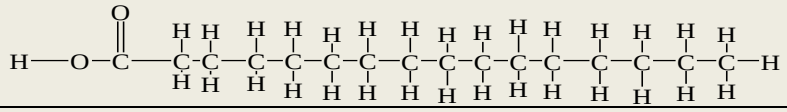
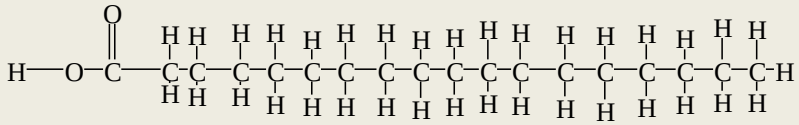
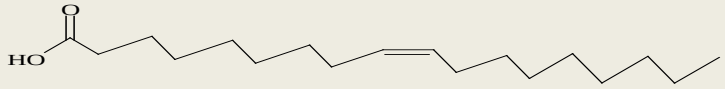
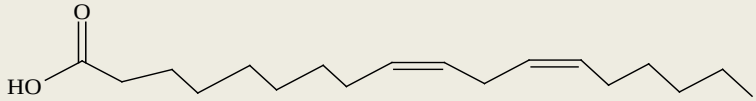
Table A2: Properties of different oils

	Fatty acid composition (wt %)															
Vegetable oil	12:0	14:0	14:1	16:0	16:1	18:0	20:0	20:1	22:0	24:0	18:1	22:1	18:2	18:3	18:4	6:0, 8:0, 10:0 and others
Cottonseed	-	0	-	28	-	1	0	-	0	0	13	0	58	0	-	-
Tobacco	-	0.09	-	10.96	0.2	3.34	-	-	-	-	14.54	-	69.49	0.69	-	0.69
Rapeseed	-	0	-	3	-	1	0	-	0	0	64	0	22	8	-	-
Safflower	-	0	-	9	-	2	0	-	0	0	12	0	78	0	-	-
Sunflower	-	0	-	6	-	3	0	-	0	0	17	0	74	0	-	-
Sesame	-	0	-	13	-	4	0	-	0	0	53	0	30	0	-	-
Lindseed	-	0	-	5	-	3	0	-	0	0	20	0	18	55	-	-
Palm tree	-		-	35	-	7	-	-	-	-	44	-	14	-	-	-
Corn	-	0	-	12	-	2	Tr	-	0	0	25	0	6	Tr	-	-
Tallow	-	-	-	23.3	0.1	19.3	-	-	-	-	42.4	-	2.9	0.9	2.9	-
Soya bean	-	-	-	14	-	4	-	-	-	-	24	-	52	-	6	-
Peanut	-	0	-	11	-	2	1	-	2	1	48	0	32	1	-	-
Coconut	48.8	19.9	-	7.8	0.1	3.0	-	-	-		4.4	-	0.8	0	65.7	8,9, 6,2
Yellow grease		0.70	0.00	14.26	1.43	8.23	0.33	0.48	-	-	43.34	-	26.25	2.51	0.47	-

Vegetable oil	Kinematic viscosity at 38°C (mm2/s)	Cetane No. (°C)	Heating Value (MJ/kg)	Cloud Point (°C)	Pour Point (°C)	Flash Point (°C)	Density (kg/l)	Carbon residue (wt %)
Corn	34.9	37.6	39.5	-1.1	-40	277	0.9095	0.24
Cottonseed	33.5	41.8	39.5	1.7	-15	234	0.9148	0.24
Crambe	53.6	44.6	40.5	10.0	-12.2	274	0.9048	0.23
Linseed	27.2	34.6	39.2	1.7	-15.0	241	0.9236	0.22
Peanut	39.6	41.8	39.8	12.8	-6.7	271	0.9026	0.24
Rapeseed	37.0	37.6	39.7	-3.9	-31.7	246	0.9115	0.30
Safflower	31.3	41.3	39.5	18.3	-6.7	260	0.9144	0.25
Sesame	35.5	40.2	39.3	-3.9	-9.4	260	0.9133	0.24
Soya bean	32.6	37.9	39.6	-3.9	-12.2	254	0.9138	0.25
Sunflower	33.9	37.1	39.6	7.2	-15.0	274	0.9161	0.27
Palm	39.6	42.0	-	31.0	-	267	0.9180	0.23
Babassu	30.3	38.0	-	20.0	-	150	0.9460	-
Diesel	3.06	50	43.8	-	-16	76	0.855	-

Source: S.P. Singh, Dipti Singh, Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review, Renewable and Sustainable Energy Reviews 14 (2010), 200-216.

Table A3: Description of the main fatty acid contents of vegetable oils (Tyson, 2006).

SATURATED			
Fatty acid	STRUCTURAL FORMULA	Symbol	Molecular formula
Lauric acid		C12:0	$C_{12}H_{24}O_2$
Palmitic acid		C16:0	$C_{16}H_{32}O_2$
Stearic acid		C18:0	$C_{18}H_{36}O_2$
UN SATURATED			
Oleic acid		C18:1	$C_{18}H_{34}O_2$
Linoleic acid		C18:2	$C_{18}H_{32}O_2$

Appendix B: Standard Specifications of Biodiesel

Table B1: Standard Specifications of Biodiesel: USA and European

Property	Unit	USA	EU	Recommended Test method
		ASTM D 6751	EN 14214	
Density, 150C	Kg/m3	-	860 -900	ASTM D 445
Kinematic viscosity, 40oC	mm2/s	1.9 -6.0	3.5 -5.0	
Flash point	oC	≥ 120	≥ 130	ASTM D 93
Cloud point	oC	-	-	
Total sulphur 100%	w%	≤ 0.05	≤ 0.01	ASTM D 5453
Sulphated Ash	w%	≤ 0.02	≤ 0.02	ASTM D 874
Water content	mg/Kg	-	≤ 500	
Total contamination	mg/Kg	-	≤ 24	
Water and sediment	% vol.	≤0.05		ASTM D 2709
Corrosion (Cu) @50oC		≤ No.3	class 1	ASTM D 130
Cetane number	Mg	≥ 47	≥ 51	ASTM D 613
Acid number	KOH/g	≤ 0.8	≤ 0.5	ASTM D 664
Oxidation			≥ 6	
Stability 110oC	hours			
Methanol content	%w%		≤ 0.2	
Ester content	%w%		≥ 96.5	
Triglycerides	%w%		≤ 0.20	
Diglycerides	%w%		≤ 0.80	
Monoglycerides	%w%			
Free glycerol	%w%	≤ 0.02	≤ 0.02	ASTM D 6584
Total glycerol	%w%	≤ 0.24	≤ 0.25	ASTM D 6584
Iodine value	$gI_2/100g$		≤ 120	
Phosphorus	mg/Kg	≤ 10	≤ 10	ASTM D 4951

Source: Adopted from (Biodiesel industries Australia, 2003)

Table B2: Specification of EN 14214 comparing biodiesel to conventional diesel

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

Table B3: Physico-Chemical Properties of Biodiesel from Different oil raw material

Feed stock	Kinematic Viscosity (at 40°C)	Density (g/cm^3)	Saponification number	Iodine value	Acid value (mg KOH/g)	Cetane Number	Heating value (MJ/kg)
soybean	4.08	0.885	201	138.7	0.15	52	40
rapeseed	4.3-5.83	0.88-0.888			0.25-0.45	49-50	45
sunflower	4.9	0.88	200	142.7	0.24	49	45.3
Palm	4.42	0.86-0.9	207	60.07	0.08	62	34
peanut	4.42	0.883	200	67.45		54	40.1
Corn	3.39	0.88-0.89	202	120.3		58-59	45
Camelina	6.12-7	0.882-0.88		152-157	0.08-0.52		
Canola	3.53	0.88-0.9	182	103.8		56	45
Cotton	4.07	0.875	204	104.7	0.16	54	45
pumpkin	4.41	0.8837	202	115	0.48		38
jatropha curcas	4.78	0.8636	202	108.4	0.496	61-63	40-42
Pongamina pinnata	4.8	0.883			0.62	60-63	42
Sea mango							
Palanga	3.99	0.869					41
Tallow		0.856	244.5	126	0.65	59	
Nile tilapia				88.1	1.4	51	
poultry		0.867	251.23	130	0.25	61	
used cooking oil	4				0.15		

Appendix C: Experimental Result

Table C1: Viscosity of wado seed oil

Dynamic viscosity (mpa.sec) at 40^{o}C					Dynamic Viscosity Avg.	Density (kg/m$^{3)}$	Kinematic viscosity, (mm2/sec)
39.4	41.6	40.9	42.3	42.8	41.4	980	42.2

Table C2: Saponification value of WSO

Run	N_{HCL}	V_{bHCL}	V_{aHCL}	V_b-V_a	mass of Oil (g)	SV (mgKOH/g)
1	0.46	45.2	29.4	15.8	2	204.00
2	0.46	43.9	28	15.9	2	205.1577
3	0.46	31.9	16	15.9	2	202.842
						204.00

Table C3: Acid Value of WSO

N_{KOH}	V_{KOH} (ml)	mass of oil (g)	AV	FFA Composition
0.085	13.21	5	12.5984	6.2992
0.085	13.45	5	12.8273	6.41365
0.085	12.98	5	12.3743	6.18715
			12.6	6.3

Table C4: Calibration of bomb calorimeter

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

Table C5: Heating Value of WSO

m' min	Δn	Δv	F	c	t_o	t_m	t_m+c-t_o	Unburnt wire	Sum of b	HHV cal/g	HHV MJ/kg
9	3.5E-07	0.012	1.25	0.0150	1.53	5.75	4.25	4	15	9448.744	39.56

Table C6: Acid value for different process variable of the esterification process

Run	Actual factors			Acid value (mg KOH/g)	
	Methanol to oil ratio	Catalyst to oil ratio	Reaction Temperature	Actual value	Predicted value
1	0.2	0.5	1	11.4	10.22546
2	0.2	0.5	3	5.74	4.239548
3	0.2	1.5	1	12.1	14.53533
4	0.2	1.5	3	13.4	10.56942
5	0.3	0.5	1	5.88	6.008812
6	0.3	0.5	3	3.1	2.962905
7	0.3	1.5	1	7.07	5.868687
8	0.3	1.5	3	6.37	5.868687
9	0.17	1	2	8.39	4.84278
10	0.33	1	2	3.2	11.88607
11	0.25	0.16	2	3.5	3.524799
12	0.25	1.84	2	5,47	3.792966
13	0.25	1	0.32	8.7	8.997906
14	0.25	1	3.68	2.1	2.05854
15	0.25	1	2	2.84	4.362331
16	0.25	1	2	2.71	2.694074
17	0.25	1	2	3.11	2.694074
18	0.25	1	2	2.61	2.694074
19	0.25	1	2	2.63	2.694074
20	0.25	1	2	2.92	2.694074

Table C7: Physico-chemical properties of the treated (Esterified) wado seed oil

Physico-chemical properties	Unit	Value
Density	Kg/m3	910
Viscosity (400C)	mm2s-1	38.97
Acid value	mgKOH/g	2.1
FFA	%	1.05
HHV	MJ/kg	39.05
Melting Point	0C	38.8

Table C8: Fatty Acid methyl ester (Biodiesel) composition for different processes variables

Run	Actual Factors			% FAME	
	M	C	T	Actual value	Predicted value
1	3	0.5	50	48.50	50.70
2	3	0.5	60	54.74	58.16
3	3	1.5	50	60.32	64.89
4	3	1.5	60	70.60	69.11
5	9	0.5	50	77.03	80.92
6	9	0.5	60	90.35	88.18
7	9	1.5	50	90.40	89.38
8	9	1.5	60	93.18	93.38
9	0.954622	1	55	33.40	29.39
10	11.04538	1	55	74.60	75.22
11	6	0.159104	55	77.50	75.20
12	6	1.840896	55	94.00	93.81
13	6	1	46.59104	88.24	83.66
14	6	1	63.40896	92.12	93.10
15	6	1	55	94.01	94.31
16	6	1	55	94.20	94.31
17	6	1	55	94.12	94.31
18	6	1	55	94.42	94.31
19	6	1	55	94.04	94.31
20	6	1	55	94.50	94.31

Table C9: Physicochemical properties of the FAME produced by base transesterification from WSO

Run	M	C	T	% FAME	Phsicochemical properties								
					ρ Kgm^{-3}	μ (mm^2s^{-1})	AV (mgKOHg-1)	SV (mgKOHg-1)	HHV (MJ/kg)	IV $(gI_2(100g)^{-1})$	CN	FP (^{0}C)	CP (^{0}C)
1	3	0.5	50	48.50	888	5.55	0.602					179	8
2	3	0.5	60	54.74	888	6.0	0.552					180	7
3	3	1.5	50	60.32	860	4.6	0.4023					184	8
4	3	1.5	60	70.60	870	4.96	0.601					182	7
5	9	0.5	50	77.03	870	5.46	0.583					188	7
6	9	0.5	60	90.35	882	4.64	0.464					190	6
7	9	1.5	50	90.40	880	5.48	0.596					190	8
8	9	1.5	60	93.18	886	4.51	0.402					188	7
9	1.0	1	55	33.40	874	4.92	0.682					178	7
10	11.1	1	55	74.60	870	5.56	o.543					196	7
11	6	0.2	55	77.50	880	5.95	0.414					183	8
12	6	1.8	55	94.00	874	5.95	0.384					193	8
13	6	1	46.6	88.24	890	7.2	0.533					186	8
14	6	1	63.4	92.12	859	3.9	0.451					196	6
15	6	1	55	94.01	880	3.9	0.225	185	41.01	55.67	36.74	194	7
16	6	1	55	94.20	887	4.2	0.323	201	39.86	88.6	71.46	198	6
17	6	1	55	94.12	880	3.8	0.296	197	40.1	88.4	54.12	196	6
18	6	1	55	94.42	870	4.1	0.301	179	40.82	84.73	57.73	200	6
19	6	1	55	94.04	870	4.6	0.262	193	40.6	61.13	60.83	196	5
20	6	1	55	94.50	880	4.4	0.294	186	40.42	92.27	54.88	195	5