JIMMA UNIVERSITY

JIMMA INSTITUTE OF TECHNOLOGY

FACULTY OF CIVIL AND ENVIROMENTAL ENGINEERING

ENVIROMENTAL ENGINEERING CHAIR

BIODIESEL PRODUCTION FROM BLENDS OF WASTE COOKING OIL AND CONSORTIUM OF MICROALGAE

BY

DEJENEBEKELEBEDADA

A THESIS SUBMITTED TOENVIRONMENTAL ENGINEERING CHAIR, FACULTY
OF CIVIL AND ENVIRONMENTAL ENGINEERING, JIMMA INSTITUTE OF TECH
NOLOGY, JIMMA UNIVERSITY IN PARTIAL FULFILLMENTS
 FOR THE REQUIREMENTS OF THE DEGREE OF MASTERS OF SCIENCE
 IN ENVIRONMENTAL ENGINEERING

March, 2018

Jimma, Ethiopia

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Mainadvisor:DejeneBeyene (PhD)

Co-advisor: DidaAbera(PhDCandidate)

March, 2018

Jimma, Ethiopia

DECLARATION

I, Dejene Bekele, hereby declare that the thesis work, entitled "biodiesel production from blends of used waste cooking oil and consortium micro algae" is entirely my original work done for the award of Master of Science (MSc) degree in Environmental Engineering by the Jimma University. To the best of my knowledge, the work has not been presented for the award of MSc. degree or any other degree either in Jimma University or any other Universities. Thorough acknowledgment has been given where reference has been made to the work of others.

Submitted by:

Name _____ Signature _____ Date _____

Approval by advisors:

This Thesis has been submitted for examination with my approval as University supervisor.

Approval by mainadvisors:

Name: _____ Signature_____Date _____

Approval by co-advisor:

Name_____Signature _____Date _____

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Name_____ signature _____Date_____

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Internal Examiner

Name_____ signature _____Date_____

External Examiner

Name_____ signature _____Date_____

APPROVAL SHEET

Jimma University Jimma Institute of Technology, Faculty of Civil and Environmental Engineering. Environmental Engineering Chair Name of the Student: Dejene Bekele Bedada. Program of Study: MSc. in Environmental Engineering.

Title: biodiesel production from blends of used waste cooking oil and consortium micro algae. I declare that the proposed research work has not been done anywhere else before or is not part of any ongoing work. We have agreed to supervise the proposed research work.

We have evaluated the contents of the research, found to be satisfactory, complete, and according to the standards and formats of the University. We have also verified that the work has not been done anywhere else before.

Submitted by   Dejene Bekele   _____   _____
                       Researcher   Signature   Date

Major Advisor:DejeneBeyene (PhD)`_____   _____
                  Name   Signature   Date

Co-Adviser: Dida Abera (PhD Candidate)_____   _____
                  Name   Signature   Date

Decision/suggestion of Department Graduate Council

 _____   _____   _____
 Chairperson DGC   Signature   Date

ACKNOWLEDGMENTS

ABSTRACT

Biodiesel as an alternative fuel for diesel engines is becoming increasingly important due to depleting petroleum reserves and the environmental consequences of exhaust gases (co_2, nitrogen and sulfur oxides) from Petroleum fuelled engines. The main environmental advantages of biodiesel are its sustainability in using as renewable fuel thus promoting independence from fossil fuel and maintaining the level of greenhouse gas (CO_2) in the atmosphere. As a future prospective fuel, biodiesel has to compete economically with petroleum diesel fuels. Diverting food crops to fuel production may result in high food prices as it will significantly reduce the areas available for food production and remove forested lands to increase land for the production of energy crops that will have negative impact on biodiversity by devoting large tracts of land for monoc ular cultivation.The objective of this study was to investigate the production of biodiesel from blends of waste cooking oil and algal biomass using methanol with alkali as catalyst. Pretreated waste cooking oil was mixed with crude oil extracted from algal bio-mass at the ratio of 1, 2 and 3 to obtain the desired biodiesel. Optimum temperature, alcohol to molar ratio, waste cooking oil to microalgae ratio and catalyst concentration on Tran's esterification process (biodiesel production) was investigated during experimental process. Physiochemical properties of biodiesel obtained from blends of waste cooking oil and algal biomass were determined. A total of 31.6 % of oil was extracted from fresh algae through the soxhlet apparatus as motioned in material and method. Four factors at three levels were considered in the alkali catalytic transesterfication process. The fuel properties tested are ASTM and EN standards and we are found to be very close to those of petroleum diesel. Study on fuel property using HPLC or GC analysis, blending conditions, engine performance and emission tests and techno economic analysis should be carried out in future studies. Waste cooking oil and algae to biogas production of biodiesel from microalgae to use as substitute of petroleum fuel and mitigate environmental pollutions caused by fossil fuel consumption.

Key words*: Cooking Oil,Emission, fossil fuel, Microalgae Biodiesel, transesterification*

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ACRONYMS

ANOVA	Analysis of Variance
AV	Acid Value
ASTM	American Society for Testing and Materials
B100	Biodiesel 100 %
C/H	Carbon hydrogen ratio
Cao	Calcium oxide
CN	Cetan number
CO	Carbon monoxide
CO_2	Carbon dioxide
CRD	Completely Randomize Design
EPA	Environmental pollution Assessments
EN	European Committee for Standardization
ETBE	Ethyl tertiary butyl ether
FAME	Fatty acids methyl esters
FFA	Free fatty acid
GC-MS	Gas chromatography-mass spectrometry
H_2SO_4	Sulfuric Acid
IPCC	Intergovernmental panel on climate change
JiT	Jimma institute of Technology
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
NO_2	Nitrogen oxides
NOx	Nitrous oxide
O_3	Ozone
PH	Power Hydrogen
Rpm	Revolution per minute
RS	Rectified Spirit
SPSS	Statistical Package for Social Studies
SSF	Simultaneous Scarification and Fermentation
WCO	Waste cooking oil

CHAPTER ONE

INTRODUCTION

1 .1 Background of the study

Biodiesel, short from for "biological oil", is one of the alternative fuels that are produced from renewable resources. Specifically, it is a mono alkyl ester produced from vegetable oil, canola oil, soybean oil or animal fats. One pressing issue faced by the modern societies is to develop renewable energy for trans- partition. The energy crisis due to depletion of global oil reserve, increased consumption rate, incessant oil price hike and growing concerns over climate change (emission of Greenhouse Gases) are all driving the global community to hunt for alternative and sustainable energy sources. One of the efforts considered in response to the energy crisis is finding substitute for petroleum oil. Non-fossil fuel alternatives are favored because of their common availability, renewability, sustainability, bio degrablability, job creation, regional development and reduced environmental impacts (Barnwal and Sharma, 2005).

Biodiesel, defined as the mono-alkyl esters of vegetable oils or animal fats, is an environmentally attractive alternative to conventional petroleum diesel fuel (petro-diesel). Produced by trans- esterification with a mono hydric alcohol, usually methanol, biodiesel has many important technical advantages over petro-diesel such as inherent lubricity, low toxicity, derivation from a renewable and domestic feedstock, superior flash point and biodegradability, negligible sulfur content and lower exhaust emissions. It can be used in a 100 per cent pure fuel formulation or as a blended component with petroleum derived diesel. The most common blend is called B20, which is 20 per cent biodiesel and 80 per cent petroleum diesel. Essentially, no engine modifications are required, and biodiesel maintains the payload capacity and range of petroleum-derived diesel (Nation Biodiesel Board, 2006).

Biodiesel production has generated heated debate of energy security for food crisis. This debate has changed the direction of biodiesel research into the use of non-edible oil sources referred to as second generation biodiesel feedstock such as Jatropha oil, Pongamia oil, Rapeseed Oil, Mahua oil, Olive oil, Rice Bran oil, Linseed oil, Soya bean oil, Palm oil,

Cotton seed oil, Beef Tallow, Lard, Guang-Pietc and others which are easily available in developing countries and are very economical comparable to edible oils.

Biomass of non-edible oil plants are well adapted to low fertility and moisture demand to grow, as well as no competition with human food, so that waste cooking after oil expelling may be used as fertilizer for soil enrichment .However, the yield and properties of biodiesel products produced from different feedstock would be quite different from each other, so that choosing a right feedstock and optimum extraction methods through experimental verification was strongly needed.(Khandelwal et *al*.,2012).

In many research publications, biodiesel is produced from the refined edible oil using methanol and alkaline catalysts. Alkaline hydroxides are the most effective transesterification catalysts as compared to acid catalysts. However, the problem with alkaline catalyzed trans-esterification of vegetable oils is possible only if the acid value of oil is less than four. High percentage of free fatty acid in the oil reduces the yield of esterification process; such oils are mainly used for making low cost soap. Therefore, it is considerably more costly to separate the catalyst from the produced monoesters(Kefyalew *et al*., 2016).

One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids. The availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial determinant delivering a competitive biodiesel price. Thus, nonedible oil sources are preferred as feed stock for the production of biodiesel. The use of non-edible oils as alternative feedstock is picking up as the demand for biodiesel is expected to increase sharply in the near future. Currently, only very few non edible sources of biodiesel are known compared to the number of non-edible oily plant species identified, so that exploration of cheap and non-edible sources of biodiesel such as frying oil can help to increase the production and use of biodiesel in the developing countries particularly in Ethiopia since this plant affects and invaded many ecosystems and communities in Ethiopia.Therefore, the present work utilized waste cooking oil and algae oil as a catalyst and methanol was used for the production of biodiesel. The effect of different process parameters (temperature, waste cooking and algae oil ratio, alcohol to oil molar ratio, and catalyst concentration) were investigated and characterization of the extracted oil and produced biodiesel was conducted (Kefyalew *et al*., 2016).

1.1.1 Advantages and Disadvantages of Biodiesel

1.1.1.2 Advantages

Biodiesel has attracted considerable interest as an alternative fuel or extender for petro-diesel for combustion in compression ignition (diesel) engines. Biodiesel is miscible with petro-diesel in any proportion and possesses several technical advantages over ultra-low sulfur diesel fuel such as the following (National Biodiesel Board, 1998).

- Renewable fuel, obtained from vegetable oils or animal fats
- Low toxicity, in comparison with diesel fuel
- Lower emissions of contaminants: carbon monoxide, particulate matter, polycyclic aromatic hydrocarbons, aldehydes
- Lower health risk, due to reduced emissions of carcinogenic substances
- No sulfur dioxide (SO_2) emissions
- Higher flash point (100 $^\circ$C minimum), leading to safer handling and storage

1.1.1.3 Disadvantages of Biodiesel

- It is the only alternative fuel that can be used in a conventional diesel engine, without modifications disadvantages
- Used cooking oils and fat residues from meat processing may be used as raw materials
- There are certain disadvantages of using biodiesel as a replacement for diesel fuel that must be taken into consideration. However, these disadvantages are significantly reduced when biodiesel is used in blends with diesel fuel (Knothe, 1997).
- Slightly higher fuel consumption due to the lower calorific value of biodiesel
- Slightly higher nitrous oxide (NOx) emissions than diesel fuel
- Inferior low-temperature operability versus petro-diesel
- High feed stock cost
- It is less stable than diesel fuel and therefore long-term storage (more than six months) of biodiesel is not recommended.

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1.2 Statement of the Problem

Continued use of petroleum sourced fuels is now widely recognized as unsustainable because of depleting supplies and the contribution of these fuels to the accumulation of carbon dioxide in the environment. Renewable, carbon neutral, transport fuels are necessary for environmental and economic sustainability. Biodiesel derived from oil crops is a potential renewable and carbon neutral alternative to petroleum fuels. Unfortunately, biodiesel from oil crops and animal fat cannot realistically satisfy even a small fraction of the existing demand for transport fuels. In this regard, microalgae appear to be the source of renewable biodiesel that is capable of meeting the global demand for transport fuels. Like plants, microalgae use sun light to produce oils but they do so more efficiently than plants. Oil productivity of many microalgae greatly exceeds the oil productivity of the best oil producing crops(Demirbas, 2003).

In addition, the price of biodiesel is much higher compare to conventional diesel makes it is less chosen by the customer. The main reason of high prices in production of biodiesel is because of its raw material. The availability, cost and continuity are the main criteria for a good raw material. Thus, using waste cooking oil as raw material will make the biodiesel price more comparable. The easy availability of waste cooking oil and continuity of supply make it as a good choice of raw material. Thus, the aim of this study was to produce biodiesel from blends of consortium of microalgae and waste cooking oils as substitute of petrol diesel which satisfy the criteria of economic competitive, availability, non-food feeds tock and continuity (Demirbas, 2003).

This is very important to face the frequent oil supply crises, as a way to help non-fossil fuel producer countries including Ethiopia to reduce imported energy dependence, contributing to security of supply and promoting environmental sustainability. Diverting food crops to fuel production may result in high food prices as it will significantly reduce the areas available for food production. Another concerned that the removal of forested lands for increase agriculture land for the production of energy crops will have negative impact on biodiversity by devoting large tracts of land for mono-culture cultivation The excessive consumption of fossil fuels, particularly in large urban areas, has greatly contributed to generation of high levels of pollution .

1.3 Objectives of the study

1.3.1 General objective

The general objective of this study is to investigate the production of biodiesel from blends of waste cooking oil and algal biomass using methanol with alkali catalyst.

1.3.2 Specific Objectives

1. To extract crude oil from consortium of micro algal biomass.

2. To determine optimum temperature, alcohol-to-oil molar ratio, waste cooking oil to microalgae ratio and catalyst concentration on trans esterification process (biodiesel production)

3. To determine the physicochemical properties of biodiesel obtained from blends of waste cooking oil and algae biomass such as acid value, saponification number, density, kinematic viscosity, iodine value, free fatty acid, flash point and cetin number.

1.4 Research Questions

1. How crude oil is extracted from microalgae?
2. What are the effects of temperature, alcohol-to-oil molar ratio, waste cooking oil to microalgae ratio and catalyst concentration on Tran's esterification process?
3. What are physicochemical properties of biodiesel obtained from blends of waste cooking oil and micro algal?

1.5 Significance of the Study

This study has great significance in terms of assuring the production of an alternative form of energy that is environmentally friendly from algal biomass which is a non-edible and can be abundantly cultivated and grow on lands not suitable for higher plants, using waste waters discharged from industries and households.

1.6 Scope of the Study

To determine optimum temperature, alcohol-to-oil molar ratio, waste cooking oil to microalgae ratio and catalyst concentration on trans esterification process (biodiesel production)and physicochemical properties of biodiesel obtained from blends of waste cooking oil and algae biomass.

CHAPTER TWO

LITRATURE REVIEW

2.1 Biodiesel

One pressing issue facing the modern societies is to develop renewable energy for transportation. The energy crisis due to depletion of global oil reserve, increased consumption rate, incessant oil price hike and growing concerns over climate change (emission of greenhouse gases) are all driving the global community to hunt for alternative and sustainable energy sources. One of the efforts considered in response to the energy crisis is finding substitute for petroleum oil that can integrate with existing infrastructure. The use of vegetable oil as a fuel source in diesel engines is as old as the diesel engine itself. However, the demand to develop and utilize plant oils and animal fats as biodiesel fuels has been limited until recently. Biodiesel, defined as the mono-alkyl esters of vegetable oils or animal fats, is an environmentally attractive alternative to conventional petroleum diesel fuel (petro-diesel). The technical definition of biodiesel is: "the mono alkyl esters of long fatty acids derived from renewable lipid feedstock such as vegetable oils or animal fats, for use in compression ignition (diesel) engines" (National Biodiesel Board, 1996).

Produced by trans-esterification with a monohydric alcohol, usually methanol, biodiesel has many important technical advantages over petro-diesel such as inherent lubricity, low toxicity, derivation from a renewable and domestic feedstock, superior flash point and biodegradability, negligible sulfur content and lower exhaust emissions. The term "biodiesel" itself is often misrepresented and misused. Biodiesel only refers to 100% pure fuel (B100) that meets the above definition and specific standards given by the American Society of Testing and Materials. However, it is often used to describe blends of biodiesel with petroleum diesel. Such blends are generally referred to as "B2," "B5," "B20," etc., where the number indicates the percent of biodiesel in the petro-diesel and biodiesel mixture. The most common method to produce biodiesel is through a process called "trans esterification," which involves altering the chemical properties of the oil by using methanol. Transesterfication of

plant oils with methanol is a relatively simple process that yields high conversions with only glycerin as a byproduct (Fangrui and Hanna, 1998).

2.2 Feed stocks for biodiesel Production

Biodiesel can be produced from a great variety of feeds tocks. Different types of fats and oils have been used in different countries as the raw material for biodiesel production, depending on availability, regional climate, geographical location and local soil conditions. These feeds tocks include algae, most common vegetable oils (e.g., soybean, cottonseed, palm ,peanut, rapeseed/canola, sunflower, safflower, coconut) and animal fats as well as waste oils (e.g., used frying oils).In general, biodiesel can be made from any oil/lipid source (Murugesan *et al*., 2009).

2.2.1Oilseed crops (rapeseed, soybean and sunflower)

First generation biodiesel refers to transportation fuel already established in fuel markets. They are usually produced from food crops such as rape seed, sunflower, soybean and palm oil. The first group is pure oils derived from various crops and plants such as soybean, canola (rapeseed), corn, cottonseed, flax, sunflower, peanut and palm. These are the most widely used feed stocks by commercial biodiesel producers. The oil composition from oil crops is pure which cuts down on preprocessing steps and makes for a more consistent quality of biodiesel product. However, there is an obvious disadvantage for oil crops as the biodiesel feedstock: Wide-scale production of crops for biodiesel feedstock can cause an increase in worldwide food and commodity prices (Klass, 1998).

Figure 2.1: Soybeans, Sunflower and peanut as feedstock of biodiesel (adapted from: Klass, 1998)

Besides its lower cost, another undeniable advantage of non-edible oils for biodiesel production lies in the fact that no foodstuffs are spent to produce fuel (Schwab *et al*., 1987).These and other reasons have led to medium and large-scale biodiesel production trials in several countries, using non-edible oils such as castor oil, tung, cotton, jojoba and jatropha.

Desirable characteristics of alternative oilseed feed stocks or biodiesel production include adaptability to local growing conditions (rainfall, soil type, latitude, etc.),regional availability, high oil content, favorable fatty acid composition, compatibility with existing farm infrastructure, low agricultural inputs (water, fertilizer, pesticides), definable growth season, uniform seed maturation rates, potential markets for agricultural by-products and the ability to grow in agriculturally undesirable lands and/or in the off-season from conventional commodity crops. Biodiesel fuels prepared from feed stocks that meet at least a majority of the above criteria will hold the most promise as alternatives to petro-diesel (Schwab *et al*., 1987).

Figure 2.2: Fruit of palm oil tree (left) and coconut (right) (adapted from: Schwab et al., 1987).

Rapeseeds are characterized by high contents of monounsaturated oleic acid and low levels of both saturated and polyunsaturated acids. Therefore, rapeseed oil is an ideal raw material regarding combustion characteristics, oxidative stability and cold temperature behavior.

Figure 2.3: Rape in flower (left) and rape seeds (right) (adapted from: Klass, 1998).

There exist many other potential oil crops that can be used for biodiesel production including Cotton (Gossypium hirsutum), mustard (Brassica nigra, Sinapis Alba, Brassica carinata), castor (Ricinus communis), gold-of-pleasure or false flax (Camelina sativa), Linseed (Linum usitatissimum), Tigernut (Cyperus esculents) and Cardoon (Cynara cardunculus).

Figure 2.4: Potential oil crops for biodiesel production) (adapted from: Kumar et al., 2003).

There, it is estimated that the potential availability of non-edible oils amounts to about one million tons per year including Sal oil, Mahua oil, neem oil and karanja oil as the most

abundant oil sources. These oil sources from non-edible plants are of special interest due to not directly concurring with vegetable oil for human food use and due to the fact that many plants can be grown in arid to semi-arid regions poorly suited for food crops. Non-edible oilseeds are not currently utilized on a large scale, but such oils can be an important component of local economies (Kumar *et al*., 2003).

2.2.2 Animal Fats as feedstock for the production of biodiesel

Animal fats are also an interesting option especially in countries with plenty of livestock resources such as Ethiopia Animal fats may include materials from a variety of domesticated animals, such as cows, chickens, pigs and other animals such as fish and insects. Animal fats are normally characterized by a greater percentage of saturated fatty acids in comparison to oils obtained from the plant and algae. Animal fats are generally considered as waste products, so they are normally less expensive than commodity vegetable oils, which make the attractive as feed stocks for biodiesel production. The problem with these sources is the discontinuity of supply. Naturally, all animal fat is only a co-product and therefore is often restricted as it has not been produced primarily for a biodiesel production program. Never the less all these animal fats are characterized by high amounts of saturated fatty acids resulting in methyl esters with poor cold temperature properties, limiting widespread application of this type of fuel, particularly for winter-time use (Wen *et al*., 2003).

But the high degree of saturation makes animal fat methyl esters excellent fuels regarding heating value and cetan number. The ethical aspect of using animal parts for transport fuel may lead to public indignation. Due to these problems, the use of animal fats is not expected to contribute largely to biodiesel production in the future.

2.2.3 Microalgae as feedstock for biodiesel production

Microalgae are microscopic single-cell aquatic organisms with the potential to produce large quantities of lipids (oils) that are well suited for use in biodiesel production. Microalgae cultivation is the first step in the production of biodiesel. At present, there are two main systems of cultivating microalgae: "open pond system and close photo bioreactors system". In open-pond systems, there is no control of water temperature and lighting conditions, algae are invaded by other algal species and bacteria and growing season dependents on the

climatic location and limits to the warmer months. The open-pond systems have low costs and the high production capacity (Demirbas, 2008).

Figure 2.5: The pond microalgae production plant (adapted from: Demirbas, 2008).

The second possibility of cultivating algae is in a close photo bioreactor system, a pond system which offers a close environment to culture microalgae with technological equipment covered by a greenhouse. These systems allow the cultivation of more species which are protected from other species from outside, smaller mainly for economic reasons and extend the growing season. Algae can be also grown in a photo bioreactor (tanks with a light source, polyethylene sleeves or bags and glass or plastic tubes) which incorporates some type of light source. In a closed system, everything the algae need to grow (CO_2, nutrients, water, light) must be introduced into the system (Demirbas, 2008).

The use of microalgae can be a suitable alternative because algae are the most efficient biological producer of oil and a versatile biomass source and may soon be one of the most important renewable fuel sources due to the higher photosynthetic efficiency, higher biomass productivities, a faster growth rate than higher plants (which is also important in the screening step), highest CO_2 fixation (provides greenhouse gas mitigation benefits) and O_2 production, grow in liquid medium which can be handled easily, can be grown in variable climates and non-arable land including marginal areas unsuitable for agricultural purposes (e.g., desert and seashore lands thereby not competing with food production), in non-potable water or even in a waste treatment, use far less water than traditional crops and do not

displace food crop cultures; their production is not seasonal and can be harvested daily (Demirbas, 2008).

Figure 2.6: Close photo bioreactor system of microalgae cultivation (adapted from: (Chisti, 2007).

Most productive oil crops, such as oil palm, do not come close to microalgae in being able to sustainably provide the necessary amounts of biodiesel (Chisti, 2007). Compared with oilseeds, the harvesting and transportation costs of microalgae are relatively low. Depending on the species, microalgae can accumulate up to 60% oil Perry weight under stress conditions. Therefore, microalgae have attracted increasing attention for their potential as producers of biodiesel or other lipid-based biofuels (Beer, *et al*., 2009; Scott *et al*., 2010; Wijffels and Barbosa, 2010).

2.3 Waste Cooking Oil (WCO)

There is a large variety of waste oils originate from households and restaurants, food and non-food industries available for biodiesel production. Repeated frying for preparation of food makes the edible vegetable oil no longer suitable for consumption due to high free fatty acid (FFA) content. These waste oils are inexpensive and have many disposal problems like water and soil pollution, human health concern and disturbance to the aquatic ecosystem, so rather than disposing it and harming the environment, it can be used as an effective and cost efficient feedstock for Biodiesel production. However, recycled oils have many impurities that require preprocessing to ensure a biodiesel product of consistent quality. Preprocessing also makes the biodiesel production process more complicated and costly (Canakci and Van Gerpen, 2001).
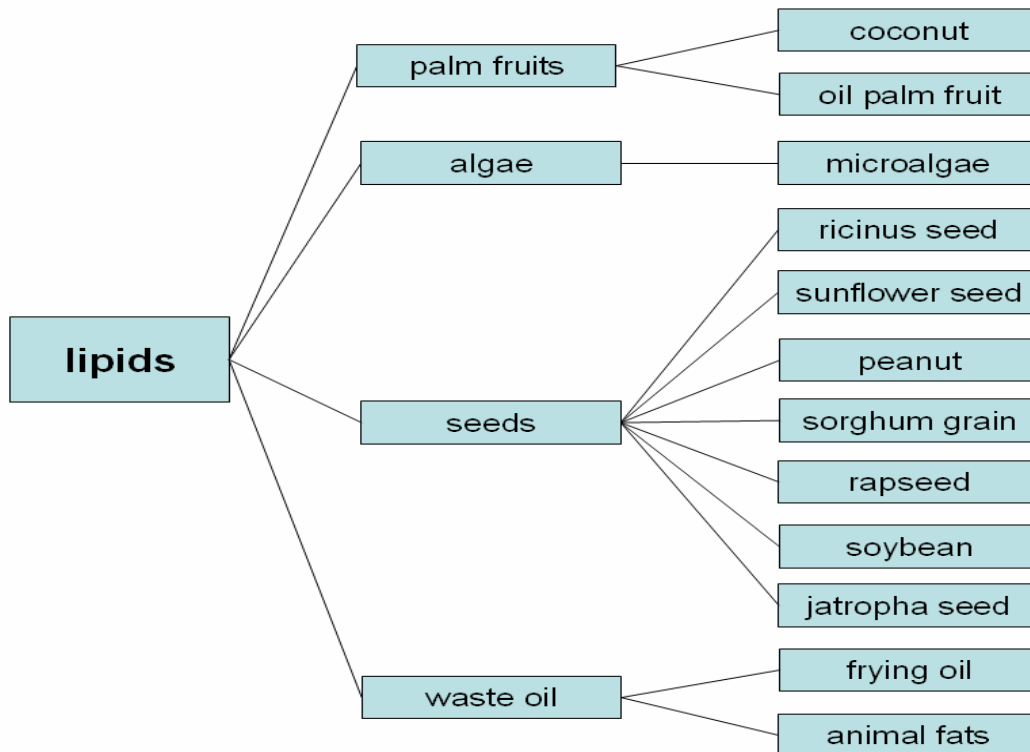
Figure 2.7: Types and classification of lipid feedstock for biodiesel production(adapted from: Canakci and Van Gerpen, 2001).

2.3.1 Alcohols Used in the Production of Biodiesel

Although trans-esterification can be done with higher or secondary alcohols, methanol and ethanol are the most commonly used alcohols in the preparation of biodiesel.

Figure 2.8: The transesterfication reaction equation (adapted from: Freedman et al., 1984)

Trans-esterification with methanol also called methanolysis is the most common method for biodiesel production. Methanol is characterized by its lower prices and its higher reactivity as compared to other alcohols. This reaction can happen by heating a mixture of 80- 90 percent oil, 10 - 20 percent methanol and small amounts of a catalyst (Freedman *et al.*, 1984).

2.4 Catalysts for Biodiesel Production

Although the trans-esterification process proceeds in the absence of catalysts, there action is usually conducted by using catalysts due to economic reasons. Non-catalytic reaction is too slow and requires high energy inputs. The advantage of a non-catalytic trans-esterification process is the creation of purer esters and soap-free glycerin. The catalysts used for the trans-esterification of triglycerides may be classified as basic, acid or enzymatic. Basic catalysts include sodium hydroxide (NaOH), potassium hydroxide (KOH), carbonates and their corresponding alcoxides (e.g., sodium meth oxide or ethoxide).Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the most common alkaline catalysts. Biodiesel is produced using homogenous basic catalysts because the trans-esterification reaction is faster, less expensive and more complete than with acid catalysts (Boocock *et al.*, 1998).

Acid catalysts include sulfuric acid, sulfonic acids and hydrochloric acid. Several types of catalysts can be used:

- ♣ Alkaline material
- ♣ Acidic material
- ♣ Transition metal compounds
- ♣ Silicates
- ♣ Lipases

Acidic and alkaline catalysis can be divided between homogeneous and heterogeneous catalysis. Heterogeneous catalysts that have been considered for biodiesel production include enzymes, titanium silicates and compounds from alkaline earth metals, anion exchange resins and guanidine's in organic polymers (Dennis *et al.,* 2010).Lipases are the most frequently used enzymes for biodiesel production (Demirbas, 2008).

2.5 Biodiesel Production Processes

2.5.1 Extraction of Oil from Microalgae

The oil extraction of the feedstock is the first step of biodiesel production processes. After drying, the micro algal oil remains in the cell by the cell wall and cell membrane. The key point of oil extraction is to break the cell wall and cell membrane to let the oil released. Chemical cool press, enzymatic extraction and supercritical fluid extraction are the methods most commonly used to extract oil from microalgae (Aresta and Dibennedatto, 2005).

In the chemical cool press method, dried micro algal feeds tocks are directly pressed by mechanical machine with the addition of some chemical solvents to get micro algal oil. The function of chemical solvents (benzene, ether and hexane)is to dissolve algal cell wall in order to release oil from the cell. About 95% oil of the total oil content of algal cell may be released without using heat energy (Oilgae, 2013).

Enzymatic extraction uses an enzyme to dissolve the algae cell wall to extract oil. Catalyst and methanol are added into the dried microalgae to convert methyl esters, which is the main content of bio-diesel. Because lipid bond of oil exist in the methyl esters, oil is extracted from the methyl esters (Mendes *et al*., 2003).

In supercritical fluid method decreasing the temperature to supercritical temperature enables co-exist of both gas and liquid forms of CO_2. This supercritical fluid is permitted into microalgae cells as organic solvent to extract oil. The quality of algae oil can be maintained through supercritical fluid extraction process at the low temperature. This method has been used in a small scale oil extraction. However, because of high production cost, it hasn't been applied for the large scale biofuel production so far (Couto *et al*., 2010).

TheOil refining process is an important treatment for preparing algae oil for the Trans esterification process so that the final biodiesel complies with the desired specifications. Thus, the extracted crude oil is usually exposed degumming, filtration, neutralization and drying out in order to remove undesirable substances, such as phosphatides, free fatty acids, waxes, tocopherols and colorants. These substances can alter oil storage life and hamper further processing. During this first refining step the oil mass (4 - 8 %) and the solvent contents are reduced. Since the refining process depends on the oil quality, the refining steps depend on the feedstock source. There also exist alternatives of refining and some refining steps are merging (Bulletin, 2009).

The first purification step of oil refining is the removal of phosphatides also known as degumming. This is necessary as phosphatides make the oil turbid during storage and promote the accumulation of water. Phosphatides can be removed by two different ways: water degumming and acid degumming. Soluble phosphatides can be removed by water degumming. Thereby water is added to the oil at 60-90 °C and the mixture is separated by centrifugal separation of the water phase and the oil phase. Acid degumming is applied to phosphatides which cannot be hydrated. Acid substances like citric or phosphoric acid are added to effectively remove both soluble and insoluble phosphatides. The second refining step is the DE acidification. The content of these FFA's in unrefined pure oil is between 0.30 and 6 %. In this step also phenol, oxidized fatty compounds, heavy metals and phosphatides are removed. The purification of all these substances is important to fuel production as these compounds alter storage life and influence Tran's esterification process. Several methods of DE acidification are in operation (Bulletin, 2009).

♣ Neutralization with alkali: FFA's are saponified with alkaline solutions and the resulting soap is separated.

♣ Distillation: For this alternative more energy is needed.

♣ DE acidification by esterification: This is done by esterification of FFA's with glycerin

♣ De acidification and extraction of colorants and odors with various solvents: (z. B. ethanol, furfural, propane).

In the third step bleaching, colorants are removed using adsorbing substances, such as bleaching earth, silica gel or activated carbon to enhance storage life of the biodiesel. But also oxygen, ozone, hydrogen peroxide and heat (200 °C) can be used for bleaching. During the deodorization step odorous substances (ketone, aldehyde) are removed by steam distillation. Finally a dehydration step has to be conducted, as traces of water may decrease conversion in the transesterfication process of biodiesel production. The removal of water is either accomplished by distillation under reduced pressure or by passing a stream of nitrogen through the fatty material (Bulletin, 2009).

2.6 Multi-feed stock Biodiesel Blends

Mixed feedstock biodiesel production may be employed to provide biodiesel with improved physical properties in comparison to the individual fuels on their own. Mixed feedstock production may also arise as a result of economic considerations. For instance, it may be economically advantageous to extend the lifetime of a comparatively more expensive feed stock through blending with a less expensive feedstock. The influence of blending various feed stocks on biodiesel fuel properties has been conducted including blends of canola, palm, soybean and sunflower oil methyl esters (Moser, 2008a).

 blends of palm, rapeseed and soybean oil methyl esters(Park *et al*., 2008b), blends of jatropha and palm oil methyl esters (Sarin et al., 2007) and blends of cottonseed, soybean and castor oil methyl esters (Meneghetti et al., 2007). In the case of jatropha–palm blends, the objective was to obtain a biodiesel blend with superior low temperature performance to PME and superior oxidative stability to jatropha oil methyl esters. Specifically, the CFPP of PME was improved from 12°C to 3°C up on blending (20:80 by volume) with jatropha oil methyl esters(neat: 0°C Sarin et al., 2007). The oxidative stability of jatropha oil methyl esters was improved from 3 to 4 hours after blending with PME (Sarin *et al*., 2007).

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The objective of another study was to evaluate the kinematic viscosities, specific gravities and IV of biodiesel fuels obtained from binary mixtures (20and 80 vol.%) of castor, soybean, cotton and canola oil methyl esters in an effort to find combinations that were satisfactory according to biodiesel standard (Albuquerque, 2009).

2.7 Tran-esterification

Trans esterification also called alcoholics is the process by which the refined oil is "cracked" and the glycerin is removed, resulting in glycerin soap and methyl or ethyl esters (biodiesel).Trans esterification changes the molecular structure of lipid molecules; there by the physical properties change. Organic fats and oils are triglycerides which are three hydrocarbon chains connected by glycerol. Biodiesel is produced by trans-esterification of triglycerides which are the main ingredients of fats and oils in the presence of an alcohol (e.g., methanol or ethanol) and a catalyst (e.g., alkali, acid, enzyme) with glycerin as a major by-product (Dube *et al*., 2008).

The mixture separates and settles out leaving the glycerin on the bottom and the biodiesel (methyl-, ethyl ester) on the top. After the reaction, the glycerin is separated by settling or centrifuging and the layer obtained is purified prior to using it for its traditional applications (pharmaceutical, cosmetics and food industries) or for the recently developed applications (animal feed, carbon feedstock in fermentations, polymers, surfactants, intermediates and lubricants) (Vicente *et al*., 2007).

2.8 Factor Affecting the Yield of Biodiesel Production

2. 8.1. Effect of Methanol to Oil Ratio

The most effective variable affecting the methyl ester production yield during the transesterfication reaction is the molar ratio of alcohol to oil. Since transesterfication is an equilibrium reaction, a large excess of alcohol is required for the reaction to move forward and avoid the reversible reaction .The amount of alcohol added to vegetable oil is one of the important factors that affect conversion efficiency as well as production cost of biodiesel. The conversion efficiency is defined as the yield of the process represented in terms of percentage. Generally the amount of alcohol required for transesterfication reaction is analyzed in terms of volumetric ratio. Stoichiometriclly, the alcohol/ oil molar ratio is 3:1.

Higher amount of alcohol is required to drive the reaction to completion at faster rate. It is observed that lower amount of alcohol requires longer reaction periods. The conversion efficiency of transesterfication reaction with increasing amount of alcohol obtained (Bournay *et al*., 2005).

2.8.2 Effect of Reaction Temperature

Temperature values for the transesterfication reaction vary depending on the literature source. It is well known that higher temperatures speed up the reaction and shorten the reaction time. Apart from that, higher temperatures usually mean obtaining higher ester yields. However; It should also be noted that if the reaction temperature is higher than the boiling point of the alcohol, it will evaporate, resulting in a lower yield. It is also an accepted fact that usually the optimum temperatures for the trans esterification range between 60^0C and 75ºC, depending on the kind of oil to be processed In the case of algae and waste cooking oil, the optimum temperature value for its methanolysis has been found to be 68ºC(Rinaldi, 2009).

2.8.3 Effect of Catalyst Type and Amount

Catalyst concentration this parameter is highly affected by the kind of catalyst used, different catalysts will require different concentrations. Even if they belong to the same group (as in the case of potassium hydroxide and sodium hydroxide), different concentrations will be necessary to attain the same yields.Therefore, the optimum value for every catalyst to be determined by titration. If the amount of catalyst is higher than the optimum, there was a decrease in the yield of methyl esters due to the formation of soap in presence of high amount of catalysts, which apart from lowering the yield increases the viscosity of the reactants (Liu *et al.,* 2009)

2.8.4 Effects of Blending Biodiesel with Other Fuels

Biodiesel can be used as a blend component in petro diesel in any proportion because it is completely miscible with ultra-low sulfur diesel fuel. Biodiesel and petro-diesel are not chemically similar: biodiesel is composed of long-chain FAAE, whereas petro-diesel is a mixture of aliphatic and aromatic hydrocarbons that contain approximately 10 - 15 carbons. Because biodiesel and petro-diesel have differing chemical compositions, they have differing

fuel properties. Once mixed, the blend will exhibit properties different from neat biodiesel (B100) or petro-diesel fuels. The most important fuel properties influenced by blending of biodiesel with petro-diesel are lubricity, exhaust emissions, cetan number (CN), flash point, oxidative stability, low-temperature operability, kinematic viscosity and energy content. Lubricity of petro-diesel is positively impacted through blending with biodiesel (Goodrum and Gellar, 2005). Exhaust emissions of ultra-low sulfur diesel fuel, with the exception of NOx, are reduced through blending with biodiesel (Lapuerta *et al*., 2008).

The CN and flash point of petro-diesel are increase dup on blending with biodiesel .When blended with petro-diesel, biodiesel does not impact flash point up to B20, but beyondB20, the flash point increases significantly. The oxidative stability of petro-diesel is negatively impacted upon blending with biodiesel. This is because the hydrocarbon constituents of petro-diesel are more stable to oxidation than FAME (especially the unsaturated FAME).The low-temperature operability of petro-diesel is negatively impacted once blended with biodiesel. The kinematic viscosity of petro-diesel increases upon blending with biodiesel. Lastly, the heat of combustion (energy content) of petro-diesel is reduced upon blending with biodiesel (Mushrush *et al*., 2004).

2.9 Separation of Biodiesel Product

The separation process is one of the most crucial parts of biodiesel production. The product from the Trans esterification process is composed of FAME, glycerine, alcohol, catalyst and unreacted glycerides (free glycerin). Due to their different chemical affinities, most of the catalyst and excess alcohol will concentrate in the lower phase (glycerin), while most of the mono-, di- and triglycerides will concentrate in the upper phase (FAME).Once the interphase is clearly and completely defined, the two phases may be physically separated. Removing glycerin from biodiesel is important since it significantly affect the quality of biodiesel. Severe consequences may result due to the high content of free and total glycerin, such as buildup in fuel tanks, clogged fuel systems, injector fouling and valve deposits (Hayyan *et al*., 2010).

The by-product glycerin is separated from FAAE using a simple gravitational settling method and left for a certain period of time. The separation process using the settling or centrifugal tank was considered to be cost effective (Gomes *et al.* 2010). Biodiesel can also be separated

by centrifugation and membrane purification .Centrifugation techniques offer a faster separation process compared to traditional settling techniques, however the high operating cost becomes a major concern. Membrane purification is the latest technology that produces a high quality of biodiesel besides being energy efficient (Dube *et al*., 2008).

2.10 Purification of Biodiesel Product

After the separation of glycerin, the FAME mixture contains impurities such as remnants of alcohol, catalyst and mono-, di-, triglycerides and other by-products. These impurities confer undesirable characteristics to FAME such as increased cloud point and pour point, lower flash point, etc. Therefore, biodiesel must be purified before being used as a fuel in order to fulfill standard specifications; otherwise the methyl esters formed cannot be classified as biodiesel. Biodiesel purification methods can be classified into two categories: wet washing and dry washing technologies. Water becomes the most popular reagent in wet washing technologies since the by-products i.e. glycerin and methanol are highly soluble in water (Javidialesaadi *et al*., 2013).

Wet washing can be conducted in three different ways: (i) washing with deionized water, (ii) washing with acid and water and (iii) washing with an organic solvent and water. Water washing using deionized water is the most effective conventional method that has been used intensively in the biodiesel purification process. The process starts by adding a small portion of deionized water to the crude biodiesel and the solution is stirred gently to avoid the formation of emulsion. The washing cycle is repeated until color less wash water is obtained indicating that all the impurities have been removed. The main drawback of having water as the washing agent is the substantial generation of waste liquid effluent and this factor contributes to a higher cost for treatment and waste disposal. In addition, water washing also contributes to a significant loss in product yield, due to the retention of product in the water phase. Water washing techniques have been improved by the addition of acid in water solution. The presence of acid in aqueous solution could reduce the purification steps as it simultaneously neutralizes the basic constituent in the product, thus producing a better quality of biodiesel (Canakci and Van Gerpen, 2001).

An organic solvent commonly used in biodiesel purification is petroleum ether. This process is usually followed with hot water washing to remove residual soap and catalyst (Ma, 1998).The conventional wet separation technologies are being progressively replaced by more promising dry washing techniques using ion exchange resins, silicates, activated carbon, activated clay and activated fiber. The process has the advantages of being waterless, having strong affinity to polar compounds, being easy to integrate into the existing plant, having a significantly lower purification time, producing no wastewater and improving the biodiesel quality (Atadashi *et al*., 2011).

2.11 Characteristics of Biodiesel

Generally the characteristics of lipid derived fuels are much more variable than properties of bioethanol, due to its different conversion process and the wide variety of feedstock sources. Ethanol is actually one very specific molecule but, the molecules biodiesel vary, depending on the origin of the feedstock type. Nevertheless, biodiesel must meet certain properties and standards after refining and transesterfication respectively to be used as fuel. The properties of biodiesel can be grouped by multiple criteria. The most important are those that influence the processes taking place in the engine (ignition qualities, ease of starting, formation and burning of the fuel-air mixture, exhaust gas formation and quality and the heating value, etc.), low-temperature operability(cloud point, pour point and cold filter plugging point), transport and depositing (oxidative and hydrolytic stability, flash point, induction period, microbial contamination, filterability limit temperature, etc.), wear of engine parts (lubricity, cleaning effect, viscosity, compatibility with materials used to manufacture the fuel system, etc.) (Knothe, 1997).

Generally, the properties of biodiesel and especially its viscosity and ignition properties are similar to the properties of petro-diesel. Although the energy content per liter of biodiesel is about 5 - 12 % lower than that of diesel fuel, biodiesel has several advantages. The higher the cetan number, the easier the fuel ignites when it is injected into the engine. Biodiesel has a higher cetan number than petrol diesel because of its higher oxygen content. This means that engines run smoother and create less noise when running on Biodiesel. Hexadecane, also known as cetan (trivial name), is the high-quality reference standard with a short ignition delay time and an arbitrarily assigned CN of 100. 2, 2, 4, 4, 6, 8, 8-heptamethylnonane is the

low-quality reference standard with a long ignition delay time and an arbitrarily assigned CN of 15 (Knothe, 1997).

Therefore, the fuel economy of biodiesel approaches that of petro-diesel. Additionally, the alcohol component of biodiesel contains oxygen (between 10 and 13 %.), which helps to complete the combustion of the fuel. The effects are reduced air pollutants such as particulates, carbon monoxide and hydrocarbons. Since biodiesel contains practically no sulfur, it can help reducing emissions of sulfur oxides. Heat of combustion is the thermal energy that is liberated upon combustion, so it is commonly referred to as energy content. Factors that influence the energy content of biodiesel include the oxygen content and carbon to hydrogen ratio .Generally, as the oxygen content of FAAE is increased, a corresponding reduction in energy content is observed. FAAE of similar chain length but lower carbon to hydrogen ratios (i.e., more hydrogen) exhibit greater energy content. Biodiesel is sensitive to cold weather and may require special anti-freezing precautions, similar to those taken with standard diesel. (Chuepeng and Komintarachat, 2010).

Therefore, winter compatibility is achieved by mixing additives, allowing the use down to minus 20 °C. Another problem is that biodiesel readily oxidizes. Thus, long-term storage may cause problems, but additives can enhance stability. Biodiesel also has some properties similar to solvents which make it to attack plastic and rubber components such as seals and fuel lines. This causes problems in vehicles which have not been approved or which are filled with biodiesel for the first time after a long mileage with fossil diesel. In this case biodiesel acts like a detergent additive, loosening and dissolving sediments in storage tanks. Residues of the fossil fuel are released, causing the filter to become blocked. It is therefore advisable to change the fuel filter after several tank fillings with biodiesel. Conventional diesel engines operate readily with up to 100 % biodiesel fuel but using blends above 20 % may require modest costs in order to replace some rubber hoses that are sensitive to the solvent character of biodiesel. The elemental composition (carbon – C, hydrogen – H and oxygen – O), the C/H ratio and the chemical formula of diesel and biodiesel produced from different feed stocks is shown in Table 2.1.The elemental composition of biodiesel varies slightly depending on the feedstock it is   produced from. (Barabás andTodoruţ, 2010).

Table 2.1: Elemental composition of diesel fuel and biodiesel, % (m/m) (modify from: Barabás&Todoruţ, 2010).

Fuel Type	C	H	O	C/H	Empirical formula
Diesel	86.5	13.6	0	6.24	$C_{15.05}H_{27.94}$
Diesel	77.2	12.0	10.8	6.45	$C_{19.03}H_{35.17}O_2$
SME	77.2	11.9	10.8	6.60	$C_{19.05}H_{34.98}O_2$
PME	76.35	11.26	12.39	6.16	$C_{18.07}H_{34.93}O_2$

2.12 Fuel Property Measurement

Replacement of existing fuels with new fuel formulations requires understanding the critical fuel properties to insure that the new fuels can be used. Discussed in this section are some key fuel properties as well as the methods to measure these properties. The properties discussed are specific gravity, kinematic viscosity, flash point, boiling point (distillation test), cetane number, cloud point, pour point, and copper strip corrosion (Knothe, 2005).

2.12.1 Specific Gravity

The specific gravity is a relative measure of the density of a substance. It is defined as the ratio of the density of the substance, ρ, to a reference density, ρ/ref. The equation for the specific gravity (SG) is SG = ρ/ρref. The most common reference density used in the measurement of specific gravity is the density of water at 4˚C, which corresponds to a reference density of 1 g/c.

2.12.2 Flash Point

The flash point is defined as the "lowest temperature corrected to a barometric pressure of 101.3kPa (760 mm Hg), at which application of an ignition source causes the vapors of a specimen to ignite under specified conditions of test." This test, in part, is a measure of residual alcohol in the B100. The flash point is determined by heating a sample of the fuel in a stirred container and passing a flame over the surface of the liquid. If the temperature is at or above the flash point, the vapor will ignite and an easily detectable flash can be observed. The flash need not correspond to a sustained flame. The "fire point" is sometimes used to designate the fuel temperature that will produce sufficient

vapor to maintain a continuous flame. The flash point is a determinant for flammability classification of materials. The typical flash point of pure methyl esters is > 200 ° C, classifying them as "non-flammable". However, during production and purification of biodiesel, not all the methanol may be removed, making the fuel flammable and more dangerous to handle and store if the flash point falls below 130ºC. Excess methanol in the fuel may also affect engine seals and elastomers and corrode metal components.(Knothe, 2005).

2.12.3 Cetane Number

Perhaps the most important measure of ignition characteristics of diesel and/or biodiesel fuels is the cetane number, since it directly pertains to ignition within compression ignition engines. Thus, it is the approximate equivalent of octane rating for gasoline (petrol). Cetane number is a measurement of the combustion quality of diesel fuel during compression ignition. It is a measure of a fuel's ignition delay, the time period between the start of injection and the first identifiable pressure increase during combustion of the fuel. In a particular diesel engine, higher cetane fuels will have shorter ignition delay periods than lower cetane fuels. In short; the higher the cetane number, the more easily the fuel will combust in a compression setting (such as a diesel engine).

2.12.4 Acid Number

It is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point." The acid number is a direct measure of free Fatty acids in B100. The free fatty acids can lead to corrosion and may be a symptom of water in the fuel. The acid Number is a relative indicator of the acidic impurities, degradation and/or oxidation of the fuel. Free fatty acids arise in part through the hydrolysis of the feedstock fats and oils. Improper processing or oxidation may also lead to higher values.

2.12.5 Kinematic viscosity

Viscosity is one of the most important properties of biodiesel. Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. Fuel atomization is also affected by fuel viscosity. Diesel fuels with high viscosity tend to form larger droplets on injection which can cause poor combustion, increased exhaust smoke and emissions. Viscosity influences the ease of starting the engine, the spray quality, the size of the particles (drops), the penetration of the injected jet and the quality of the fuel-air mixture combustion Alptekin and Canakci (2009). Fuel viscosity has both an upper and a lower limit. The fuel with a too low viscosity provides a very fine spray, the drops having a very low mass and speed. This leads to insufficient penetration and the formation of black smoke specific to combustion in the absence of oxygen (near the injector) (Băţaga, 2003).

2.12.6 Density

Fuel density is the mass of unit volume, measured in a vacuum. It's the weight per unit volume. Oils that are denser contain more energy. For example, petrol and diesel fuels give comparable energy by weight, but diesel is denser and hence gives more energy per litre. Biodiesel is generally denser than diesel fuel with sample values ranging since density is strongly influenced by temperature; the quality standards state the determination of density at 15 °C. Fuel density directly affects fuel performance, as some of the engine properties, such as cetane number, heating value and viscosity are strongly connected to density.

2.12.7 Iodine value

 It is an index of the number of double bonds in biodiesel, and therefore is a parameter that quantifies the degree of unsaturation of biodiesel. It is reported in terms of the grams of iodine that will react with 100 grams of a fat or oil under specified condition. It is a value of the amount of iodine, measured in grams, absorbed by 100 grams of given oil. It is commonly used as a measure of the chemical stability properties of different biodiesel fuels against such oxidation. It is useful parameter in studying oxidative rancidity of triacylglycerol's since, higher the unsaturation; greater is the possibility of rancidity.

$$Iodine\ value\ = \frac{12.7(B-S)\ N}{weight\ of\ the\ sample(g)} ……………………………………….3.2$$

Where; B = Volume in ml of standard sodium sulphate solution required for the blank.

S = Volume in ml of standard sodium thiosulphate solution required for the sample.

N = Normality of the standard sodium thiosulphate solution,

W = Weight in g of the material taken for the test

2.12.8 Ash Percentage

Ash is a measure of the amount of metals contained in the fuel. High concentrations of these materials can cause injector tip plugging, combustion deposits and injection system wear. The ash content is important for the heating value, as heating value decreases with increasing ash content. Ash content for bio-fuels is typically lower than for most coals, and sulphur content is much lower than for many fossil fuels.

2.12.9 Saponification value

A known quantity of oil is refluxed with an excess amount of alcoholic KOH. After saponification, the remaining NaOH is estimated by titrating it against a standard acid.

$$Saponification\ value = \frac{28.5x\ (T2-T1)}{W} ……………………………………… (3.3)$$

Where: T2 = Volume in ml of 0.5N acid required for the blank.

T1 = Volume in ml of 0.5N acid required for the sample.

W = Weight in g of the sample taken.

2.12.10 Determination of Free Fatty Acid (FFA)

The free fatty acid, FFA of the oil was calculated empirically from the acid value determined above using the equation

$$\%FFA = AV/2 ……………………………………………………………………… (3.4)$$

AV=acid value

2.12 Current Diesel Production in Ethiopia

Biodiesel is a good alternative fuel for diesel engines because it is environmentally friendly and renewable in nature. Researchers focus more on the production of biodiesel using edible oils but the use of non-edible oil for biodiesel production has contributed immensely to its cost reduction. The combustion characteristics of biodiesel are similar as diesel and the engine power output with biodiesel is found to be equivalent to that of diesel. Therefore, from this review, we concluded that the biodiesel is a better alternative renewable fuel for the diesel (Kefyalew et al., 2016).

Although production of bio-diesel is not yet started, various types of plant species which can be used for producing bio-diesel grow in the country. Jatropha, which is very important feed-stock for bio-diesel grows in many parts of the country and used as a hedge and medicinal plant. Assessments, conducted in Amhara indicate that there are about 11 million wild and planted Jatropha plants in the regional State. The plant grows in the Southern and other places and being used for many purposes as well. It has various names depending on the locations it grows. In some areas it is called ''Ayderkie'', which means Draught Resistant, and in some places it is called ''Yedinber Shimagilie'', which means Border Mediator since it is widely used as hedge. Another plant which grows in many parts of Ethiopia and important feed-stock for producing bio-diesel is castor oil. Imported Palm tree seedlings are planted in 100 ha area in the Gambella Regional State for producing oil and soap around Tepi area (Kefyalew *et al., 2016).*

Ethiopia is endowed with natural resource suitable for bio-diesel production. In this regard, at national level, an estimated area of 23.3 million ha land is available for development of bio-diesel. Regionally, the available land in million ha is: Oromia 17.2, Benishangul-Gumuz 3.1 Gambela 2.8, Somali 1.5, Amhara 1, Southern Nations Nationalities 0.05, Tigray 0.007. Statistical information for Afar and Hareri is not available. It should be noted that there is information gap in some of the regions; nevertheless, the potential is expected to be higher than the available record. Based on the government development strategy local and(Bataga et al, 2003) foreign private investors have started growing plants for producing bio-diesel (Kefyalew *et al., 2016).*

CHAPTER THREE

MATERIALS AND METHODS

3.1 Algal Sample Collection and Oil Extraction

A consosium of algal samples were collected from Jimma Institute of Technology oxidation pond and Boye stream in Jimma. A wet algal biomass of about 5 kg was obtained from Boye stream in three rounds. Similarly 9 kg of wet algal biomass was obtained from Jimma Institute of Technology oxidation pond using microscreens by centrifugation. The algae paste was dried in an oven at 105 $^{\circ}$C to constant weight and desiccated overnight. The dried algal biomass was grounded using a mortar-and-pestle and sieved through a 500-micron mesh screen. The dried and grounded algal biomass (5 g) was taken in solvent mixture (100 ml) of acetone and the contents were refluxed for 4 hrs. After the extraction, the contents were cooled and filtered (or centrifuged) to separate the biomass and washed the biomass with 25 ml of acetone twice to extract the residual lipids present in the biomass. The extracts were pooled and taken in a separating funnel and washed with 1% aqueous sodium chloride solution (50 ml) twice. The solvent were removed by using rota-evaporator under vacuum to get the algal oil. The weight of algal oil was taken to determine the oil content in biomass. If the biomass is available in smaller quantities, the content may be reduced accordingly. All experiments were conducted in triplicate.

Figure 3.1: Wet algal biomass

Figure 3.2: Dry in the oven (a), algae grinder (b) and algae powder (c)

The major raw materials used during the experiment for biodiesel production were algae oil, waste cooking oil, methanol (analytical grade) and sodium hydroxide catalyst, physicochemical property test study chemicals as; potassium hydroxide, hydrochloric acid, phosphoric acid, phenolphthalein, sodium chloride and distilled water. The algae oil was obtained by sox let extraction of dried algae biomass using hexane as a solvent. The chemicals were purchased and obtained from Neway Private Limited Company and from bio-chemical engineering laboratory; in Addis Ababa institute of technology.

3.1.1 Oil Extraction from powdered Microalgae

The extraction was performed in sox let extractors by using hexane has solvent. The powdered Microalgae were then subjected to sox let extraction. Hexane 20ml was mixed with 6g dried ground algae to extract oil. In temperature of 75℃ the mixture was recycled and processed by kept in sox let device for 24 h up to for settling. The extracted oil was evaporated in vacuum to release hexane and using rotary evaporator. At the end the solvent was distilled off using rotary evaporator by giving a white color (Couto *et al*., 2010).

3.2 The Process of Extraction oil from consortium algae

```
┌─────────────────────┐
│  Algal biomass      │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│ Drying Algal (Freeze│
│ drying)             │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐        ┌──────────────┐
│ Extracting oil (soxhlet│◄──── │  n-hexane    │
│ extraction)         │        └──────────────┘
└─────────────────────┘
          │
          ▼
┌─────────────────────┐        ┌────────────────────────────┐
│ Algae Oil purification/│     │ Physicochemical analysis   │
│ Degumming           │        │   □ Acid value of oil      │
└─────────────────────┘        │   □ specific gravity       │
          │                    │   □ Kinematic Viscosity    │
          ▼                    │   □ Flash point            │
┌─────────────────────┐        │   □ Moisture content       │
│ Neutralization      │        │   □ Ash content            │
└─────────────────────┘        └────────────────────────────┘
          │                              ▲
          ▼                              │
┌─────────────────────┐                  │
│ Purified Oil        │──────────────────┘
└─────────────────────┘
```
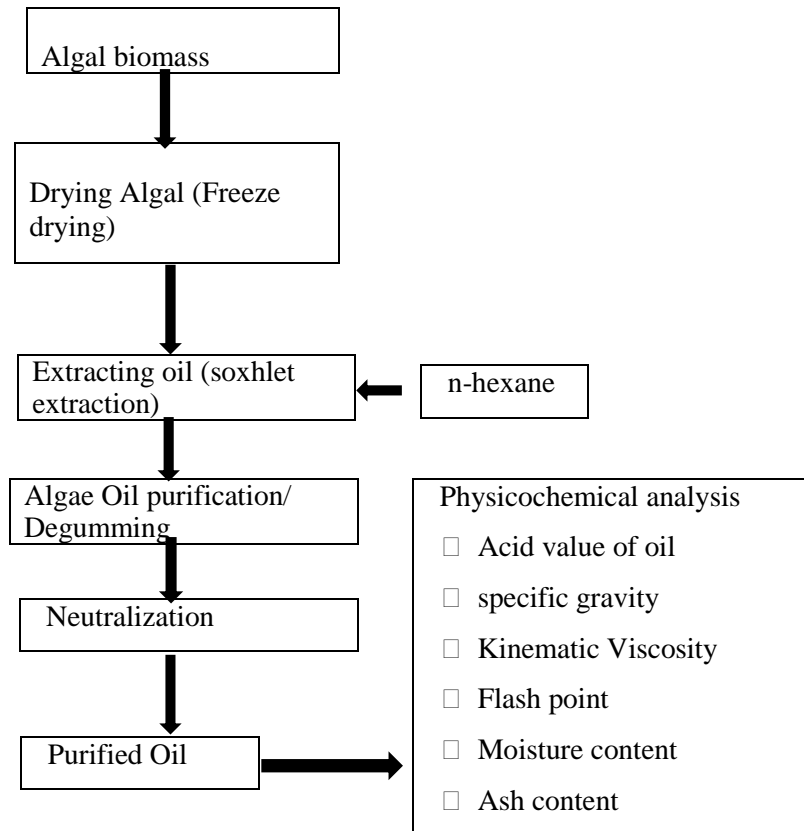
Figure 3.3: oil extraction processes

a   b   c

Figure 3.4: Algae powder in the filter paper (a), sox let device (solvent) (b) and separation of algae and hexane (c)

Oil Content Determination

To determine or calculate the oil content of the powdered algal biomass, the following method wasempl oyed.

$$Oil\ content\ of\ algae\ (\%) = \frac{(weight\ of\ oil\ obtained\ or\ extracted)}{(weight\ of\ dried\ algae\ used)} \times 100\% \cdots\cdots (3.1)$$

3.3 The Process of waste cooking oil

3.3.1 Pretreatment of waste cooking oil

3.3.1.1 Physical pretreatment

The waste cooking oil which was collected from restaurants was filtered using filter paper to remove the large particles and impurities. Then for the removal of small particles, the oil was centrifuged at 8000 rpm for 20 minutes to obtain oil without solid impurities and particulates.

| A | b | c | d |

Fiure 3.5: Waste cooking oil (a), waste cooking oil is centrifuged (b), waste crude oil (c) and pure cooking oil (d)

3.3.1.2 Chemical Pretreatment

In order to remove the water content from the pure cooking oil, sodium sulfate as dehumidifier was used. First, sodium sulfate was poured into the physically treated oil, and then it was left for a period of time to absorb the water content of the oil. After 72 hours, sodium sulfate which was deposited at the bottom was settled down. Lastly after the settled of sodium sulfate of dehumidifier the pure cooking oil is filter (Barnwal *et al*., 2005)
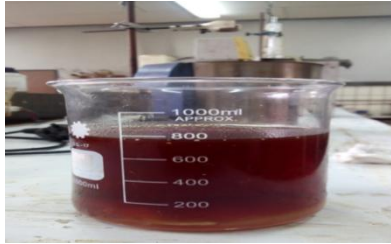
Figure 3.6: Chemical Pretreatment WCO oil
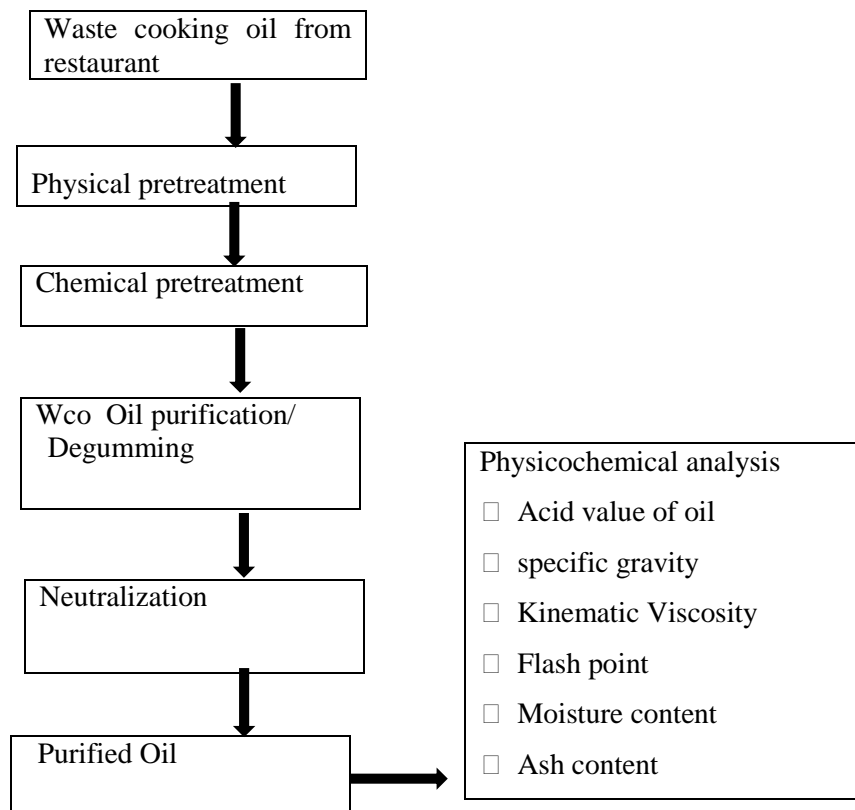
Figure 3.7: waste cooking oil processes

3.4 Purification of Crude Oil the two raw materials

This step was used to remove phosphorus compounds of crude oil using a phosphoric acid and hot distilled water. The oil was heated to 70 ^{o}c. 3% distilled water (v/v of oil) which was heated to 80 ^{o}C and 2% phosphoric acid (v/v of oil) was mixed with the heated oil. The mixtures were stirred at speed of 200 rpm for 1 hour at a temperature of 70 ^{o}c. The impurities were separated using a centrifuge at a speed of 800 rpm for 20 minutes.(Atadashi *et al*., 2011).

3.5 Neutralization algae oil and WCO oil

After determining the free fatty acid (FFA) of oil, the free fatty acid was neutralized by 0.05N of NaOH. Neutralization was done by heating the oil at 70 ^{0}C. The mixture of oil and NaOH solution was stirred at 200 rpm at a temperature of 70 ^{o}C for 1 hour. The mixture was washed with a distilled water to remove a trace NaOH and produced soap. Finally, trace water was removed in an oven drying at a temperature of 105 ^{0}C.

Figure 3.8: Neutralization

3.6 Trans esterification

Methanol and potassium hydroxide was pre-mixed to prepare potassium meth oxide and then added to oil in the reactor with a mixing speed of 400 rpm for 2 hours at 50 ^{0}C. The molar ratio of oil to methanol was 1:10. The mixture was left overnight to settle forming two layers, namely: biodiesel phase (upper layer) and the glycerin-rich phase (Vicente *et al*., 2007).

a   b   c
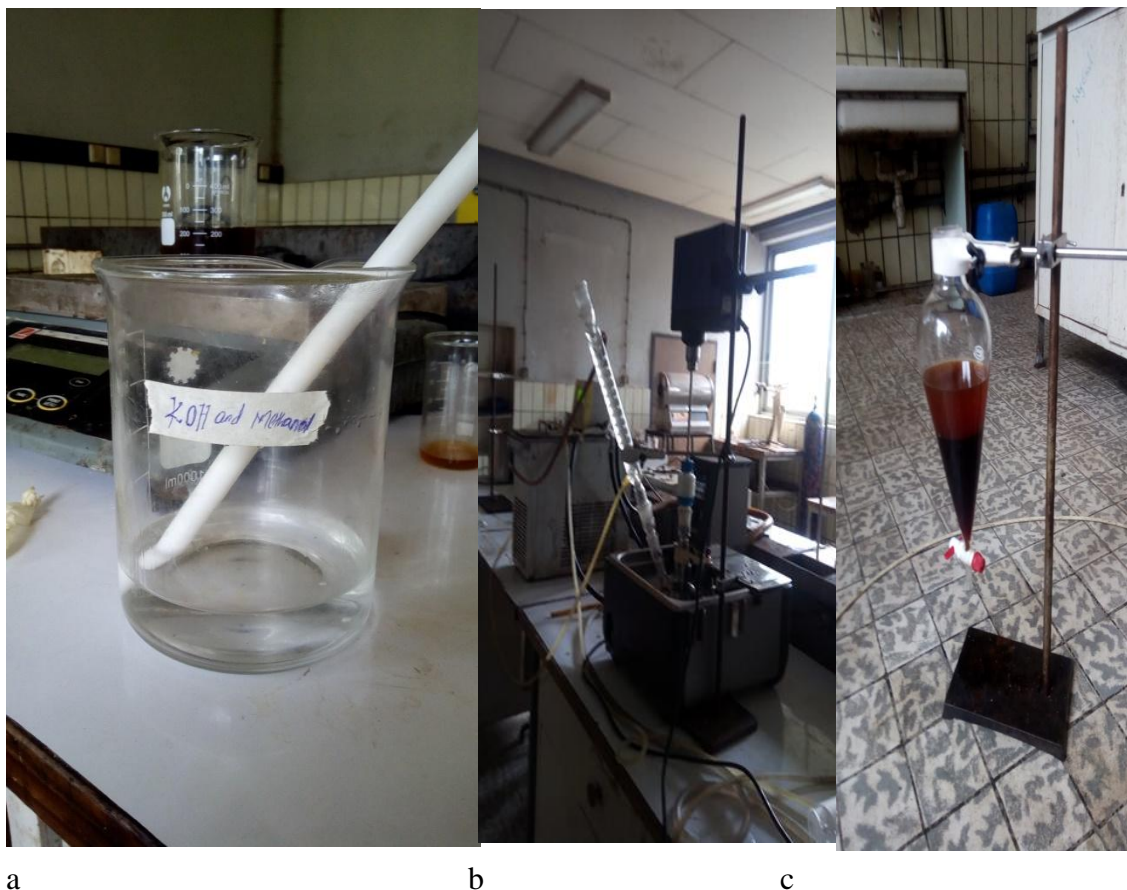
Figure 3.9: KOH, and methanol (a), stirred device (b) and biodiesel oil (c)

3.7 Purification of biodiesel: Washing, Neutralizing and Drying

The mixture of fatty acids methyl esters (FAME) obtained from the Trans esterification reaction was purified in order to comply with established quality standards for biodiesel. The FAME was washed by successive steps using distilled water to remove the remains of methanol, catalyst and glycerin since these contaminants are water-soluble. The first washing step was carried out with acidified water to neutralize the mixture of esters. Two additional washing steps was carried out using distilled water alone.

Finally the trace of water was   eliminated using dryer. Biodiesel production was measured by using measuring cylinder pH was measured and stored for analysis.(Javidialesaadi *et al*., 2013).

| A | b | c |

Figure 3.10: Washing biodiesel (a), pure biodiesel (b) and c) pure biodiesel (c)

3.8 Physicochemical Properties of Extracted Oil and waste cooking oil

American Society for Testing and Materials (ASTM) standard fuel tests was carried out on the biodiesel obtained from blends of waste cooking oil and microalgae. Specific gravity and viscosity measurements was made using the thermal-hydrometer apparatus and viscos meter following ASTM standards .The biodiesel was analyzed for cloud point and pour point using Baskeyl Seta point Cloud and Pour Point apparatus following ASTM standards. The oil was analyzed for as specific gravity, kinematic viscosity, acid value, percentage of FFA content and moisture content.These parameters directly or indirectly may affect the quality of the biodiesel.

3.8.1 Determination of Specific Gravity (SG) by Hydrometer Method

To determine the specific gravity of the oil, a 50 ml sample that is heated to a temperature of 25^0C and filled into graduated cylinder. Dens meter was inserted into the graduated cylinder to measure the SG of the oil and the reading was taken. On the other hand the specific gravity or relative density of the oil can be determined by taking the ratio of the mass of the 50ml oil at t^0Cto the mass of an equal volume of water at 20^0C. Usually it is expressed as "sp gr at t°C/20°C".

3.8.2 Determination of Kinematic Viscosity

A viscometer was inserted into a water bath with a set temperature and left for 30minutes. The sample was added to the viscometer and allowed to remain in the bath as long as it reaches the test thermometer. The sample is allowed to flow freely and the time required for the meniscus to pass from the first to the second timing mark is taken using a stop watch. The procedure is repeated a number of times and the average value are taken which is then multiplied with the viscometer calibration to give the kinematic viscosity.

$$Kinematic\ Viscosity\ of\ oil\ (v) = \frac{Dynamic\ Viscosity\ of\ oil\ (n)}{Density\ of\ oil\ (p)} \dots\dots\dots\dots\dots\dots 3.2$$

Figure 3.11: Determination of Kinematic Viscosity

3.8.3 Determination of Acid Value

To determine the acid value of oil a titration solution of 0.1N of KOH in distilled water was prepared. 2g of oil was added to a beaker and heated at 70^oC for 3 minutes. Then, 20ml of anhydrous ethanol (99.5%w/w), 20ml of diethyl ether and 5 drops of phenolphthalein was

added into the titration beaker that contains sample oil. Then oil sample was mixed thoroughly with a mixture of 20ml of ethanol, 20ml of diethyl ether and 5 drops of phenolphthalein. Finally, titration solution, 0.1N of KOH was added 1 drop at a time until the first color (until pinkish color appeared) change was observed. Once the color change was observed, the titration volume (ml) was recorded and the recorded volume was used to calculate the acid value using the equation;

$$AV = N * V * M/W \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3.3)$$

Where;   N= normality of aqueous solution of KOH

V= Volume of titrant used for titration (ml)

M = Molecular weight of KOH

W = the weight of oil sample

Figure 3.12: Determination of Acid Value

3.8.4 Determination of Flash Point

A sample of the biodiesel was heated in a close vessel and ignited. When the sample burns, the temperature was recorded; the pen sky-martens cup tester measures the lowest temperature at which application of the test flame causes the vapor above the sample to ignite. The biodiesel was placed in a cup in such quantity as to just touch the prescribed mark on the interior of the cup. The cover was then fitted onto the position on the cup and Bunsen burner is used to supply heat to the apparatus at a rate of about 5°C per minute. During heating, the oil is constantly stirred. As the oil approaches its flashing, the injector burner is lighted and injected into the oil container after every 12 second intervals until a distinct flash

was observed with in the container. The temperature at which the flash occurred is then recorded, it was repeated three times and the average taken.

Figure 3.13: Determination of Flash Point

3.8.5 Determination of Free Fatty Acid (FFA)

The free fatty acid, FFA of the oil was calculated empirically from the acid value determined above using the equation

$$\%FFA = AV/2 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3.4)$$

AV=acid value

3.8.6 Determination of Moisture Content

A dish was weighed with and without oil. The dish with oil was dried in an oven at 105°C for 7 hours, weighing each 2 hours till constant weight was obtained and finally the weight was taken and compared with the initially recorded weight. The percentage weight in the oil was calculated using the formula;

$$Moisture\ content\ =\ W1 - \frac{W2}{W1} * 100\% \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3.6)$$

Where; W1 = Original weight of the sample

W2 = Weight of the sample after drying

Figure 3.14: Determination of Moisture Content

3.8.7 Ash Content Determination

Furnace was used to determine the ash content of the oil. A burning cup containing 20g oil was placed in a furnace for 4 hour which was set at a temperature of 550 ^{0}C. After burning the residue sample was weighted and ash content was calculated

$$Ash\ content\ \%(W/W) = \frac{mass\ of\ oil\ after\ burning}{Initial\ mass\ of\ oil} \times 100\% \cdots\cdots\cdots\cdots\cdots\cdots\ (3.7)$$

a) weight of sample with corrodible   b) the ash of in the corrodible

Figure 3.15: Ash Content Determination

3.9 Transesterfication Process/ Conversion to Biodiesel

a) Stirred device   b) biodiesel with glycerol oil   c) washing of biodiesel

Figure 3.16:Transesterification reaction & Separation of biodiesel from glycerol

3.10 Design of Experiment

A four variable central composite design for response surface methodology was used to study the combined effects of catalyst concentration, methanol to oil molar ratio algae to WCO and bind effects of catalyst concentration, methanol to oil molar ratio algae to WCO oil reaction temperature on the amount of biodiesel yield over three levels. The range and levels of the variables used for optimization are shown in table 3.1. Process variables revised were reaction temperature, molar ratio methanol to oil and weight percentage of catalyst. The reaction time and mixing intensity were fixed at 2 hours and 500 rpm respectively for all experimental runs. The central composite design is suitable for the exploration of quadratic response surfaces and generates a second degree polynomial model, which in turn is used optimizing a process using a small number of experimental runs. This design requires an experimental number   of runs according to:

$$N = K^2 + K + C_p \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3.8)$$

Where:. K is the factor number which is three in this case Cp is the number of replications at the center point which is also three in this case. (Gerpen,2004).

The design which was developed using Design Expert ® 6.0.8 (Statease, Inc. Minneapolis,

USA), resulted in 30 experimental runs as shown in Table 3.2. The 30 experimental runs wer e ized to maximize the effects of unexplained variability in the observed responses due to ous fators. The levels of the independent variables as shown in Table 3.1 were selected base d on the operating limit of biodiesel production process conditions and previous research Works.The upper temperature level (68°C) is near to the theoretical boiling point of methanol , and calyst concentration of 3 % by weight of oil was based on literature data. The lower mo lar ratio (3:1) was the theoretically declared maximum yield giving mlar ratio (Gerpen, 2004).

To avoid systematic errors, the order in which the runs were made was randomized. The relation between the coded and actual values is described as follows:

$$x_i = (X_i - X_o)/_{\Delta X_i} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.9)$$

Where x_i and X_i are the coded and actual values of the independent variable respectively. X_o is the actual value of the independent variable at the center point, and ΔX_i is the step chan ge of X_i a second degree polynomial was fitted to the experimental data using the statistical pack age design Expert ® 6.0.8 to estimate the response of the dependent variable and predict the point. The second degree polynomial was expressed as follows:

$Y= b_0+b_1X_1+b_2X_2+b_3X_3+b_{12}X_1X_2 + b_{13}X_1X_3+b_{23}X_2X_3+b_{11}X_1^2+b_{22}X_2^2+b_{33}X_3^2$

Where Y is predicted response, X_1, X_2 & X_3 are independent variables, b_o is offset term, b_1, b_2, b_3 are linear effects, b_{11}, b_{22}, b_{13} are interaction terms.The independent variables and l evels used for base catalyzed transesterification and conducting the 30 experimental runs was presented in table 3.1 and table appendix respectively.

Table 3.1The factors for three levels central composite design

Independent Variables	Symbols	Unit	Coded & Actual Levels		
			-1	0	+1
Amount of catalyst	C	%	1	2	3
Reaction temperature	B	^{o}C	60	64	68
Methanol to oil ratio	A	%	3	6	9
Algae oil to WCO oil ratio	D	%	1	2	3

3.10.1 Feed Material Requirement for the transesterification process

For each experimental run of the transesterification process, 50ml of purified oil was used.The amount of catalyst and methanol required was calculated as follows:

3.10.1.1 Amount of Methanol required

The amount of methanol required when the molar ratio of methanol to oil is 3:1

$$\frac{mole\ of\ methanol}{mole\ of\ oil} = \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3.10)$$

$$\frac{Given\ mass\ of\ \frac{methanol}{Molecular}\ of\ methanol}{given\ mass\ of\ \frac{oil}{molecular}\ mass\ of\ oil} = 3$$

$$\frac{Density\ of\ methanol \times Volume\ of\ methanol/Molecular\ mass\ of\ methanol}{Density\ of\ oil\ \times volume\ of\ oil/Molecular\ mass\ of\ oil} = 3$$

$$\frac{\frac{0.791g}{ml} \times Volume\ of\ methanol\ /32.04g/mol}{\frac{0.94g}{ml} \times 50ml/912g/mol}$$

Volume of methanol = 6.26ml

Similarly,

Volume of methanol required when the molar ratio of methanol to oil is 6:1and 9:1 w ascalculated and obtained as 12.52ml & 18.79ml respectively.

3.10.1.2 Amount of Catalyst required

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

$$Mass\ of\ catalyst\ (NaOH)/(0.54g \times 50ml) \times 100\% = 1\%$$

$$\frac{Mass\ of\ catalyst\ (NaOH)}{denity\ of\ oil \times volume\ of\ oil} \times 100\% = 1\%$$

Mass of catalyst (NaOH) = 0.47g

Similarly, the amount of catalyst required when catalyst weight to oil ratio is 2% & 3% was Calculated & obtained as 0.94g & 1.41g respectively.

3.10.2.3 Statistical Analysis

The design expert software was used for the analysis of variance (ANOVA). Response surface method of central composite was used to generate surface plots using the fitted equation obtained from the regression analysis, holding one of the independent variables constant. Experimental values of conversion of the oil to biodiesel at the design points at different parameters was obtained and from those values the yield was calculated and recorded on table 3.2 The response of the trans esterification process which is biodiesel yield was calculated as ;

$$biodiesel\ yield\ (in\%) = \frac{weight\ of\ biodiesel\ obtained \times 100\%}{weigt\ of\ oil\ used} \dots\dots\dots\dots\dots\dots\dots\dots 3.12$$

3.11 Experimental Methods

All experimental works except freeze drying of the wet algal biomass were done in organic laboratory of Addis Ababa University, AiT for biodiesel extraction. Freeze drying of the wet algal biomass was done in by Jimma Institute of Technology (JiT) Environmental Engineering Department Laboratory.

The general experimental setup is shown in figure 3.3 below. The algae biomass is collected from the two sources by filtering using a 60 micrometer filter and dried in a freeze dryer. Oil was extracted from the dried and ground algae using sox let extraction method with a solvent n-hexane. After the oil obtained is refined and analyzed for its physicochemical properties, it was subjected to a chemical reaction trans esterification with meth oxide (a mixed solution of methanol and sodium hydroxide). After the Trans esterification reaction is completed the crude biodiesel was separated from the glycerol using a separator funnel and the methanol was distilled to be recycled. Hot water was applied to remove the impurities from the biodiesel and was dried in an oven to get a pure biodiesel. Finally, the obtained biodiesel was checked for its physicochemical properties and compared with the international standard.
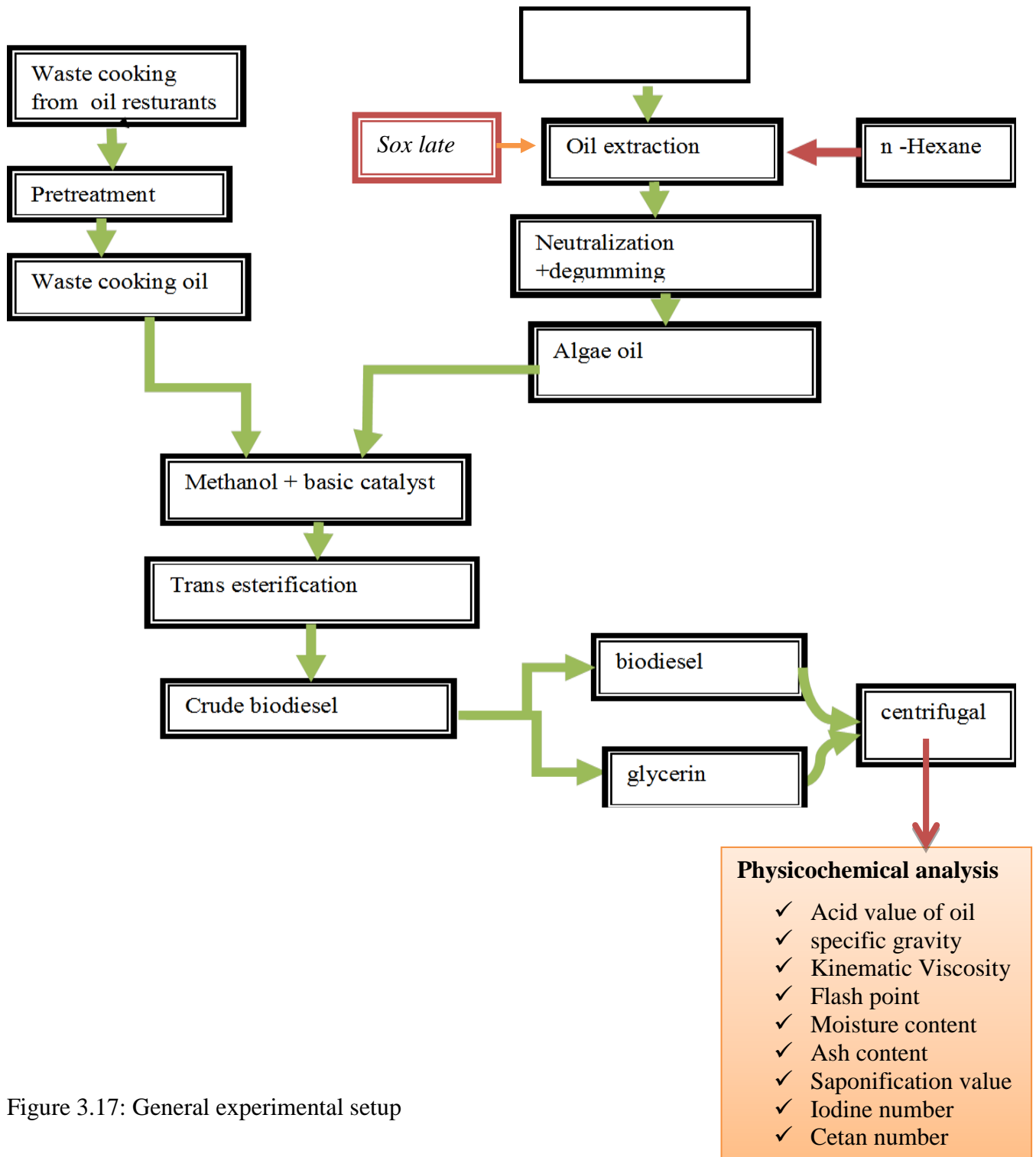
Figure 3.17: General experimental setup

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Oil Extraction and Characterization

4.1.1 Oil Extraction

From the 2kg grounded algal mass 633.72g of oil was obtained after the oil was extracted and Sepraed from the solvent (hexane) 684.2ml were obtained. The oil content of the powder ed mass was calculated using equation 3.1.The result showed that 31.6% of dried mass of the Sample (the algae) is oil.

According to a study made by Ayalew (2014) a 798.4g of oil can be obtained from 2.5 kg grounded algal biomass. After oil extraction and separation from the solvent (hexane), 850 ml of algal oil was obtained. This indicates that 32% of the dried algal biomass is oil. The current study is almost the same with this finding.

4.1.2 Waste cooking oil

From the 1L the waste cooking oil filtered using filter paper to remove the large particles and impurities. Then for the removal of small particles, the oil was centrifuged at 12000 rpm for 5 minutes700 ml of oil was obtaining oil without solid impurities and particulates. In order to remove the water content, sodium sulfate as dehumidifier was used. First, sodium sulfate was poured into the physically treated oil, and then it was left for a period of time to absorb the water content of the oil. After 72 hours, sodium sulfate which was deposited at the bottom was slowly removed (Barnwal *et al*., 2005).

4.2 Characterization of the two blends Oil

4.2.1 Density of the Oil

The specific gravity was measured by densimeter and obtained to be 0.92g/cm^3.from the sample empirical formula explained in equation 3.2, the density of the oil was obtained to be 0.92g/cm^3 at room temperature and 0.921 g/cm^3 at 40^{0}c temperature.Then 920 kg/m^3 at room temperature and 921 kg/m^3 at 40 ^{o}C temperature.

4.2.2 Kinematic Viscosity of the Oil

The dynamic viscosity of the oil was measured using Sine Wave (SV10, 2011, Australia vibro vis meter at 40^0c and recorded as 3.82m.pa.s = $3.82 * 10^3$ kg/m.s. The kinematic viscosity can be calculated using the equation 3.2 and the result was obtained to be 41.47mm^2/s. The result shows that the oil obtained is highly viscous & needs transesterification so as to minimize its viscosity.

4.2.3 Acid Value of the Oil

The acid value of the oil was determined using the method stated under section 3.2.2. The results were recorded in table 4.1 as shown below.

Table 4.1: Titration results for acid value test

Run Number	Mass of oil (g)	Titration volume (VKOH) (ml)	Color change	Acid Value (mg KOH/g oil)	FFA
1.	5	3.7	Yellow to pink	4.15	2.075
2.	5	2.2	Yellow to pink	2.46	1.23
3.	5	2.2	Yellow to pink	2.46	1.23
Average		2.7		3.02	1.51

As it can be shown in table 4.1 the titration volume at which the first color change observed on average was 2.7 ml. The acid vlaue of the oil was calculated using equation 3.3 and the result was obtained to be 3.02mg KOH/g oil.

4.2.4 Free Fatty Acid of the Oil

The free fatty acid of the oil is half of the acid value of the oil. Using equation 3.4 the free fatty acid is calculated and obtained to be 1.51%. The result shows that the oil needs pretreatment to reduce the amount of free fatty acid so as to overcome soap formation during transesterificatio n reaction.

4.2.5. Saponification Value of Oil

The procedure used to determine saponification value of oil was stated in section 3.2.2. The titration results for saponification test are illustrated in Table 4.2.

Table 4. 2: Titration results for Saponification value test

Run Number	Mass of oil (g)	NHCl	VbHCl	VaHCl	VbHCl-VsHCl	Saponification Value (mgKOH/g oil)
1	2	0.5	23.7	11.4	12.3	172.5075
2	2	0.5	23.7	11	12.7	178.1175
3	2	0.5	23.7	10	13.7	192.1425
Average value						180.9225

The saponification value was then calculated using equation 3.4 & gives an average saponification value of 180.9225 mgKOH/g of oil.

4.2.6 Moisture Content of the Oil

As it can be shown in table 4.3Moisture content of the oil was determined using equation 3.6 and it is obtained to be 0.03%.The result shows that further removing of the moisture is required to avoid soap formation in transesterification reaction.

Table 4.3: Titration results for Moisture Content of the Oil

Run number	Mass of oil (g)	Original weight of the sample(W1) (g)	Weight of the sample after drying (W2) (g)	Moisture content value %
1.	2	2	1.998	0.1
2.	2	2	2	0
3.	2	2	2	0
Average		2	1.999	0.03

4.2.7 Ash content of the Oil

As it can be shown in table 4.4Using equation 3.7 the ash content of the oil was determined to be 0.0605%. The physicochemicalproperties of the oil are summarized in table 4.3 below.

Table 4.4: Titration results for Ash content of the Oil

Run number	Mass of oil (g)	Mass of oil after burning (g)	Initial mass of oil (g)	Value 0f ash content
1.	2	0.001	2	0.05
2.	2	0.0002	2	0.01
3.	2	0.00001	2	0.0005
Average			2	0.0605

4.2.8 Determination of Iodine value (IV)

The iodine value of the FAME was determined using the empirical formula suggested by other researcher for determination of higher heating value by using equation 3.8 to 3.10. After rearrangement the iodine value was calculated from equation 3.11. Equations 3.8 were developed for the calculation of the higher heating value (HHV) of vegetable oils and FAME from their viscosity (V). Relationships derived from physical properties of vegetable oil and biodiesel fuels. The equations between viscosity and higher heating values are for vegetable oils.

$$HHV = 0.0317v + 38.053$$

For FAME; $\quad HHV = 0.4625v + 0.015(IV)]$

$$HHV = 49.43 - [0.041(SN) + 0.015(IV)]$$

$$IV = \frac{HHV - 49.43 + 0.041(SN)}{0.015}$$

$$IV = 118.402G\ I^2/100g$$

4.2.9 Cetane Number

Perhaps the most important measure of ignition characteristics of diesel and/or biodiesel fuels is the cetane number, since it directly pertains to ignition within compression ignition engines. Thus, it is the approximate equivalent of octane rating for gasoline (petrol). Cetane number is a measurement of the combustion quality of diesel fuel during compression ignition. It is a measure of a fuel's ignition delay, the time period between the start of injection and the first identifiable pressure increase during combustion of the fuel. In a particular diesel engine, higher cetane fuels will have shorter ignition delay periods than lower cetane fuels. In short; the higher the cetane number, the more easily the fuel will combust in a compression setting (such as a diesel engine).

The cetane number of the FAME was determined using the empirical formula suggested by equation 3.12, using the result of saponification number (SN) and the iodine value (IV) of the FAME. The other researcher for determination of higher heating value by using equation 3.8 to 3.10.

$$CN = 46.3 + (^{54.58}/_{SN}) - 0.225(IV)$$

$\quad = 46.3 + (54.58/180.9225 \text{ mg koH/g} - 0.225(118.402)$

$\quad = 19.9616$

4.2.10 Determination of Flash Point

A sample of the biodiesel was heated in a close vessel and ignited. When the sample burns, the temperature was recorded; the pesky-martens cup tester measures the lowest temperature at which application of the test flame causes the vapor above the sample to ignite. The biodiesel was placed in a cup in such quantity as to just touch the prescribed mark on the interior of the cup. The cover was then fitted onto the position on the cup and Bunsen burner is used to supply heat to the apparatus at a rate of about 5°C per minute. During heating, the oil is constantly stirred. As the oil approaches its flashing, the injector burner is lighted and injected into the oil container after every 12 second intervals until a distinct flash was observed with in the container. The temperature at which the flash occurred is then recorded, it was repeated three times and the average taken.

Table 4.5 Summary of physicochemical properties of the oil

S.n.	Physicochemical property	Units	Value	Remark
1.	Density	kg/m^3	921	
2.	Kinematic Viscosity	mm^2/s	41.47	
3.	Acid value	mg KOH/g oil	3.02	
4.	Free fatty acid	%	1.51	
5.	Saponification value	mg KOH/g	180.9225	
6.	Moisture content	%	0.03	
7.	Ash content	%	0.0605	
8	Iodine number	G I^2/100g	118.402	
9	Cetane number		19.9616	
10	Flash point	C^0	168.33	

4.3 Biodiesel Production and Analysis of Effects of the Parameters

4.3.1 Transesterfication Process

The transesesterification process was carried out using the method discussed in section 3.3.4. The actual results obtained from the 30 runs were recorded in table 4.6 and used to analyze the variance.

4.3.2 Statistical Analysis

The design expert software was used for the analysis of variance (ANOVA). Response surfac method of centeral composite was used to generate surface plots using the fitted equation obt ained from the regression analysis, holding one of the independent variables constant. Experi mental values of conversion of the oil to biodiesel at the design points at different parameter was obtained and from those values the yield was calculated and recorded on table 4.4.The re sponse of the transesterification process which is biodiesel yield was calculated using equati on 3.12;

Table 4.6 Actual and predicted values of biodiesel yield

Run	Factors				% of Biodiesel		Residuals
	Methanol to oil ratio	Temprature	Catalyst	Algae oil to waste cooking oil ratio	Actual	Predicted	
1.	6.00	64.00	0.00	2.00	72.00	73.69	-1.69
2.	6.00	64.00	2.00	2.00	91.00	91.59	-0.59
3.	3.00	68.00	1.00	1.00	76.00	72.06	3.94
4.	3.00	68.00	1.00	3.00	89.00	91.22	-2.22
5.	3.00	60.00	1.00	1.00	69.00	69.84	-0.84
6.	9.00	68.00	1.00	3.00	92.00	89.49	2.51
7.	6.00	64.00	2.00	2.00	56.00	57.97	-1.97
8.	3.00	68.00	3.00	1.00	79.00	78.87	0.13
9.	9.00	60.00	3.00	3.00	57.00	55.06	1.94
10.	0.00	64.00	2.00	2.00	59.00	58.72	0.28
11.	6.00	72.00	2.00	2.00	61.00	65.19	-4.19
12.	9.00	68.00	3.00	3.00	73.00	70.09	2.91
13.	6.00	64.00	2.00	2.00	58.00	57.47	0.53
14.	6.00	64.00	4.00	2.00	61.00	62.87	-1.87
15.	3.00	60.00	1.00	3.00	60.00	57.34	2.66
16	3.00	60.00	3.00	3.00	64.00	63.99	6.944E-
17	6.00	64.00	2.00	2.00	79.00	79.39	-0.39
18	9.00	60.00	1.00	1.00	66.00	65.94	0.056
19	6.00	64.00	2.00	2.00	65.00	65.44	-0.44
20	6.00	64.00	2.00	2.00	68.00	68.39	-0.39
21	12.00	64.00	2.00	2.00	90.00	89.44	0.56
22	6.00	64.00	2.00	0.00	55.00	55.94	-0.94
23	9.00	68.00	1.00	1.00	80.00	79.17	0.83
24	9.00	60.00	3.00	1.00	77.00	79.17	-2.17
25	3.00	60.00	3.00	1.00	81.00	79.17	1.83
26	9.00	60.00	1.00	3.00	78.00	79.17	-1.17
27	6.00	56.00	2.00	2.00	79.00	79.17	-0.17
28	9.00	68.00	3.00	1.00	80.00	79.17	0.83
29	6.00	64.00	2.00	4.00	72.00	73.69	-1.69
30	3.00	68.00	3.00	3.00	91.00	91.59	-0.59

The model equation that correlates the response (yield of the oil to biodiesel) to the transesterification process variables in terms of actual value after excluding the insignificant terms was given below. The predicted (coded factor) model for percentage of biodiesel content (yield) is shown in equation 4. 2 below:

Final Equation in Terms of Coded Factors:

Yield $= +79.17 + 6.14 * A - 0.13 * B - 2.49 * C - 8.38 * D - 3.01 * A2 - 3.37 * B2 - 1.4 * C2 - 1.62 * D2 + 0.31 * A * B + 0.44 * A * C - 3.56 * A*D - 2.56 * B * C + 2.94 * B*D + 1.56 * C * D$

Where,   A   - Molar ratio of Methanol to oil

                        B   - Temperature

                        C   - Catalist

                        D   - Algea to wco oil Ratio

Final Equation in Terms of Actual Factors:

Yield $= -780.19444 + 6.48148 *$ Methanol Ratio $+ 26.56944 *$ Temperature $+ 40.31944 *$ Catalyst $- 44.90278 *$ Algae Ratio $- 0.33488 *$ Methanol Ratio2 $- 0.21050 *$ Temperature2 $- 1.45139 *$ Catalist2 $- 1.61806 *$ Algae Ratio2 $+ 0.026042 *$ Methanol Ratio $*$ Temperature $+ 0.14583 *$ Methanol Ratio $*$ Catalist $- 1.18750 *$ Methanol Ratio $*$ Algae Ratio $- 0.64063 *$ Temperature $*$ Catalist $+ 0.73437 *$ Temperature $*$ Algae Ratio $+ 1.56250 *$ Catalyst $*$ Algae Ratio

Table 4.7: Analysis of variance for response surface quadratic model

Response 1 Yield
ANOVA for Response Surface Quadratic Model
Analysis of Variance Table (Partial sum of Square – Type III)

Source	Sum of Squares	Df	Mean Square	F Value	P- value Prob > F	
Model	3415.26	14	243.95	36.16	< 0.0001	Significant
A	638.44	1	638.44	94.64	< 0.0001	
B	0.38	1	0.38	0.056	0.8173	
C	104.71	1	104.71	15.52	0.0017	
D	1683.38	1	1683.38	249.53	< 0.0001	
A2	135.90	1	135.90	20.14	0.0006	
B2	297.00	1	297.00	44.02	< 0.0001	
C2	31.52	1	31.52	4.67	0.0499	
D2	68.55	1	68.55	10.16	0.0071	
AB	1.56	1	1.56	0.23	0.6383	
AC	3.06	1	3.06	0.45	0.5123	
AD	203.06	1	203.06	30.10	<0.0001	
BC	105.06	1	105.06	15.57	0.0017	
BD	138.06	1	138.06	20.47	0.0006	
CD	39.06	1	39.06	5.79	0.0317	
ResidualLack of	87.70	13	6.75			
fitPure Error	76.87	8	9.61	4.43	0.0588	Not significant
	10.83	5	2.17			
Cor Total	3502.96	27				

The Model F-value of 36.16 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, C, D, A^2, B^2, C^2, D^2, AD, BC, BD, CD are significant model terms. Values greater than 0.1000 indicate the model terms

are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The "Lack of Fit F-value" of 4.43 implies there is a 5.88% chance that a "Lack of Fit F-value" this large could occur due to noise. Lack of fit is bad we want the model to fit.

As it can be seen from p-values of the model coefficients, the value of temperature in both linear and quadratic is much less than 0.001. This indicated that temperature is the most significant factor in determining the model than the rest. 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 4.7). 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. The actual values versus predicted values obtained using the developed correlation is plotted in the figure below.

Table 4.8: Model summary

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Press
Linear	6.82	0.6950	0.6420	0.5575	1550.23
2FI	5.83	0.8349	0.7378	0.6042	1386.54
Quadratic	2.60	0.9750	0.9480	0.8301	595.30
Cubic	2.04	0.9929	0.9680		

+ Case(s) with leverage of 1.0000: PRESS statistic not defined

"Model Summary Statistics": Focus on the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared".

The quality of the model developed was evaluated based on the correlation co efficient value,R2.The R2 value was 0.9929. This indicated that 99.29% of the total variation in the biodiesel yield was attributed to the experimental variable studied.The closer the R2 value to unity, the better the model will be as it will give p redicted values which are closer to the actual values for the response.
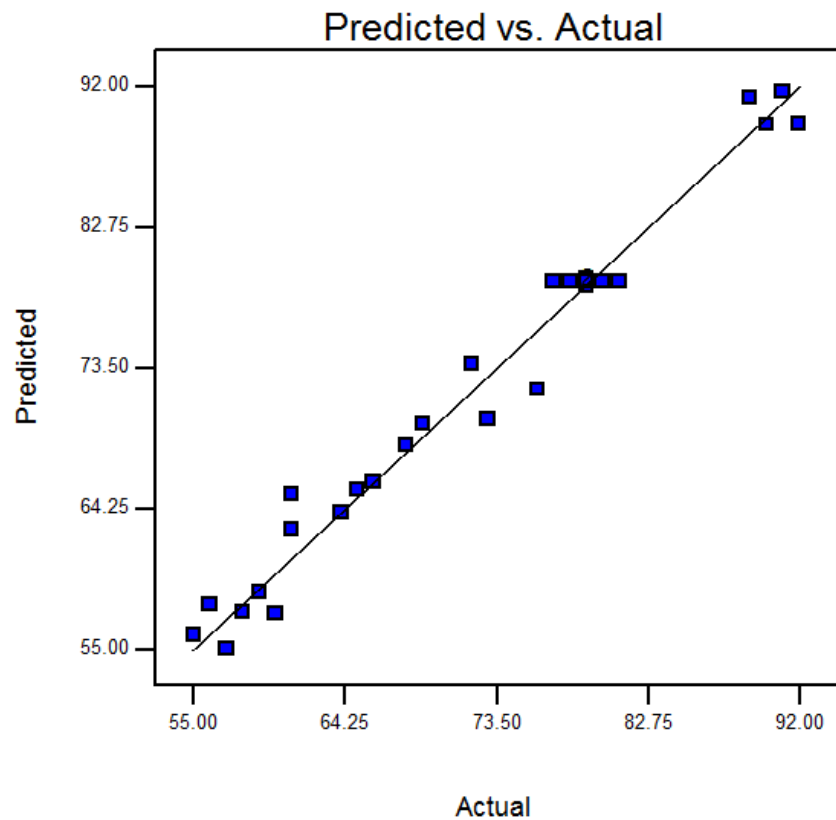
Figure 4.1 Actual vs. predicted value of biodiesel

The graph of the predicted values obtained using the developed correlation versus actual values is shown in Figure 4.1. The
 plot contains a line of unit slope which is 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 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 the design expert software was successful in creating the correlation between the four process variables to the biodiese
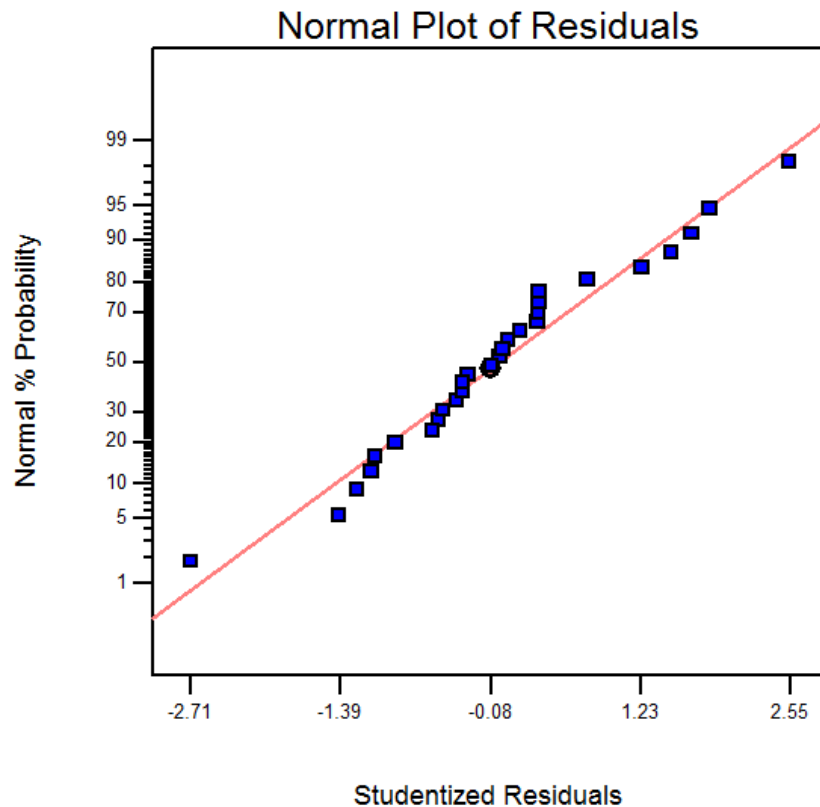
Figure 4.2: Normal plots of residuals

To identify the statistical properties of the model, the CCD normal probability plot of the residuals shows the normality of the model. Figure 4.2 shows the diagnostic graph of the model.The data points should be approximately linear. A nonlinear pattern indicates in the error term which may be corrected by transformation. From figure 4.2 there is no any sign of any abnormality in the model.

4.4 Effect of process parameters

Based on the analysis of variance, the transesterification reaction was significantly by various interactions between the process variables. This result demonstrated the advantage of using design of experiments in capturing the interactions 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.
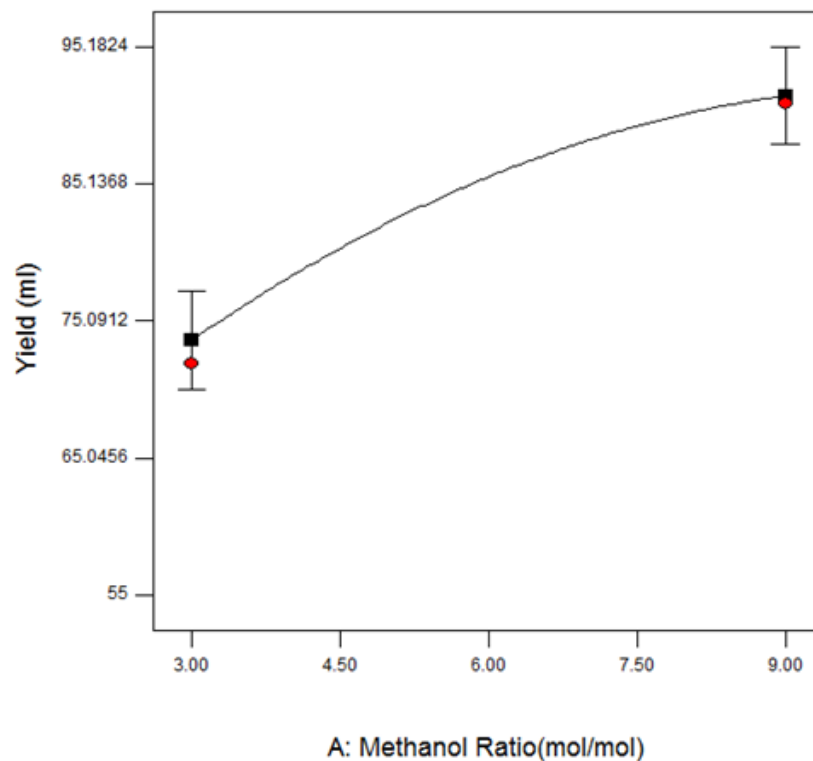
Figure 4.3: Effect of methanol-to-oil molar ratio on biodiesel yield

The methanol-to-oil ratio is one of the important factors that affect the conversion of triglyceride to biodiesel. Stoichiometriclly, 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 biodiesel as products. The results obtained in this study are in agreement with this. As shown in Figure 4.3, the methanol-to-oil ratio showed positive influence to the yield of methyl ester, the yield started to increase as the ratio is increased. The increase is due to the positive sign in the experimental model an higher ratio of methanol used allow for complete conversion of the oil to biodiesel.

4. 4.1 Effect of catalyst concentration

From Figure 4.4, it was observed that the catalyst concentration influenced the biodiesel yield in a positive manner up to a certain concentration. Beyond this concentration the yield decreased with increase in potassium hydroxide concentration. When the catalyst amount

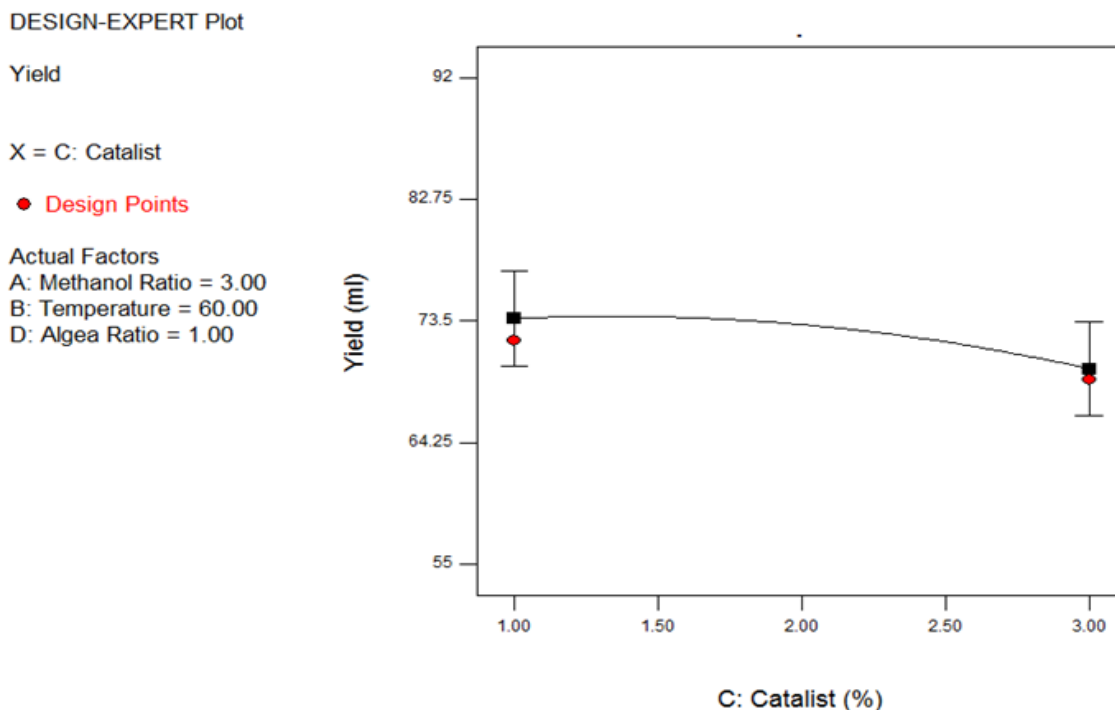was improved, which is the interactive (active) site of the catalyst increased biodiesel yield was decrease.

DESIGN-EXPERT Plot

Yield

X = C: Catalist

● Design Points

Actual Factors
A: Methanol Ratio = 3.00
B: Temperature = 60.00
D: Algea Ratio = 1.00

Figure 4.4: Effect of catalyst concentration

4.4.2 Effect of Temperature

As it can be shown below in Figure 4.5 when the temperature increase the viscosity of the oil decrease and the reaction is facilitated which leads to the increase on the yield of biodiesel. But after the temperature reached to an optimum value the yield start to decline. The increase in the methyl ester content up to an optimum temperature might have been due to the decrease of viscosity of the oil with an elevation of reaction temperature, which results in an increase in the solubility of the oil in the methanol, leading to an improvement in the contact between the oil and the methanol. Hence, the reaction was faster at a higher temperature. But at a maximum reaction temperature the transesterfication process yield was too low. This might be due to the fact that the required methanol to oil ratio doesn't kept in the reactor because at higher temperature (temperature near or above the boiling point of methanol) the methanol is evaporated and not fully recovered by the reflux condenser. In

addition at higher temperature the saponification is higher and this hinders the separation of glycerol (Bournay *et al*., 2005).
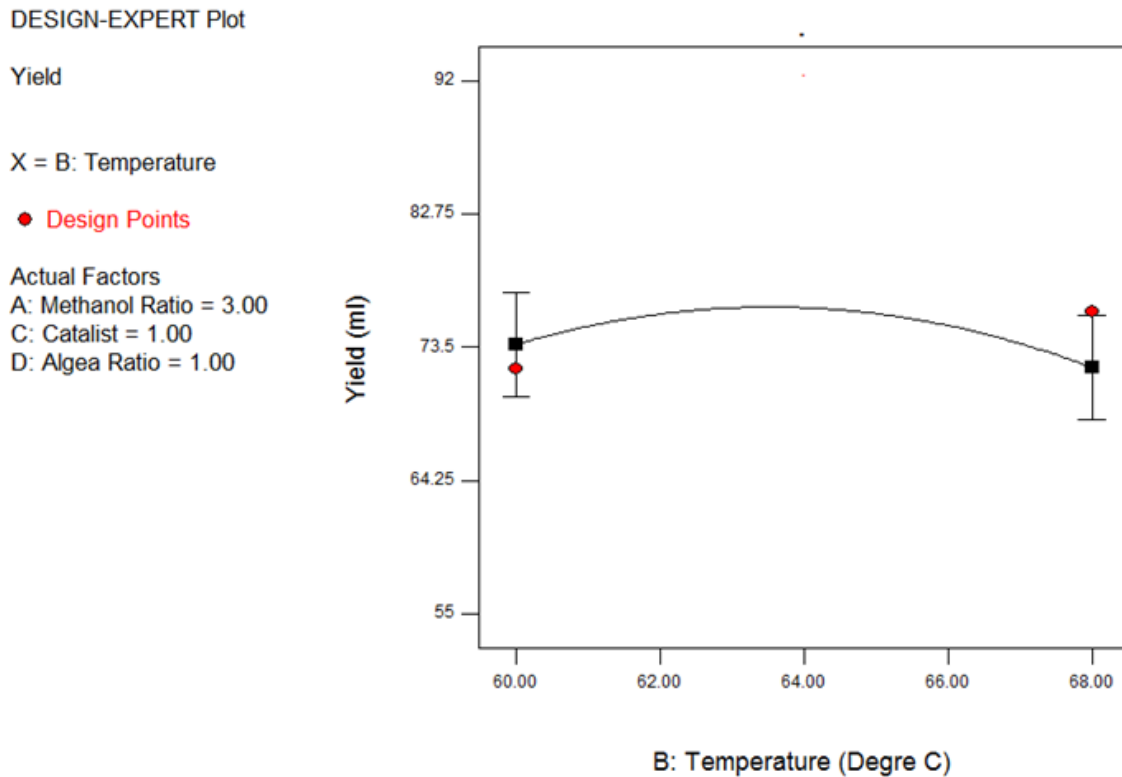

Figure 4.5: Effect of Temperature

4.4.3 Effect of Algae oil to WCO oil Ratio

TheAlgae oil to WCO oil Ratio decrease clearly influences the reaction rate and biodiesel yield in positive manner. The Algae oil to WCO oil Ratio decrease at 1 volume gives high yield of biodiesel. Through increase in Algae oil to WCO oil Ratio lead to low yield of biodiesel.

DESIGN-EXPERT Plot

Yield

X = D: Algea Ratio

● Design Points

Actual Factors
A: Methanol Ratio = 3.00
B: Temperature = 60.00
C: Catalist = 1.00
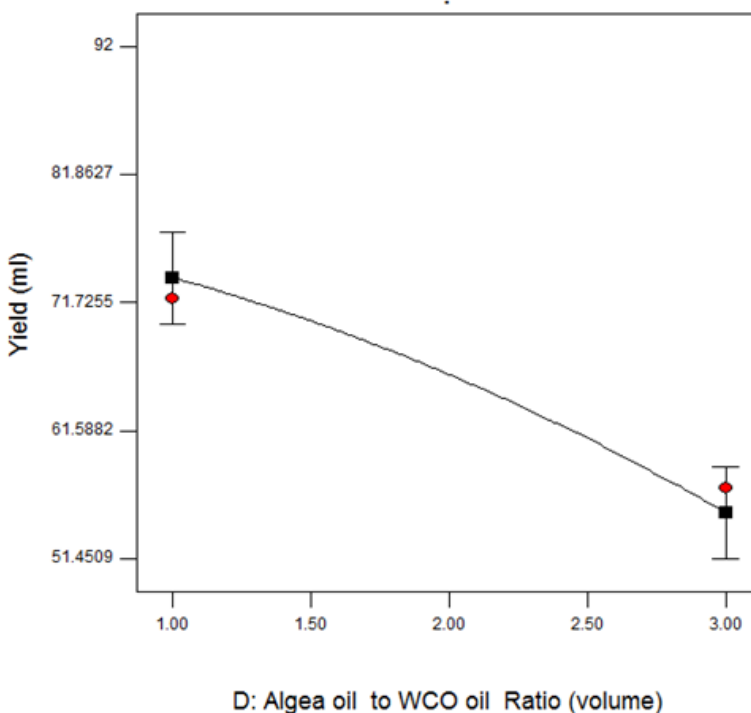
Figure 4.6: Effect of Algae oil to WCO oil Ratio

4. 4.4 Interaction Effect on the Yield

Contour plots and 3D Figures 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. The relationship between independent and dependent variables of the developed model in the response surface plots at the stationary value of 9:1 methanol-to-oil molar ratio, 1% catalyst concentration and 1 hr. reaction time is shown in Figure 4.7.
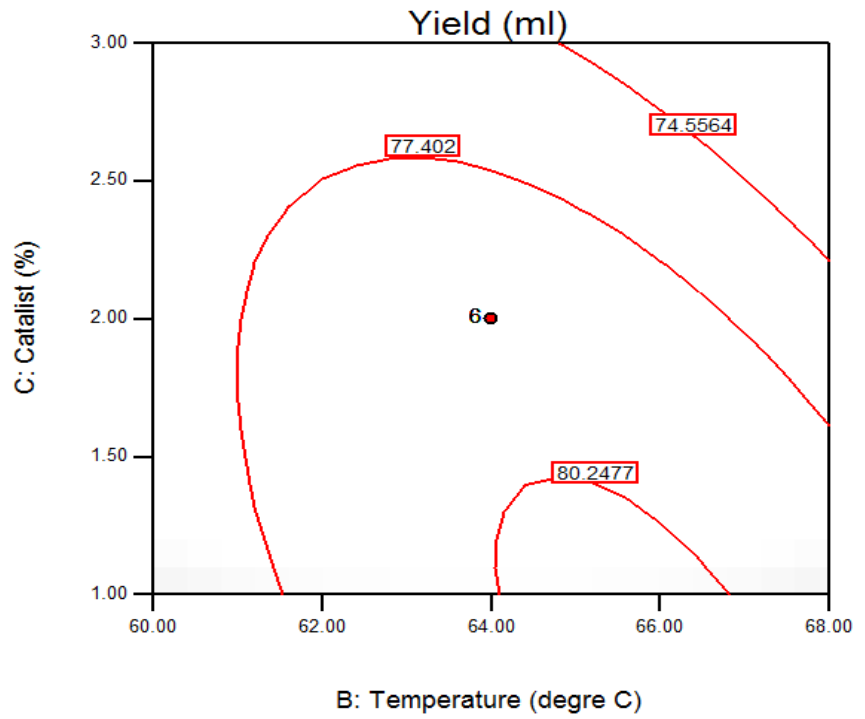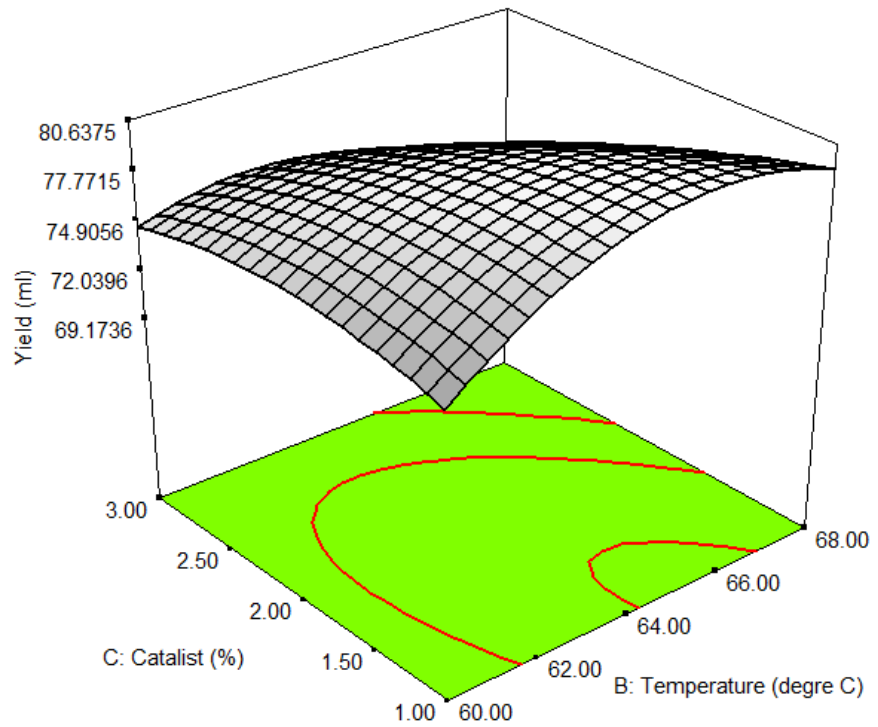
DESIGN-EXPERT Plot

Yield
• Design Points

X = B: Temperature
Y = C: Catalist

Actual Factors
A: Methanol Ratio = 6.00
D: Algea Ratio = 2.00

DESIGN-EXPERT Plot

Yield
X = B: Temperature
Y = C: Catalist

Actual Factors
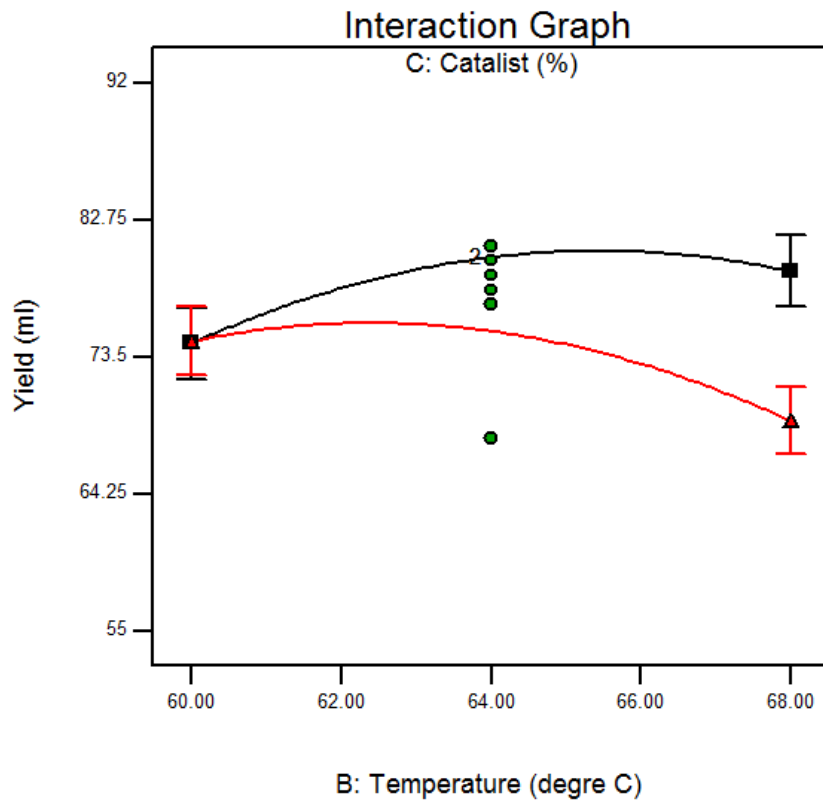A: Methanol Ratio = 6.00
D: Algea Ratio = 2.00

Figure 4.7 Effect of temperature & catalyst on biodiesel yield

From Figure 4.7., it can be seen that the yield of the biodiesel increased for an increase in temperature up to the optimum degree at a lower catalyst concentration but as both the temperature and the catalyst increase the cumulative effect led to increase in the yield. This could be due to the fact that only the temperature was enough to make the reaction go forward.
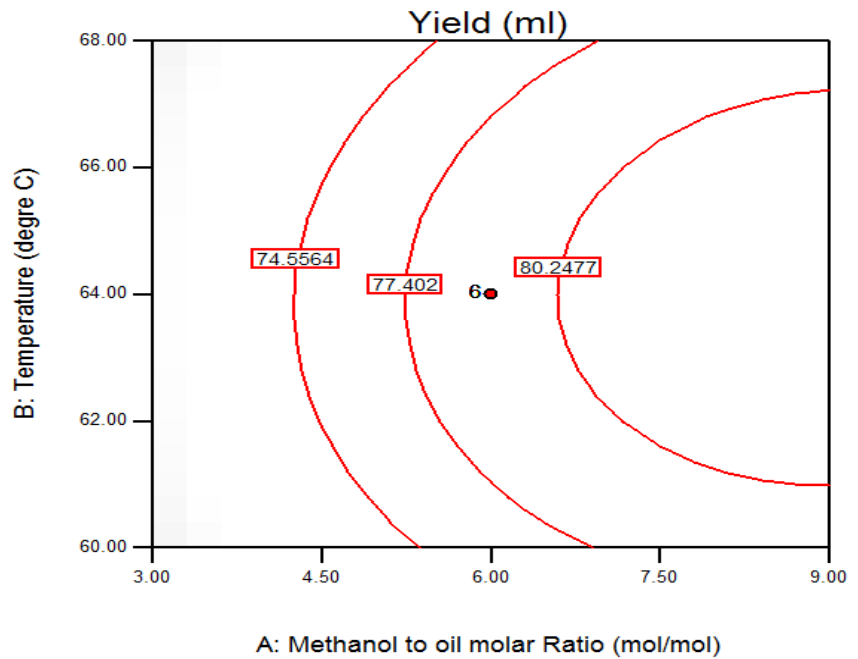
DESIGN-EXPERT Plot

Yield
• Design Points

X = A: Methanol Ratio
Y = B: Temperature

Actual Factors
C: Catalist = 2.00
D: Algea Ratio = 2.00

Yield (ml)
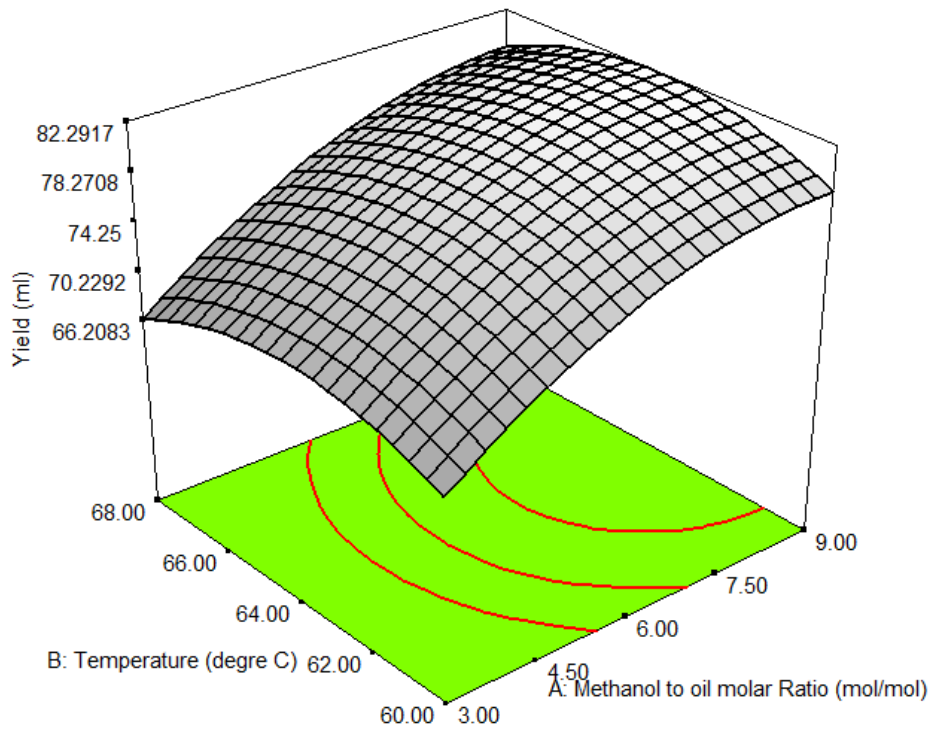
DESIGN-EXPERT Plot

Yield
X = A: Methanol Ratio
Y = B: Temperature

Actual Factors
C: Catalist = 2.00
D: Algea Ratio = 2.00

DESIGN-EXPERT Plot

Yield

X = A: Methanol Ratio
Y = B: Temperature

● Design Points

■ B- 60.000
▲ B+ 68.000
Actual Factors
C: Catalist = 2.00
D: Algea Ratio = 2.00

Interaction Graph
B: Temperature (degre C)

Yield (ml)

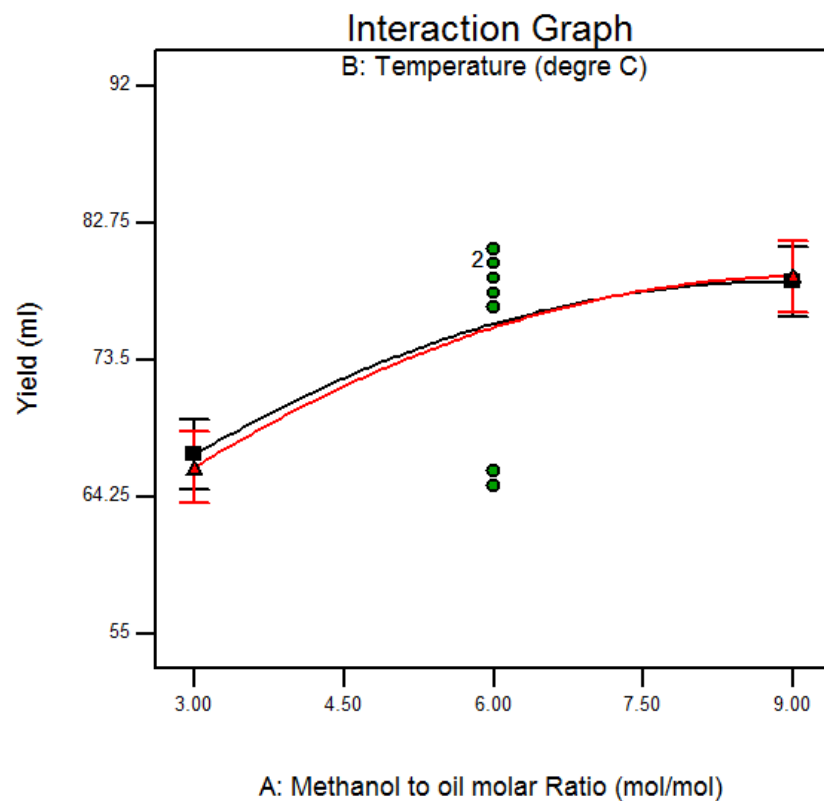A: Methanol to oil molar Ratio (mol/mol)

Figure 4.8 Effect of temperature & methanol to oil molar ratio on biodiesel yield

Figure 4.8 shows the effect of temperature and methanol to oil molar ratio on biodiesel yield when the catalyst concentration is 1%. As the temperature of the reaction increased at lower oil to molar ratio, the yield of biodiesel increased. The biodiesel yield also increases as the methanol to oil ratio increased to an optimal level.
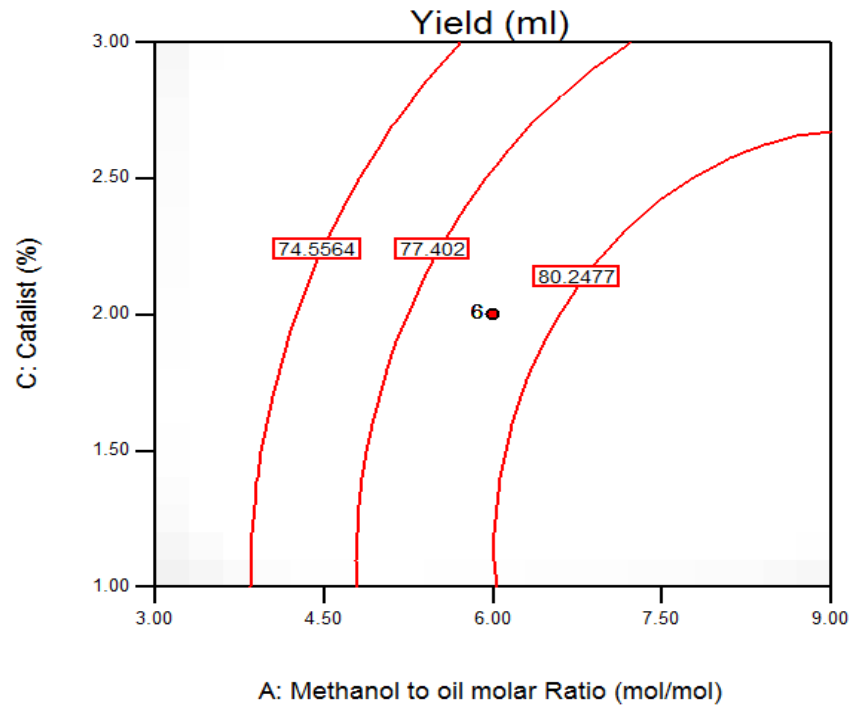
65

Yield
• Design Points

X = A: Methanol Ratio
Y = C: Catalist

Actual Factors
B: Temperature = 64.00
D: Algea Ratio = 2.00

Yield (ml)

C: Catalist (%)

74.5564   77.402   80.2477

6

A: Methanol to oil molar Ratio (mol/mol)

DESIGN-EXPERT Plot

Yield
X = A: Methanol Ratio
Y = C: Catalist

Actual Factors
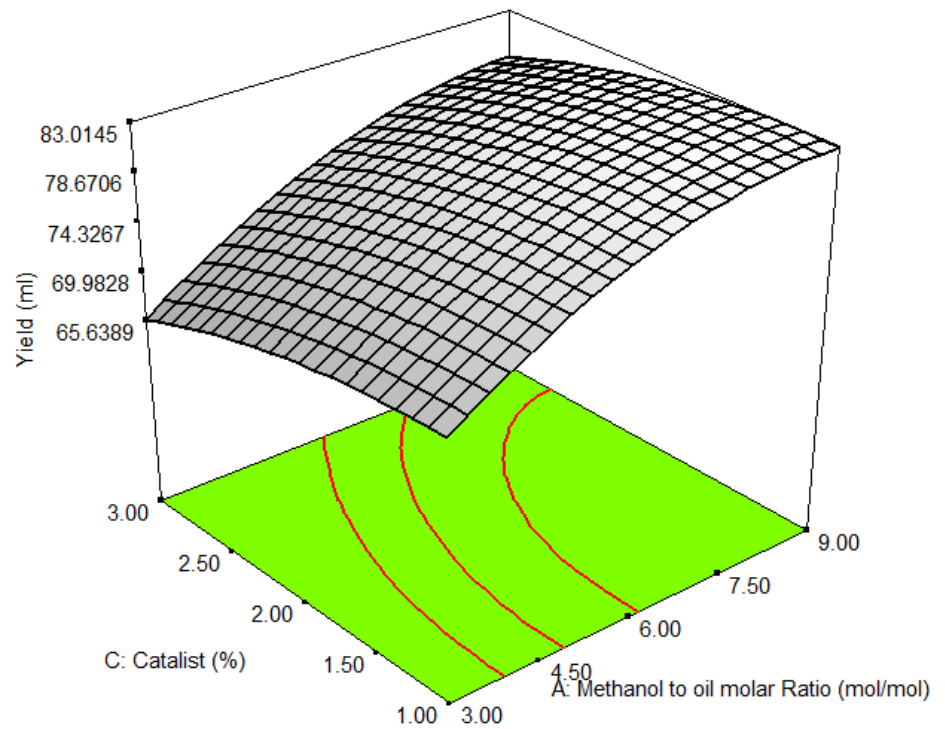B: Temperature = 64.00
D: Algea Ratio = 2.00

Yield (ml)

83.0145
78.6706
74.3267
69.9828
65.6389

C: Catalist (%)

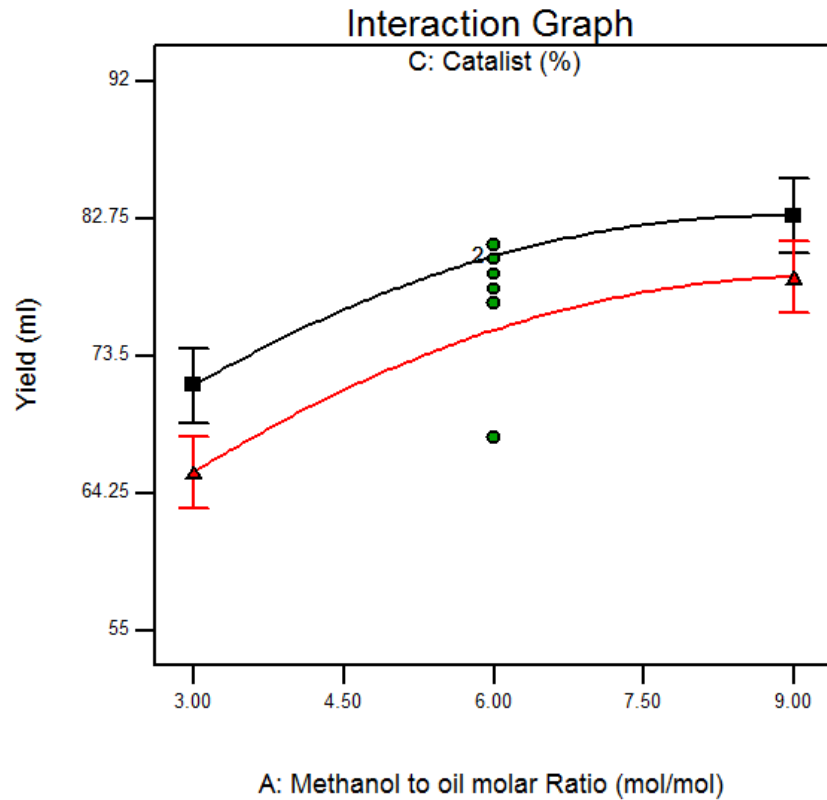A: Methanol to oil molar Ratio (mol/mol)

66

Figure 4.9 Effect of methanol to oil molar ratio & catalyst on biodiesel yield

From Figure 4.9 it can be seen that the biodiesel yield increase when the catalyst concentration increase. But after an optimal concentration level, the yield starts to increase. Similarly when the methanol to oil ratio increased at first, the yield also increased. However after the methanol to oil ratio reached an optimal level the yield started to decline. The increase of yield to an optimal level as the catalyst increases could be due to the increase on miscibility of methanol and triglyceride in the oil which facilitates the transesterfication reaction.However for further increase of catalyst the yield started to decline this could be due to the formation of soap which hinders the separation of glycerol from biodiesel. On a similar manner, when the methanol to oil ratio increased the yield also increased while a further increase in the molar ratio reduced the biodiesel yield (Freedman *et al*., 1984).

Yield
• Design Points

X = A: Methanol Ratio
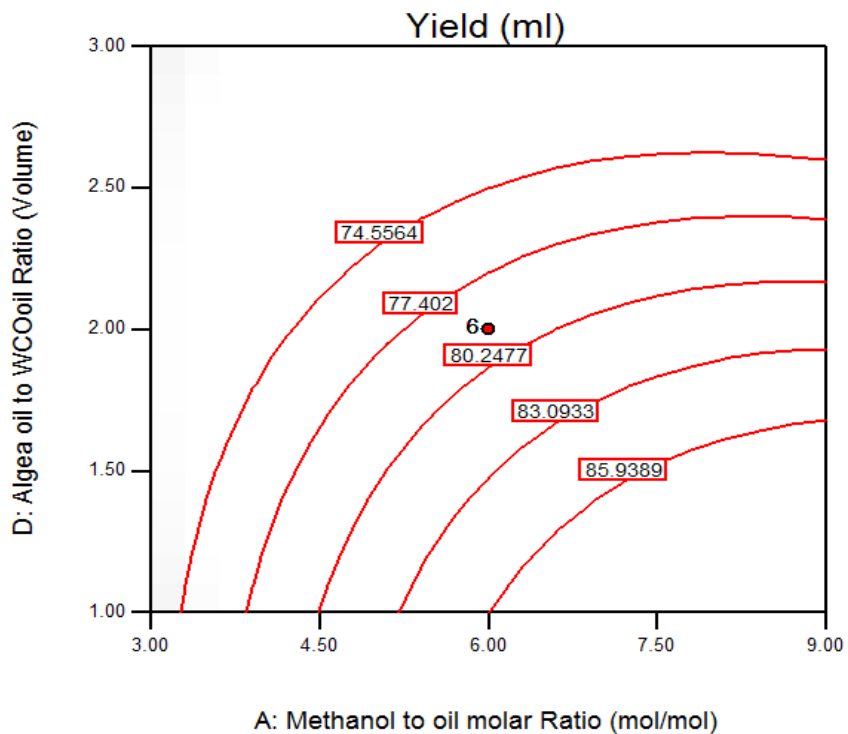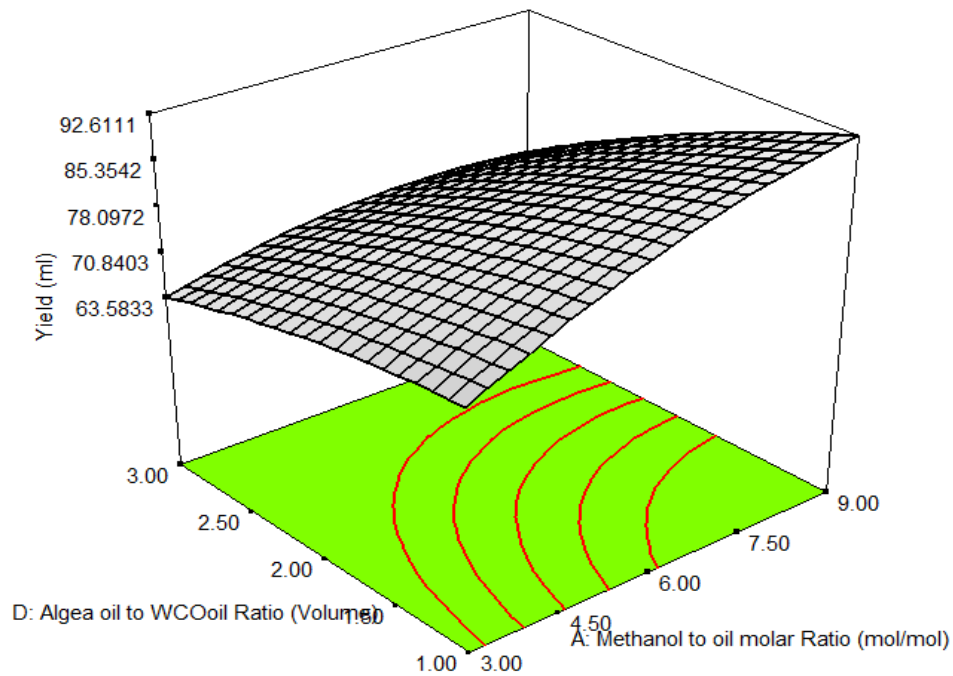Y = D: Algea Ratio

Actual Factors
B: Temperature = 64.00
C: Catalist = 2.00

Yield (ml)

DESIGN-EXPERT Plot

Yield
X = A: Methanol Ratio
Y = D: Algea Ratio

Actual Factors
B: Temperature = 64.00
C: Catalist = 2.00
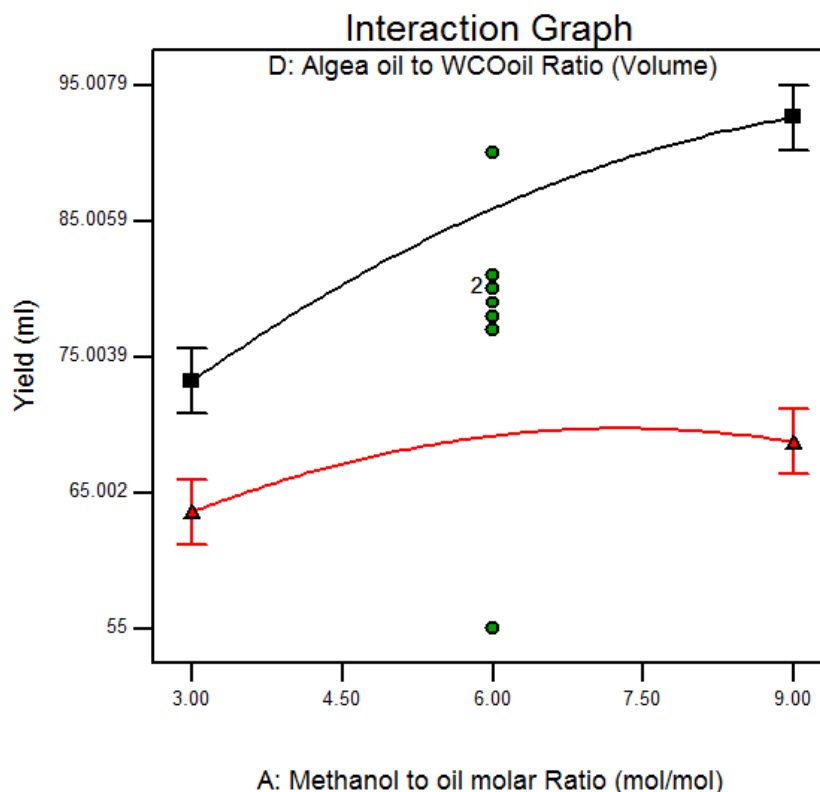
Figure 4.10 Effect of methanol to oil molar ratio & Algae and wco oil on biodiesel

From Figure 4.10 it can be seen that the biodiesel yield increase when the Algae oil to wco oil concentration increase. But after an optimal concentration level, the yield starts to increase. Similarly when the methanol to oil ratio increased at first, the yield also increased. However after the methanol to oil ratio reached an optimal level the yield started to decline. The increase of yield to an optimal level as the Algae oil to wco increases could be due to the increase on miscibility of methanol and triglyceride in the oil which facilitates the transesterfication reaction. However for further increase of Algae oil to wco the yield started to decline this could be due to the formation of soap which hinders the separation of glycerol from biodiesel. On a similar manner, when the methanol to oil ratio increased the yield also increased while a further increase in the molar ratio reduced the biodiesel yield.

DESIGN-EXPERT Plot

Yield
X = B: Temperature
Y = D: Algea Ratio

Actual Factors
A: Methanol Ratio = 6.00
C: Catalist = 2.00

Figure 4.11 Effect of temperature & Algae oil to wco oil on biodiesel yield

From Figure 4.11., it can be seen that the yield of the biodiesel decreased for an increase in temperature up to the optimum degree at a lower Algae oil to wco concentration but as both the temperature and the Algae oil to wco increase the cumulative effect led to a decrease in the yield. This could be due to the fact that only the temperature was enough to make the reaction go forward.

DESIGN-EXPERT Plot

Yield

X = B: Temperature
Y = D: Algea Ratio

● Design Points

■ D- 1.000
▲ D+ 3.000
Actual Factors
A: Methanol Ratio = 6.00
C: Catalist = 2.00

Interaction Graph

D: Algea oil to WCOoil Ratio (Volume)

Yield (ml)

B: Temperature (degre C)
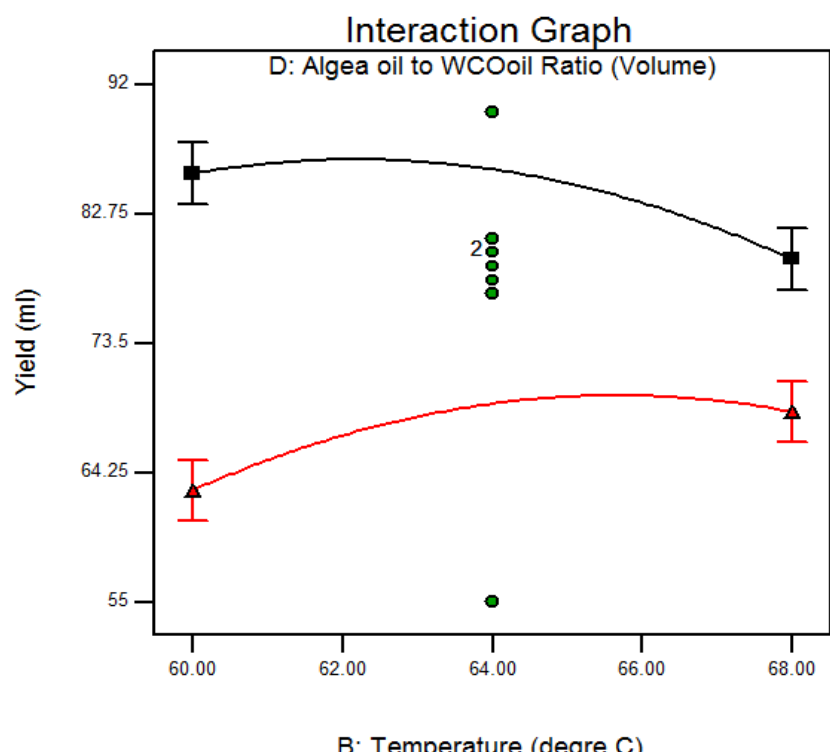
DESIGN-EXPERT Plot

Yield
● Design Points

X = C: Catalist
Y = D: Algea Ratio
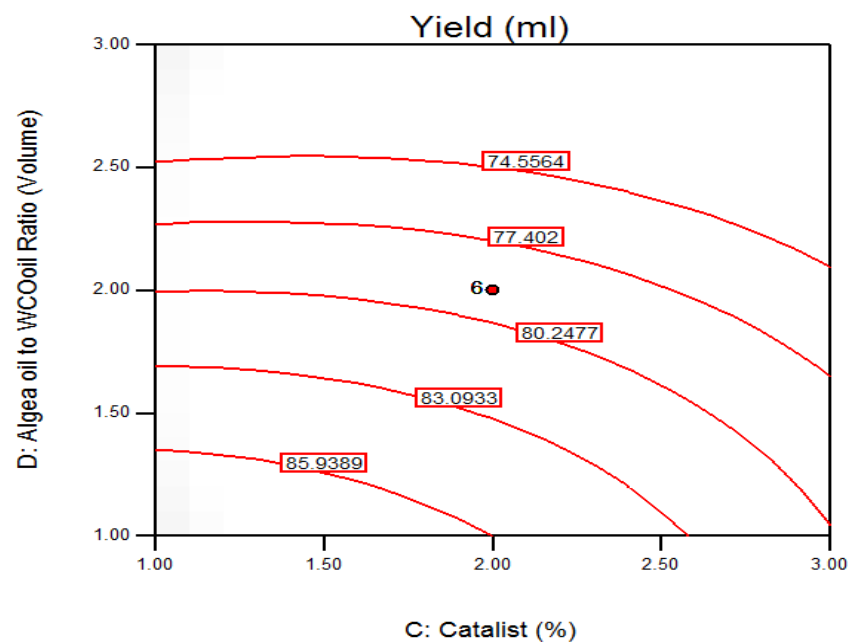
Actual Factors
A: Methanol Ratio = 6.00
B: Temperature = 64.00

Yield (ml)

74.5564

77.402

80.2477

83.0933

85.9389

D: Algea oil to WCOoil Ratio (Volume)

C: Catalist (%)

71

Yield
X = C: Catalist
Y = D: Algea Ratio

Actual Factors
A: Methanol Ratio = 6.00
B: Temperature = 64.00

DESIGN-EXPERT Plot

Yield

X = C: Catalist
Y = D: Algea Ratio
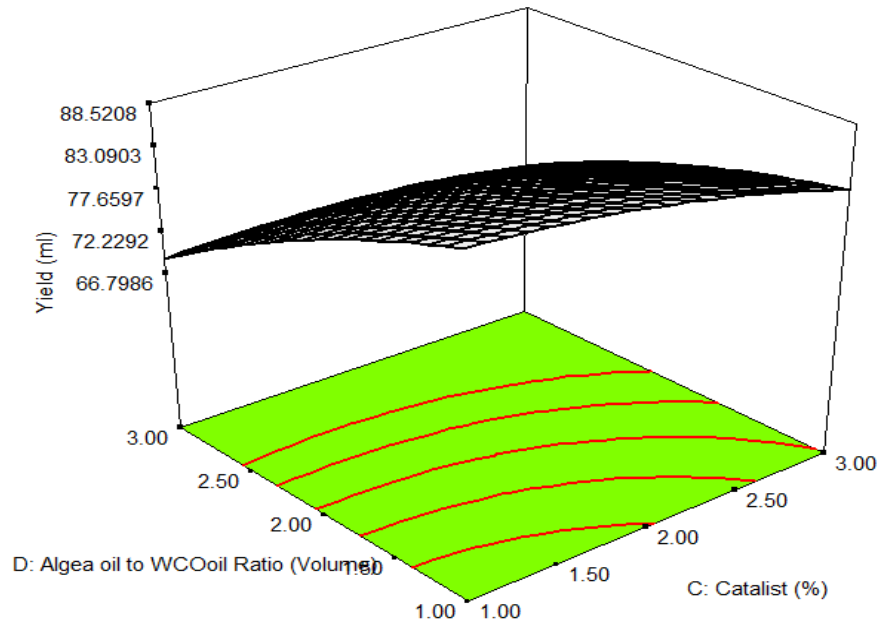
● Design Points

■ D- 1.000
▲ D+ 3.000
Actual Factors
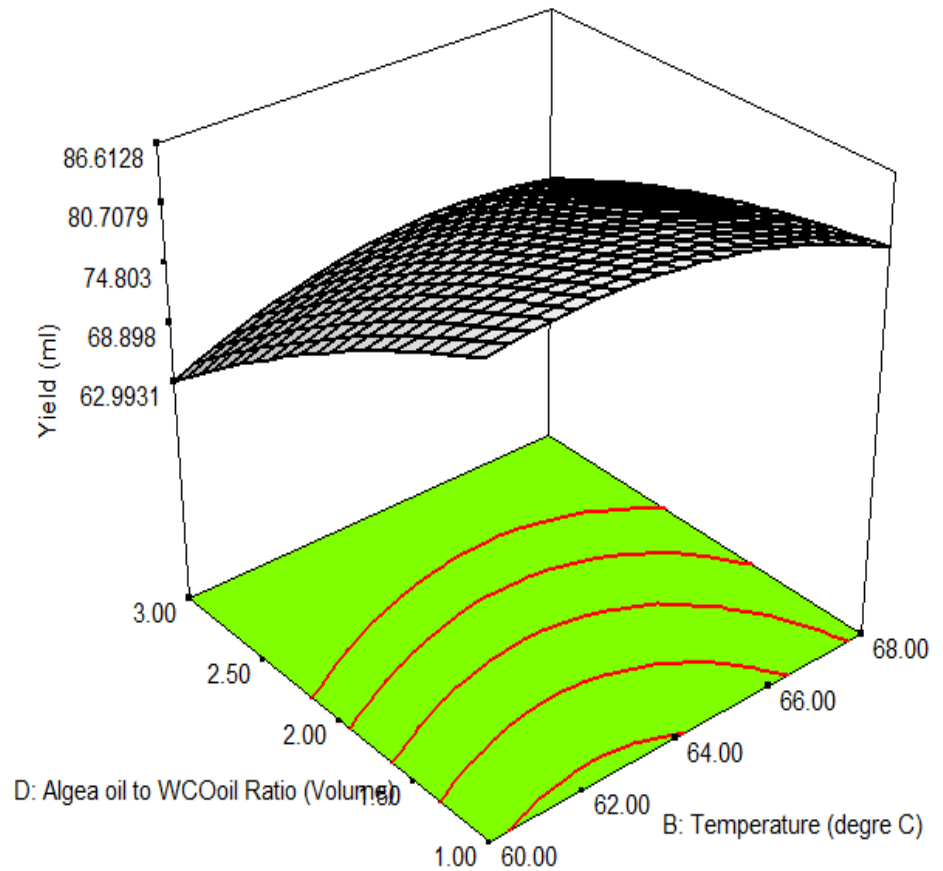A: Methanol Ratio = 6.00
B: Temperature = 64.00
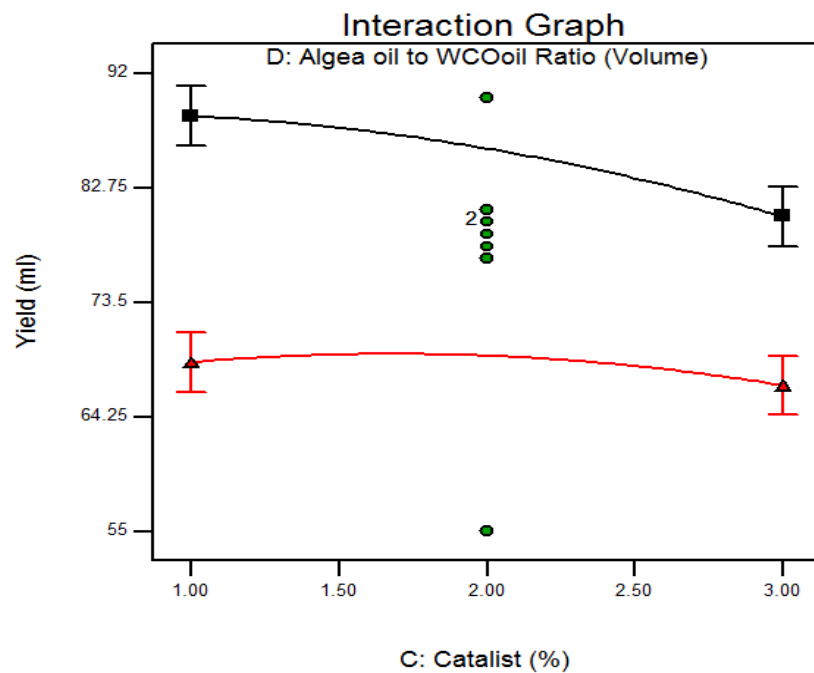
Figure 4.12 Effect of Algae oil to wco oil ratio & catalyst on biodiesel yield

From Figure 4.12. it can be seen that the yield of the biodiesel decreased for an increase in Algae oil to wco up to the optimum degree at a lower catalyst concentration but as both the Algae oil to wco and the catalyst increase the cumulative effect led to adecrease in

the yield. This could be due to the fact that only the Algae oil to wco was enough to make the reaction go forward.

4.5 Optimization of Process Variables

The optimization function in Design Expert 6.0.8 software was employed for the optimization of process variables. The goal of the four variables temperature, catalyst concentration, Algae oil to WCO oil ratio and methanol to oil molar ratio was set in range and the goal of the response was set to maximize. Accordingly, the optimum result predicted was 79.1667 ml at the process variable of reaction temperature 62.34 0C, catalyst concentration of 2.98 % and methanol to oil ratio of 5.90 and Algae oil to WCO oil ratio 1.90.

Table 4.9 optimization of process variables

Constraints Name	Goal	Lower limit	Upper Limit	Lower Weight	Upper weight	Importance
`Methanol Ratio	is in range	3	9	1	1	3
Temperature	is inrange	60	68	1	1	3
Catalyst	is in range	1	3	1	1	3
Algae Ratio	is in range	1	3	1	1	3
Yield	Maximize	55	92	1	1	3

Solutions

Solutions number	Temperate	Catalyst	Molar Ratio	Algae Ratio	Yield	Desirability	Remark	Solutions number
1	62.34	2.98	5.90	1.90	79.1667 ml	1.000	selected	

Methanol Ratio* (has no effect) =5.90   Temperature* (has no effect) =62.34

Catalist* (has no effect) = 2.98   Algea Ratio* (has no effect)

=1.90

Desirability =1.000
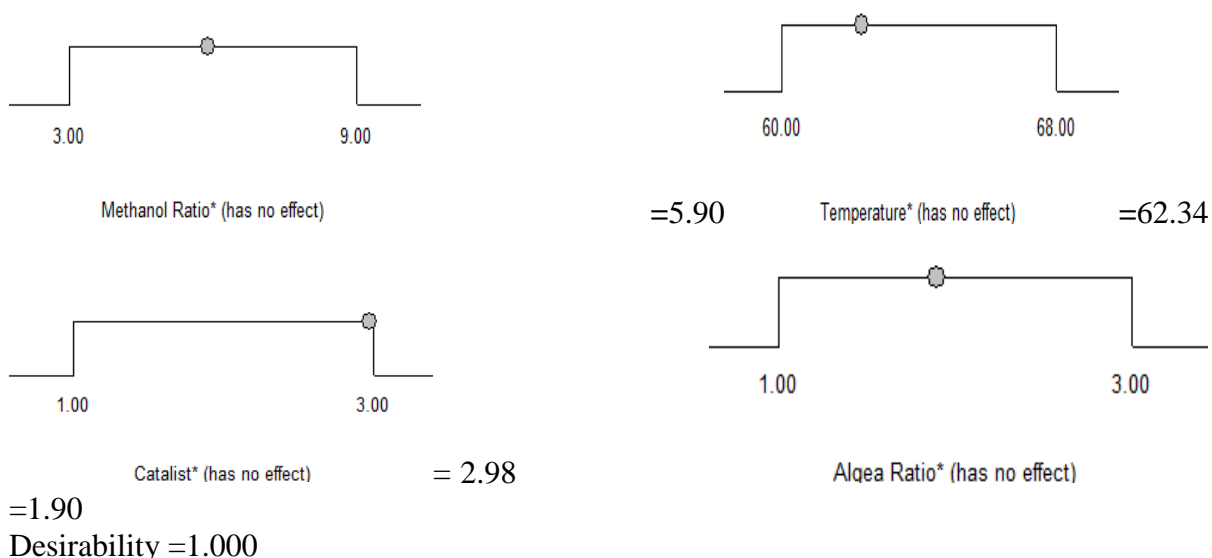
Figure 4.13 Optimization of process variables

To check the optimum process value experiment was conducted at specified parameters yield obtained through the experiment at temperature of 62.34, catalyst concentration of 2.98, a gas to cook oil ratio 1.90 and methanol to oil molar ratio of 5.90 was 79.1667 ml which is near to the value obtained using the design expert software.

4.6 physiochemical properties of biodiesel

The physicochemical properties of the biodiesel determined titration and empirical formulas.

Table 4.10: Physicochemical properties of biodiesel

Physiochemical properties	Unit	Value
SG (15 ^{0}c)	g/cm^3	0.88
Density (40 ^{o}C)	g/cm^3	0.89
Acid Value	mgKOH/g	0.89
FFA	%	0.445
HHV	MJ/Kg	42.37
Iodine Value	I^{2}g/100g	12.9
Saponification value	mgKOH/g	146.1
Viscosity (40 ^{0}c)	Mm^{2}s^{-1}	9.05
Flash point	0C	180

4.6.1 Specific Gravity

Both the SG and density was measured by digital density meter. SG of biodiesel was found to be 889kg/m^3. The density of biodiesel produced were found to be 890kg/m^3.the salts are compared with the range specified byEN14124(860-900) kg/m^3 and with the ASTMD6751 for FAME870-890 kg/m^{3}is acceptable. The change in the density shows that the density of the biodiesel decreased with increase molar ratio. This was probably due to a decreased in residualtriglycerides. THE density of the biodiesel decreased with influence of the catalyst amount and temperature.

4.6.2 Viscosity

Viscosity is the most important of FAME since itaffects the operation of fuel injection equipment's particularly at low temperature when the increases in Viscosity affect the fluiditymm2/sec. at 40^{0}C.Generaly the Kinematic viscosity of FAME was higher compared to that of fossil diesel (3,6mm^2/sec) the implication was that FAME has lubricating effect in engines which will be an added advantage to user. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injection. As the result were presented in Table 4.10 the Kinematic viscosity value 9.05.

4.6.3 Acid value

The acid values of biodiesel product were found to be 0.82 mg KOH/g' the result indicates that acid value of the diesel decreased significantly after transit sterilization 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 factor affecting storage ability. Oxidation is usually accompanied by an increase in acid value and viscosity of the fuel. In the presence of water the ester can hydrolyzed to long chain FFA, which also causes the acid value to increase. the acid value or neutralization number is a measure of mineral acid and free fatty acid contained in a fuel sample. It is expressed in mg KOH required to neutralize 1g of fatty acid methyl ester and it sets to maximum value of0.5 and 0.8mgKOH/g in the EN-14214 and ASTMD664 specification respectively.

4.6.4 Higher heating value

The heating value depends on the composition of the fuel. Since all the oil have very nearly the same carbon, hydrogen, and oxygen contents the gross and net heating value of each fuel per unit mass will be closed to each other. Biodiesel has lower energy content (lower heating value) than conventional diesel fuel. The heat of combustion refers to the measure of energy content in the fuel. Heating value of fuels is an important measure of its releasing energy for producing work. As the results presented in Table 4.10 the highest calorific value was 43.37MJ/kg which is in agreement with standard specification limit EN14214(>35MJ/kg).

4.6.5 Iodine value

The iodine index is measured as iodine adsorbed as iodine(g) per 100g of sample, and is related to the level of un saturation (double bond) present in the oil i.e. the higher the un saturation content the higher iodine index. Iodine value is used to measure the chemical stability property of substance against oxidation and the higher the iodine value the higher the number of double bond hence lesser stability. It can be observed from table4.10 that the iodine value is 12.9 g12/100g. The result was in the acceptable value as the upper limit for EN14214 standard is 120g12/100g. The ASTM requirement is maximum of 115. In general the result of iodine value of FAME yield revealed higher value compared with that of fossil diesel (9.5 g12/100g). This shows that the fossil diesel is more stable compared to the FAME. However the double bonds in a biodiesel help attract oxygen to the compound and aid proper burning of biodiesel over fossil and affect the FAME to polymerase easily.

4.6.6 Cetane Number

Cetane Number Is a dimensionless indicator of the ignition quality of a FAME ,if the Cetane number is high ,combustion can occur before the fuel and air are properly mixed, resulting in incomplete combustion and smoke, and if is low, engine roughness, misfiring, higher air temperatures ,slower engine warm-up, and also incomplete combustion occur. As the result shown in Table 4.10 the cetane number were found to be 46.77 and the result were similar with standard specification limit of ASTM, diesel engines will operate on fuels with Cetane number> 47(ASTM D623).

4.6.7 Flash Point

Flash point is the lowest temperature by which a fuel vapors will ignite in air. A nonflammable FAME should have flash point high enough to within the standard limit for save storage purpose. High content of methanol will lower the flash point and viscosity of the FAME and thus lead to dangerous storage stabilities. The higher the flash the saver the fuel and viceversal. As result shown in Table 4.10 the flash point were found to be 170 ^{0}C.the result was in agreement within the lower limit of standard with120 ^{0}C (EN14214) and 130 ^{0}C (ASTM D6751) and similar with previous study. The flash point of FAME was higher than that of fossil diesel (70 ^{0}C) and therefore, it could be said that FAME is safer to handle than fossil diesel. The flash point determined in oil was very high as compared to its methyl ester and diesel. The blending of Algae oil to WCO with petroleum diesel is known the flash point.

In general, the quality of the FAME fuel can be significantly influenced by several factors including: quality of feedstock, fatty acid composition the vegetable oil, type of production and refining process employed and purification steps.Properties like iodine number and viscosity are mostly depend upon the fatty acid composition of the raw oil. Other properties :viscosity, flash point and acid value are highly depends on to the purification process.to get rid of these contaminants,several purification techniques such as gravitational setting, distillation, evaporation, washing with distilled water has been employed to ensure the achievement of highly purified biodiesel.

4.6.8 Moisture Contents of Biodiesel

Determination of moisture contents of biodiesel was done in similar manner with that of oil m oisture content determination as discussed in Sections 3.2.2. Moisture content of the biodiesel was determined using equation 3.6 and recorded as 0.017%

4.6.9 Ash content of biodiesel

The same producer was employed in determinations of ash contents of biodiesel as it was discussed in ash content determination of algae and waste cooking oil. Using equation 3.7 the ash content of the biodiesel was calculated and obtained to 0.003%.

Table 4. 11: Biodiesel summary

Properties	Algae to WCO oil ratio FAME Values	ASTM D6751	EN14214
Density (kg/m3)	890	870–890	860–900
Kinematic Viscosity at 40oc (mm^2/sec)	4.5	1.9-6.0	3.5-5.0
Flash point (^{0}C)	170	130 Minimum	120 Minimum
Heating value MjKg-1	43.37		>35
Cetane number	46.77	> 47	
Acid Values(mg KOH/g)	0.82	≤ 0.8	≤ 0.5
Iodine values (I2g100g-1)	12.9	Maximum of 115.	120
Moisture Content (%w/w)	0.017	<0.03	
Ash Content(%w/w)	0.003	<0.03	<0.02

The density of the oil was reduced from 921 kg/m3 to 890 kg/m3 after the transesterification process and the result is within the limit of both the ASTM and EN14214. The kinematic viscosity measured for the biodiesel was found to be 4.5mm2/s. The kinematic viscosity of the original oil at 40 0C was 41.47mm2/s. As the result indicates, the methanolysis significantly reduces the kinematic viscosity of the primary algal oil by approximately one-nenth of its initial value. The results are still within the limit of the ASTM specification i.e. (1.9 – 6.0 mm2/s).the flash point was incerse from 168.33 ^{0}c to 170 ^{0}c after the transesterification process and the result is within the limit of both the ASTM and EN14214. The left of parametres the same to vibrate of the above discusion

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The waste oil are inexpensive and have many disposal problems like water and soil pollution, human health concern and disturbance to the aquatic ecosystem, so rather than disposing it and harming the environment, it can be used as an effective and cost efficient feedstock for biodiesel production. Extracted oil was further used for biodiesel production by transesterification process. Four factors at three levels were considered in the alkali catalytic transesterfication process. The individual and interaction effects of the four factors on biodiesel yield were analyzed and optimization of the process variables was made using design expert 6.0.8 software.

- A total 31.6% of oil was extracted from fresh algae through the soxhlet apparatus as motioned in material and method. This oil was then converted into methyl ester by the process of transesterification. Algae cooking oil methyl ester showed the better fuel properties compared to the oil.

- The statistical and experimental design was done by using design expert 6.0.8 software the outputs of the experiments conducted have been analyzed by employing physicochemical and instrumental parameter determination.

- Based on the experimental results, it was found that all the process variables exhibited significant individual and interaction effect on the yield of biodiesel. The effects of the methanol to oil molar ratio, catalyst concentration, and temperature and algae oil to waste cooking oil were investigated to determine the best strategy for producing biodiesel from algae oil to waste cooking.

- The fuel properties tested are within the ASTM and EN standards and were found to be very close to those of petroleum diesel.

- The results showed that transesterification improved the properties tested. Flash point, Acid value and density of the algae and waste cooking oil biodiesel were in the range of the ASTM and EN standards.

- The density and the viscosity were indicators of the biodiesel quality against the process variables. The viscosity of waste cooking oil and algae oil higher than that of diesel but similar with other researches.

- The calculated cetane number is low as compared with the standard.

- The iodine value is higher than the standard, 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 biodiesel of the blends of algae waste cooking oil has closer fuel properties to petroleum diesel.

5.2 Recommendations

The present study has enabled us to confirm that algae and WCO may be used as a resource to obtain biodiesel, which could offer more opportunities for generation of rural employment, increasing in come and protecting environment .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 should be carried out in future studies.

Additionally further research should be conducted on storage problem to increase the shelf life of biodiesel. It is also recommended to use the waste cooking oil and algae to biogas production of biodiesel from microalgae to use as substitute of petroleum fuel and mitigate environmental pollutions caused by fossil fuel consumption. Glycerol has relevance in soap industries but in this study the property of glycerol was not determined. Therefore, in addition to the production of biodiesel the property of the product glycerol should be analyzed and purified for further applications.

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APPENDICS

Table A1 centeral composite experimental design matrix

Run	Factors				Response
	Methanol to oil ratio	Temperature (^{0}C)	Catalyst (%) (wt/wt)	Algae oil to waste cooking oil ratio	
1.	6.00	64.00	2.00	4.00	55
2.	3.00	68.00	3.00	1.00	56
3.	3.00	60.00	1.00	3.00	57
4.	3.00	60.00	3.00	3.00	58
5.	9.00	60.00	1.00	3.00	59
6.	3.00	68.00	3.00	3.00	60
7.	3.00	68.00	1.00	3.00	61
8.	9.00	60.00	3.00	3.00	61
9.	9.00	68.00	3.00	3.00	64
10.	6.00	72.00	2.00	2.00	65
11.	6.00	56.00	2.00	2.00	66
12.	6.00	64.00	4.00	2.00	68
13.	3.00	60.00	3.00	1.00	69
14.	3.00	60.00	1.00	1.00	72
15.	9.00	68.00	1.00	3.00	73
16	3.00	68.00	1.00	1.00	76
17	6.00	64.00	2.00	2.00	77
18	6.00	64.00	2.00	2.00	78
19	6.00	64.00	2.00	2.00	79
20	12.00	64.00	2.00	2.00	79
21	9.00	68.00	3.00	1.00	79
22	6.00	64.00	2.00	2.00	80
23	6.00	64.00	2.00	2.00	80
24	6.00	64.00	2.00	2.00	81
25	9.00	68.00	1.00	1.00	89
26	6.00	64.00	2.00	0.00	90
27	9.00	60.00	1.00	1.00	91
28	9.00	60.00	3.00	1.00	92
29	6.00	64.00	0.00	2.00	
30	0.00	64.00	2.00	2.00	

Note:. Run of 29 and 30 the miss of response

Table A2 the amount of catalyst and methanol

methanol Oil to methanol ratio		Catalyst amount	
Ratio	Amount used (ml)		Amount used (g)
1:3	6.26	1%	0.47
1:6	12.52	2%	0.94
1:9	18.79	3%	1.41