ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY (AAiT)

SCHOOL OF CHEMICAL AND BIO- ENGINEERING

PRODUCTION AND CHARACTERIZATION OF BIODIESEL FROM AVOCADO PEEL OIL (APO)

By:

Tafere Aga

A thesis submitted to the school of graduate studies of Addis Ababa University in partial fulfillment of the requirement for the Masters degree in chemical engineering (process engineering stream)

Advisor: Dr. Eng. Abubeker Yimam

Addis Ababa

Ethiopia

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The undersigned have examined the thesis "Production and Characterization of Biodiesel from avocado Peel oil (APO)" presented by Tafere Aga, a candidate for the degree of Master Science in Chemical Engineering (Process Engineering)), and hereby certify that it is worthy of acceptance.

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DEDICATION

This thesis work is dedicated to God Almighty for his guidance and protection for the countless sacrifices made for my sake. This work also dedicated to my parents. I hereby declare that the thesis is based on my original work except for flotation's and citations which have been duly acknowledged .I also declare that it has not been previously or currently submitted for any other department at Addis Ababa University or other institute.

Tafere Aga

Signature: - ____________

Date: - 17/11/10 E.c

ABSTRACT

Biodiesel is as alternative energy source and a promising potential that grows rapidly, due to its great contribution to the environment, renewable, non-toxicity, biodegradability, essentially sulfur free and its role as a strategically source of renewable energy in substitution to diesel oil and contributes a minimal amount of net greenhouse gases.

In this study, biodiesel production from waste avocado peel oil was investigated in laboratory approach. Experimental results evaluate the major optimum process parameters for base-catalyzed transesterification on biodiesel yield as well as its properties. The most important variables affecting methyl ester yield during the transesterification reaction are the molar ratio of alcohol to oil and the reaction temperature.

From this thesis, the optimum operating conditions for the extraction of oil from avocado peel oil. For this, particle size of 2.6 mm, solvent type N-hexane and extraction time of 3-5 hr were considered. A general factorial design was applied to investigate the effect of process variables on oil yield and biodiesel. Maximum oil yield of 40.6% was obtained for particle size of 2.6 mm at extraction time of 5 hr. A 95.2% FAME conversion was also obtained using a methanol/oil ratio of 6:1, 1.21g NaOH, reaction time 67.5min and 60^0*C reaction temperature.*

The important properties (characterization) of the experimental biodiesel sample of the biodiesel (pH, specific gravity, API specific gravity, density, kinematic viscosity, cloud point, cetane number, iodine value, and high heating value) well-matched the relevant international standards for biodiesel quality, were compared to those of ASTM and EN standards for biodiesel. The comparison shows that the avocado peel oil used as a raw material for biodiesel production as an alternative fuel.

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First and foremost, I would like to thank to God for giving me health and patience to accomplish this thesis work. I would like to acknowledge my advisor Dr. Eng Abubeker Yimam for his efforts, comments, proper supervision of the thesis and reading the manuscript through my thesis. His knowledge and hands on experience in chemical engineering discipline has added greatly to the depth of information provided by this thesis. Next we would like to thankful to all Laboratory assistances in school of Chemical and Bio Engineering for their support and make the stay so pleasant. We would like to say 'thank you' to all of them.

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List of abbreviations and symbols

AAIT	*Addis Ababa Institute of Technology*
ANOVA	*Analysis of variance*
ASTM	*American Society for Testing and Materials*
API	*American Petroleum Institute*
APOs	*Avocado peel oil*
AV	*Acid Value*
BD	*Biodiesel*
Bxx	*x% biodiesel and x% petroleum diesel*
CARB	*California Air Resources Board*
CCD	*Central composite design*
CIE	*Compression Ignition engines*
CN	*Cetane number*
CSA	*central statistical agency*
CP	*Cloud point*
DOE	*Dept of Energy*
EN	*European Committee for Standardization*
EPA	*Environmental Protection Agency*
EU	*European Union*
FA	*Fatty Acid*
FAAE	*fatty acid alkyl esters*

FAME	*Fatty Acid Methyl Esters*
FAO	*Food and agricultural organization*
FFA	*free fatty acid*
FT-IR	*Fourier transforms infrared*
g	*gram*
RSM	*Response surface methodology*
HHVs	*The higher heating values*
HPLC	*High Performance Liquid Chromatography*
IV	*Iodine value*
NaOH	*sodium hydroxide*
SV	*Saponification value*
PP	*Pour point*
TG	*Triglyceride*
V	*Volume*
ρ	*Density*

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CHAPTER ONE

1. Introduction

1.1. Background

Biodiesel is the most promising alternative diesel fuel and the challenging of energy problem and sustainability in our today's world increases the number of population and sustainability have been problems due to the industrial revolution. Since it has received considerable attention due to it's a renewability, reliable, secure, biodegradability, clean, environmental eco-friendly, non-toxicity, energy efficient, less emission of gaseous and sustainable energy resources substitution of fuel which can fulfill energy security needs without sacrificing engine's operational performance thus it provides a feasible solution to the twin crises of fossil fuel depletion and environmental degradation. It meets the currently increasing huge demands of world energy which is dependent on petroleum based fuel resources. However, energy is often known as the primary success for a country's development. It is often used as an indicator to measure the level of economic growth in a country. The occurrence of oil depletion, global warming and the greenhouse effect has become an alarming condition where it is needed to search for an alternative energy source (Mazen et al, 2010).

Base catalyzed transesterification is the most commonly used technique as it is the most economical process base-catalyzed transesterification involves stripping the glycerin from the fatty acids with a catalyst such as sodium or potassium hydroxide, and replacing it with an anhydrous alcohol, usually methanol (van Gerpen, 2005).

Biodiesel is a renewable and biodegradable fuel to ensure the sustainability of energy resources, and produced from a wide range of naturally occurring fats and oils by a transesterification reaction in which the triglycerides are broken down and fatty acid methyl esters (FAMEs) are formed. The fatty acid distribution of the original oil is retained in the biodiesel, thus the physical and chemical properties of the biodiesel have some dependence on the feedstock used.

Biodiesel is a good alternative fuel for internal combustion engines, is defined as a mixture of monoalkyl esters of long chain fatty acids (FAME) derived from a renewable feedstock, such as vegetable oil or animal fat, which is one of the most promising energy sources for our country (Demirbas, 2005).

Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as methanol through transterification reaction. The reaction requires a catalyst, usually a strong base, such as sodium or potassium hydroxide, and produces new chemical compounds called methyl esters or known as biodiesel. It is a carbon free fuel because there is no overall increase in CO_2 in the atmosphere due to recycling by the growing plants used to feed the biodiesel industry. Emissions of SO_2, SO_3, CO, unburnt hydrocarbons and particulate matter are lower than that of petroleum diesel (Hiwot, 2017).

The most common process used to produce biodiesel is through transesterification, a reaction between triglycerides and an alcohol with a low molecular weight (ethanol or methanol) in the presence of a basic catalyst (NaOH or KOH), to obtain esters and glycerol . Any oil from peel, seed and also animal fat, can be used as a feed stock for the production of biodiesel. Since oils and biodiesel produced from different oils will likely have different physicochemical compositions and more importantly different properties.

Biodiesel can be used in ‘‘neat” form referred to as B100 or mixed with petroleum-based diesel. Petroleum and diesel come in the category of non-renewable fuel and will last for a limited period of time. Biodiesel is the first and only alternative fuel to commercial diesel to have a complete evaluation of emission results. Biodiesel is a good lubricant (about 66% better than petro diesel) (Koria &Thangaraj, 2010).

Biodiesel is a renewable fuel which is produced from vegetable oil or animal fat through a chemical process called transterification and can be used as either direct substitute, extender or as an additive to fossil diesel fuel in compression ignition engines. The most promising feature of biodiesel is that it can be utilized in existing design of diesel engine with no or very little modifications. It has a proven performance for air pollution reduction. Biodiesel is typically produced through the reaction of vegetable oils or animal fat with methanol or ethanol in the presence of catalyst to yield glycerol as major by- product and biodiesel chemically called methyl or ethyl ester. However, the price of biodiesel is presently more as compared to petro diesel, since higher cost of biodiesel is primarily due to the raw material cost.

There are different types of feed stocks that are used for the production of biodiesel. These includes linseed oil, palm seed oil ,waste cooked vegetable oil, sunflower seed oil, cotton seed oil, jatropha seed oil, castor beans oil and animal fats. Avocado peel oil are used for the production of biodiesel through the process called transesterification reaction which is a process by which alcohol reacts with vegetable oil in the presence of catalyst (Refaat, 2010).

Avocado peel is a waste where so many people are throwing away after using the fruit flesh. It is one of the most popular fruit in Ethiopia as a result there is a significant rise in avocado fruit consumption and consequently an increase in the avocado peel waste generation. Therefore, alternative routes are needed for this waste management. This waste cannot be used still for any consumption. The presence of nitrogen allows it to be directly used as fertilizer or as soil improver (or compost) (Hiwot, 2017). On the other hand, waste avocado peels have oil content of 8-40 % which can be used for biodiesel production. Avocado peels are used to evaluate the possibility of using and transforming waste to something valuable product, namely biodiesel there by contributing towards alternative energy supply as well as recycles what would be discarded and resolves energy scarcity.

Currently, about 84% of the world biodiesel production is met by rapeseed oil. The remaining 16 percent is from sun flower oil (13%), palm oil (1%), soybean and others (2%). Since more than 98% of the biodiesel is made from edible oil, there are many claims due to the depletion of edible oil supply worldwide. Therefore in order to overcome this problem, the feed stock for the biodiesel production must be replaced by non–edible oil, like oil extracted from waste substances. Therefore, for this study oil extracted from the waste avocado peels was used for the production of biodiesel because this have two advantage, one is waste management and second the oil is non-edible as a result it does not compete with food security (Hiwot, 2017).

Biodiesel is a clean-burning diesel fuel produced from vegetable oils, animal fats, or grease. Biodiesel as a fuel gives much lower toxic air emissions than fossil diesel. In addition, it gives cleaner burning and has less (free) sulfur content, and thus reducing emissions. Commercially, biodiesel is produced by transesterification of triglycerides which are the main ingredients of biological origin oils in the presence of an alcohol (e.g. methanol, ethanol) and a catalyst (e.g. alkali, acid, and enzyme) with glycerin as a major by-product (Hiwot, 2017).

1.2 Status of Biodiesel Production in Ethiopia

Ethiopia is among the developing countries, with over 45% of the population living below the poverty line. Significant improvements to Ethiopia’s trade balance are needed to stimulate the required economic development. One main issue is that around 65% of Ethiopian export earnings are needed to pay for the import of petroleum products. Despite the availability of huge energy resources in Ethiopia, the current level of harnessing this energy is very low. This, to a certain extent, depicts the poor socio-economic situation in the country on the one side, and a low level of awareness about the potential and value of energy by most stakeholders on the other side.

Ethiopia, being large country of diverse ecology, may harness the potential benefits from economic opportunities that may arise from biofuel production and also minimize the escalating budgetary pressure from a rise in international oil price. From international experiences, it has been shown that the production of biofuels, particularly at a large scale, may negative impacts on the society. Of course, positive impacts are also cited including response to price signals by smaller farmers and alleviating the environmental problems associated to the use of fossil fuels (Kalay, 2011). The development of biodiesel is a recent and at its initial stage there is no observable market use of biodiesel products in Ethiopia. However, within a short period of time a significant number of foreign, local and joint companies have invested in the biodiesel industry.

Currently more than 50 projects are in progress from which 14 companies are involved in the biodiesel industry and some of them have already started feedstock plantation for biodiesel production in five different regions (Benshangual Gumuz, Amhara, Oromia, SNNP and GPNRS), while others are at the pre-implementation stage (Kinfu, 2008). For example, in Benshangul Gumuz there is a major ongoing project of large scale jatropha plantation of more than 80,000 hectares. This project can produce more than 100 million liters of biodiesel per year, and if total production was converted to biodiesel, it would be equivalent to almost 15% of Ethiopia‘s current diesel consumption. Obviously, this will have a significant positive impact on Ethiopia’s trade balance. Additionally, the inward investment that this project brings will create a large number of jobs in the sectors helping to alleviate rural poverty. The search for feedstock other than jatropha is still at its ground level.

1.3. Statement of the problem

Due to the increase in population growth, finding an alternative fuel source for producing valuable products are needed more than ever. In our today's world the issues of energy shortage resulting from the depletion of world petroleum reserves, increase of petroleum prices and environmental concerns has initiate (stimulated) me to look for alternative renewable energy sources that are technically feasible, economically competitive and environmentally acceptable. A more convenient way is to use by- products (wastes) as potential sources due not only reduce the cost of production but also reduced health effect, since lack of proper management of fruit waste and not properly disposed this waste creates environmental problems in our country. A considerable amount of waste ends up in open dumps or drainage system, affecting both surface water and ground water.

Avocado peels waste largely obtained from hotels, restaurants and juice processing houses as a by-product in our country. Since this wastes can cause environmental problems unless they change or convert in to some useful products or disposed properly. Our country spends about birr10 billion annually to import petroleum products for domestic consumption (MOME). A convenient way to lower the cost of biodiesel is to use the by-product like cheaper feedstock (waste like, avocado peel oil) as a potential source of energy, rather than treat them as waste. This can be used to improve the economics of biodiesel which will lower the price of petroleum diesel.

1.4. Objectives

1.4.1. General objective

The general objective of this thesis is to produce and characterize biodiesel from avocado peels oil.

1.4.2. Specific objective

- ✓ To extract the oil from the avocado peels by Soxhlet extraction method.
- ✓ To investigate the effect of particle size, extraction temperature and extraction time on the quantity of avocado peel oil.
- ✓ Characterizing the physicochemical properties of oil that express (specific gravity, free fatty acid, pH, refractive index, acid value and density).
- ✓ To produce biodiesel from avocado peel oil through transesterification process.
- ✓ Characterizing the fuel (biodiesel) physicochemical properties such as, acid value, saponification number, density, kinematic viscosity, iodine value, flash point, cetane number, heating value and cloud point by and empirical formula.

1.5. Significance of the Thesis

The significance of this thesis is to use non-edible vegetable oil as source of biodiesel production to maintain important of food consumption oil. The use of non-edible vegetable oils for biodiesel production as compared to edible oils is very significant in developing countries because of the tremendous demand for edible oils as food and they are far too expensive to be used as fuel at present. In this context, recently biodiesel derived from vegetable oil has been shown to be a potential alternative replacing petroleum-derived diesel oil for diesel engine. Although there is continuous increase in the production of vegetable oil, however the ending stocks of vegetable oils are continuously decreasing due to increasing production of biodiesel.

Everything we do is connected to energy in one form or other. All energy sources have an impact on the environment. Concerns about the greenhouse effect and global warming, air pollution, and energy security have led to increasing interest and more development in renewable energy sources such as biofuel, solar, wind, geothermal, and hydrogen. But we continue to use the non-renewable fossil fuels and nuclear energy until now, the clear technologies that should replace this non- renewable resource are renewable source like, biodiesel which is environmentally friendly.

Eventually, with the implementation of biodiesel as a substitute fuel for petroleum-derived diesel oil, this may lead to the depletion of edible-oil supply worldwide. So, avocado peel oil is chosen as non-edible oil to produce biodiesel. It was chosen for the study because it widely available has no other commercial uses and would not compete for other uses such as consumption. It grows very well in Ethiopia.

1.6. Scope of the Thesis

The work presented in this thesis was the production of biodiesel from avocado peels oil based on the availability of raw material. Utilization of crude avocado peels oil for production of biodiesel will prevent further wastage of already existing resources and use of environmentally friendly fuel will create cleaner environment. The main scope of this thesis was mentioned as the following:

- ✓ Avocado peel collection

- ✓ Oil extraction and study of physiochemical characterization of extracted oil.
- ✓ Study of methods employed in production of biodiesel, i.e. trans-esterification
- ✓ To obtain biodiesel from the extracted oil by transesterification.
- ✓ Characterization of the produced biodiesel.

1.7. Study outline of the Thesis

The first chapter of this thesis would present an introduction to biodiesel as a renewable source. Chapter 2 is the detail literature review with information about biodiesel properties and production and techniques of production methods. Chapter 3 describes the methodology and details of the experimental work. Chapter 4 presents and discusses the obtained results from chapter 3 and all work concludes in Chapter 5 with suggestions for all future work (recommendation).

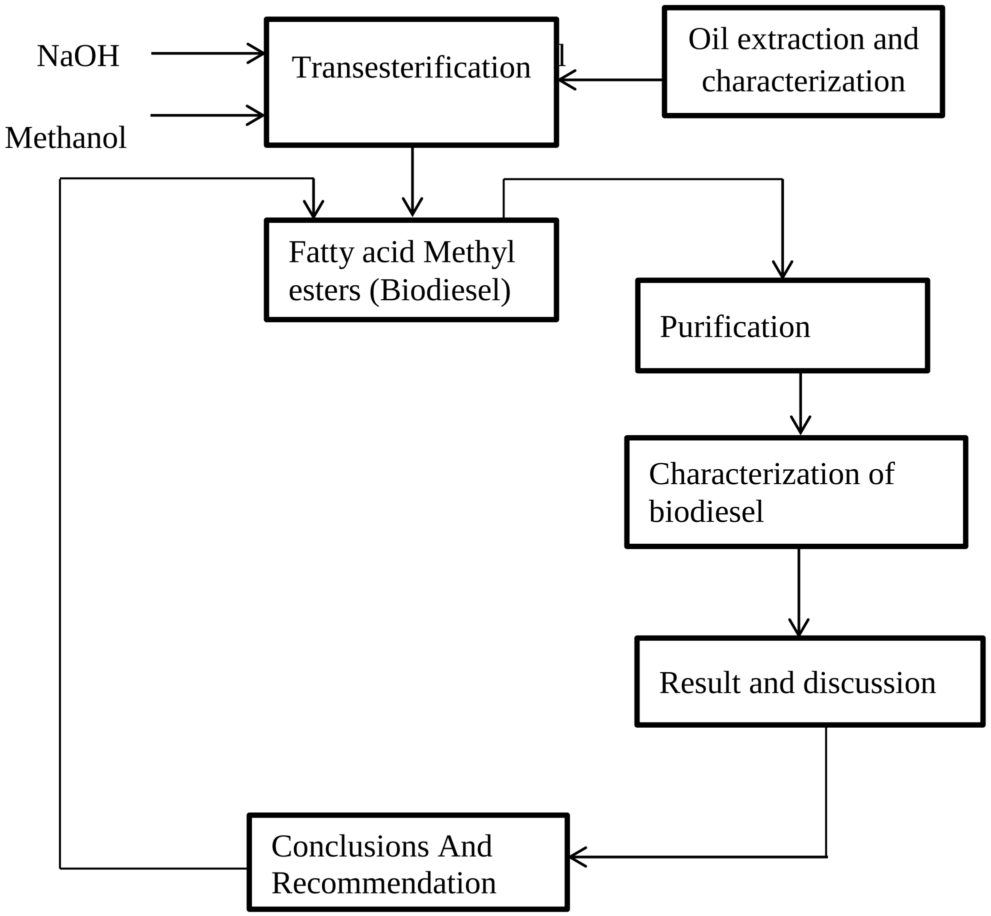


Figure 1.1: Proposed and outline for biodiesel production process.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 General Overview of Biodiesel Fuel Production

Biodiesel, a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable (virgin) oils, frying oil, animal fats, and mixtures of this is produced by transesterification reaction, with biodiesel as main product and glycerol being produced as a co-product. Biodiesel with diesel fuel offers improved lubricity and reduced emissions. Diesel fuel use worldwide is estimated to be 1.14 billion tons (330 billion gallons) per year. The United States uses an estimated 18% of that or 205 million tons (Useia, 2004). Because diesel (compression ignition) engines are more efficient than gasoline (spark ignition) engines (45% versus 30%), there is the possibility that the use of diesel engines in vehicles will increase, thereby increasing the demand for diesel fuel (DOE, 2003).

2.2. Biodiesel

Biodiesel is a renewable fuel, non-toxic and biodegradable. It is a good alternative for conventional fossil diesel fuel since it has similar properties as shown in table 2.1. However, it requires the use of additives to be suitable for motor fuel in order to overcome oxidation processes limitations (Khurshid, 2014).

Table 2.1: Comparison between biodiesel and petrodiesel properties

Types	Density at 20°C	Viscosity at 20°C (mm^2/s)	Cetane Number	LHV (MJ/Kg)	Fuel eqv.
BD	0.88	7.5	56	37.1	0.91
DIESEL	0.83	5.0	50	43.1	1

Source: (Khurshid, 2014).

The main feedstocks for the biodiesel production process through transesterification process (reversible reaction) are vegetable oils, waste cooking oil and animal fats. The reaction uses to be carried out in batch reactor provided with controlled heating and mixing process system. Biodiesel has been produced in EU since 1992. The annual production was up to 6,100,000 tones with about 120 production plants in the EU. From this, Austria, Germany, Italy, France and Sweden are the main producers of biodiesel in EU. The use of 1 kg biodiesel leads to a reduction of about 3 kg of CO_2 emissions. Since, the use of biodiesel leads to a significant reduction in CO_2 emission from 65% to 90% less compared with the use of conventional diesel (Khurshid, 2014).

Table 2.2: The advantage of biodiesel and disadvantage of fossil Diesel

Advantage and disadvantage	
Biodiesel	- Nontoxic material, better lubrication. - Renewable and biodegradable. - It free from greenhouse gasses emission. - Due to high flash point it was safe to store. - Increase combustion efficiency due to high cetane number. - Require anti freezing additive in cold weather due to its higher density.
Fossil Diesel	- Toxic. - Lower lubrication, not renewable. - Greenhouse gasses emission e.g. CO_2, NO_x, SO_x. - Low flash point. - Low cetane number. - Require less amount of anti-freezing additive in cold weather due to its lower density.

Biodiesel is an alternative fuel, which can be produced from renewable sources such as vegetable oils. It is biodegradable and nontoxic has low emission profiles and environmentally beneficial. The strongest motivation for increasing of production and consumption of biodiesel is environmental issues. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression-ignition (CI-diesel) engines with little or no modifications (Akhtar, 2011).

In the most general sense, biodiesel refers to any diesel fuel substitute derived from renewable biomass. More specifically, biodiesel is defined as an oxygenated, sulfur-free, biodegradable, non-toxic, and eco-environmentally friendly alternative diesel oil. In chemical sense, biodiesel can be defined as a fuel composed of triglycerides to mono-alkyl esters of long chain fatty acids derived from renewable sources, such as vegetable oil, animal fat, and used cooking oil and also it must meet the special requirements of the ASTM and the European standards.

The characteristics of the vegetable oils are significantly different than those of petroleum derived diesel fuels, mainly as the result of their high viscosities. The conversion of vegetable oils into biodiesel is an effective way to overcome all the problems associated with the vegetable oils. Dilution, micro emulsification, pyrolysis, and transesterification are the four main modern production technology applied to solve the problems encountered with the high fuel viscosity (El-Solh, 2011). Transesterification reaction is the most suitable process and popular method and commonly leads to mono alkyl esters of vegetable oils and fats, now called biodiesel when used for fuel purposes. The methyl ester produced by transesterification of vegetable oil has a high cetane number, low viscosity and improved heating value compared to those of pure vegetable oil which results in shorter ignition delay and longer combustion duration and hence low particulate emissions.

As fossil fuels are limited sources of energy, this increasing demand for energy has led to a search for alternative sources of energy that would be economically efficient, socially equitable, and environmentally sound. Two of the main contributors of this increase of energy demand have been the transportation and the basic industry sectors, being the largest energy consumers (Hill et al, 2006).

Biofuels appear to be a solution to substitute fossil fuels because;

- Resources for biofuels will not run out (as fresh supplies can be regrown).
- Biofuels are becoming cost wise competitive with fossil fuels.
- Biofuels appear to be more environmental eco-friendly and they are rather accessible to distribute and

- Biofuels use as applicable infrastructure and technologies exists and are readily available.

2.3. History of Biodiesel

Dr. Rudolf Diesel, who invented the first diesel engine in 1895, used only biofuel in his engine. His visionary statement was “The use of vegetable oils for engine fuel may seem insignificant today, but such oils may become in course of time, as important as petroleum and coal tar products of the present time”. The above prediction is becoming true today as more and more biodiesel is being used all over the world. Dr. Rudolf Diesel invented the diesel engine to run on a host of fuels including coal dust suspended in water, heavy mineral oil, and, vegetable oils. Dr. Diesel’s showed his first engine experiments at the world exhibition in Paris in 1900; his engine was running on 100% peanut oil. In 1911 he stated ‘‘the diesel engine can be fed with vegetable oils and would help considerably in the development of agriculture of the countries, which use it’’. In 1912, Diesel said,’ the use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of the present time’’. Since Dr. Diesel’s untimely death in 1913, his engine has been modified to run on the polluting petroleum fuel, now known as ‘‘diesel’’. Nevertheless, his ideas on agriculture and his invention provided the foundation for a society fueled with clean, renewable, locally grown fuel.

In the 1930s and 1940s, vegetable oils were used as diesel substitutes from time to time, but usually only in emergency situations. Recently, because of increase in crude oil prices, limited resources of fossil oil and environmental concerns, there has been a renewed focus on vegetable oils and animal fats to make biodiesel. The continuity and increasing use of petroleum will intensify local air pollution and magnify the global warming problems caused by carbon dioxide. In a particular case, such as the emission of pollutants in the closed environment of underground mines, biodiesel has the potential to reduce the level of pollutants and the level of potential for probable carcinogens.

In recent times, due to realization that vegetable oil has been revisited for its scope as a fuel in compression ignition engines. The high viscosity of vegetable oils compared to petroleum diesel fuel were reported due to some operational problems, which results in poor atomization of the fuel in the fuel spray and often leads to deposits and coking of the injectors and valves. The use of biodiesel was recognized much later and became technically relevant only after the energy crisis in the year 1973 and afterwards.

2.4. Biodiesel as a source of renewable energy

Biodiesel is a renewable, biodegradable, non-toxic, sulfur-free, and environmentally clean alternative diesel fuel. Biodiesel is composed by fatty acid methyl esters, produced from renewable resources, such as vegetable oils, animal fats, and waste restaurant greases. One of the attractive characteristics of biodiesel is that its use does not require any significant modifications to the diesel engine, so the engine does not have to be dedicated for biodiesel. Biodiesel has lower emissions than petroleum diesel and it does not contribute to a rise of the net concentration of carbon dioxide in the atmosphere and leads to minimize the intensity of greenhouse effects (Alimova, 2016).

The most prospective recourse of energy is renewable energy sources and it includes biomass, hydro, wind, solar (thermal and photovoltaic), geothermal, marine, and hydrogen. Every year the importance of renewable sources increases and by 2040 according to scientists forecasts almost half of world's energy supply will be from renewable sources, meanwhile, 80% of total world's electricity production will be from renewables. Fig. 2.1 compares global energy consumption in 5 different categories as petroleum, coal, natural gas, nuclear and renewables.

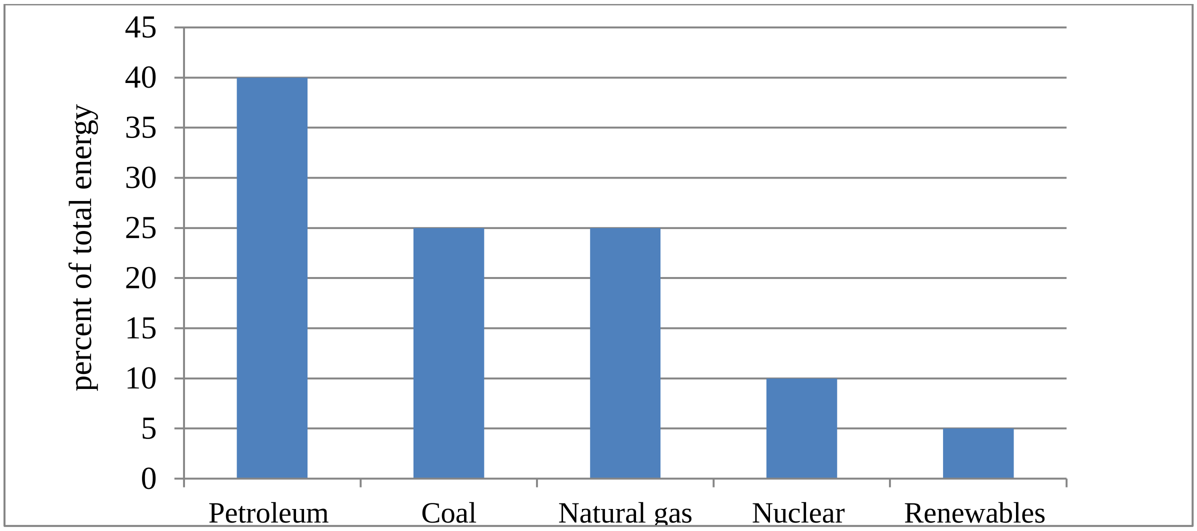


Figure 2.1 Worldwide fossil, nuclear and renewable energy consumption.

Biodiesel is the type of biofuel and it can be produced by transesterification process from vegetable oil or animal fat. Biofuels appear to be more environment friendly in comparison to fossil fuels considering the emission of greenhouse gasses when consumed. Examples of those gasses are carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). Those gasses pose risks as they tend to warm the earth's surface' (Randelli, 2007). The energy content of biofuels differs from conventional fuels. Total energy output per liter of biofuel is determined by the feedstock used, region where the feedstock is grown and production techniques applied.

Biodiesel production is a very modern and technological area for us as an alternative fuel for diesel engines because of the increase in the petroleum price, its renewability and the environmental advantages. Currently, the cost of biodiesel is high as compared to conventional diesel oil because most of the biodiesel is produced from pure vegetable oil.

Proper utilization of agricultural waste like fruit peels to produce biodiesel is a promising approach to ensure environmental protection and energy security in this era of energy crisis. Due to the depletion of petroleum reserves and the environmental impact of using fossil fuel, it is necessary to look for an alternative source of fuel. Biodiesel, derived from vegetable oil or animal fats, can be a substitute of petroleum based diesel and considered as renewable energy source. It is estimated that biodiesel could replace approximately 10% of diesel fuel consumption within Europe and 5% of Southeast Asia's total fuel demand. Since compared to commercial diesel, biodiesel is environment friendly because of its sulphur free benefit and non-toxicity, lower greenhouse gas emission and higher flash point (Duti et al, 2016).

Biodiesel is a liquid biofuel obtained by chemical processes from vegetable oils or animal fats and an alcohol that can be used in diesel engines, alone or blended with diesel oil. It is a nontoxic, biodegradable, and renewable fuel that can be used in diesel engines with little or no modification. The use of biodiesel for transportation applications are a relatively new phenomenon but is gaining acceptance and growing rapidly.

2.5. Biodiesel as a Fuel

Biodiesel was registered as a fuel and fuel additive with the environmental protection agency (EPA) and meets clean diesel standards established by the California air resources board (CARB). Neat (100 percent) biodiesel has been designated as an alternative fuel by the department of energy (DOE) and the U.S. department of transportation. In petrodiesel the energy content can vary up to 15% but in biodiesel it is much less variable. Pure biodiesel contains up to 10-12% oxygen by weight, while diesel contains almost 0% oxygen. The presence of oxygen allows more complete combustion, which reduces hydrocarbons, carbon monoxide, and particulate matter emission. However, higher oxygen content increases nitrogen oxides emissions.

The primary reason, why biodiesel is suitable as an alternative fuel for petrodiesel, lies in the cetane number (CN). The cetane number indicates the ignition quality of a diesel fuel. It measures a fuel's ignition delay, which is a period between the start of injection and start of combustion (ignition) of the fuel. Fuels with a higher cetane number have shorter ignition delays, providing more time for the fuel combustion process to be completed (Akhtar, 2011).

2.6. Properties of Vegetable Oils and Biodiesel

2.6.1. Properties of Vegetable Oils

Vegetable oils mainly contain triglycerides (90 to 98%) can be used as alternative fuels because they are biodegradable, nontoxic, and clean fuels. Vegetable oils and their derivatives as diesel engine fuels lead to substantial reductions in sulfur, carbon monoxide, polycyclic aromatic hydrocarbons, smoke and particulate emissions. The viscosity of liquid fuels affects the flow properties as well as vaporization, and air/fuel mixture formation (A K and Davies P, 2010,).

The viscosities of vegetable oils are greatly affected by temperature. It has been reported that the viscosity of oils and fats decreases almost linearly with temperature. The significant fuel properties of vegetable oils indicate that the kinematic viscosity of vegetable oils varies in the range from 27– 67 ^{0}C St at 40 ^{0}C. The high viscosity of oils is due to their large molecular mass in the range of 600–900, which is an order of magnitude almost 4 times higher than that of diesel. The flash point of vegetable oils is very high (above 180^{0} C) and the heating values are in the range of 36– 40 MJ/kg, as compared to diesel fuels which is about 42-45 MJ/kg. The cetane numbers are in the range of 30–45.

2.6.2. Properties of biodiesel

Biodiesel is a clear amber-yellow liquid with a viscosity similar to that of petro diesel. Biodiesel is non-flammable and, in contrast to petro diesel, is non-explosive, is biodegradable and non-toxic, and it significantly reduces toxic and other emissions when burned as a fuel. The most important parameters affecting the ester yield during the transesterification reaction are the molar ratio of alcohol to oil and reaction temperature. The viscosity values of oil methyl esters decrease sharply after transesterification. Biodiesels are characterized by their viscosity, density, cloud and pour points, flash point, pH, sulfur content, free fatty acid, acid value, and higher heating value (HHV).

Table 2.3 Technical properties of biodiesel

Common name	Biodiesel (BD)
Common chemical name	Fatty acid methyl ester
Chemical formula range	C_{14}–C_{24} methyl esters or C_{15}-25H_{28}-48O_2
Kinematic viscosity range (mm^2/s, at 40 ^0C)	3.3–5.2
Density range (kg/m^3, at 15 ^0C)	860–894
Boiling point range (^0C)	> 202
Flash point range (^0C)	147–177
Vapor pressure (mm Hg, at 25 ^0C)	< 5
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable.

Source: - (Vazquez, 2014)

The current derivative of our natural products and it is more advantages when compare with other engines. As demand increases, the production of the required agricultural products can be increased to compensate.

Table 2.4: - Availability of modern transportation fuel

Fuel type	Availability	
	Current	Future
Gasoline	Excellent	Moderate-poor
Biodiesel	Moderate	Excellent
Compressed natural gas (CNG)	Excellent	Moderate
Hydrogen fuel cell	Poor	Excellent

Source: - (Vazquez, 2014)

2.7. General overview of Avocado

The avocado (*Persea Americana* Mill.) is a polymorphic tree species that originated in a broad geographical area from the eastern and central highlands of Mexico and Central America belongs to the Lauraceae family, genus perseal and comprises two subgenres: Persea and Eriodaphne (Barreira, 2013). Currently, avocado is a fruit that has been cultivated in many parts of the world, especially tropical countries. Avocado is a fruit from a tree that has a variable growth and development, reaching a height of a tree between 5 and 15 m in its natural habitat may grow at different altitudes. Such habitat is classified as subtropical-tropical evergreen. The weight of the fruit is between 120 and 2.5 kg and the harvesting period varies from 5 to 15 months. The tree has 25 to 30 years old that can be axillaries or terminal. Avocados are existed in different shape, size, and color depending on their variety. Avocado fruit can be consumed directly as a high energy food source because of content of lipids that significantly higher than in other fruit. Besides, avocado fruit is also a good source of oil. Avocados fruits depending on the variety and the growth conditions it contain from 8 to 40% amount of oil, the percentage varying with the variety, growing area and seasonal conditions (Islas et al, 2013). Only ripe olives have higher oil content. The value of avocado oil is related to its fatty acid composition.

Avocado oil is reported to have the beneficial health properties. Compared to other fruits, avocados contain very little sugar (Usda, 2011). One-half an avocado contains only about 0.2 g sugar (e.g., sucrose, glucose, and fructose). Avocado fruit has an energetic fruit with great nutritional value as a source of carbohydrate, protein, fiber and it contains essential micronutrients for human consumption such as vitamins and is considered a major tropical fruit, since it is rich in protein and contains fat soluble vitamins lacking in other fruits, including Vitamins A, and B, and median levels of vitamins D and E. It contains different oil levels in the pulp, thus it is widely used in pharmaceutical and cosmetic industries, and for obtaining commercial oils similar to olive oil, because of their similar fatty acid composition. In addition, the oil of an avocado leaves has contains significant amounts of minerals that could also be consumed as for its medical properties and health benefits, especially due to the compounds present in the lipid fraction (Duarte, 2016).

Table 2.5: composition of avocado peel oil

Minerals	Fatty acid fraction (%)
Palmitic	4 – 25
Palmitoleic	6-10
Stearic	0-3
Oleic	45-80
Linoleic	6-20
Linolenic	Max.14
Free Fatty Acid	Max.6

The differences form and yield of the oils from the local avocado peel could be attributed to the differences in their drying methods and their fatty acid composition. Avocado peel with oven drying method able to maintain the oil content compared to that dried with direct sun-drying.

2.7.1. Review of avocado production in the world

The avocado (*Persea Americana*) is a native of Central America and the West Indies. It was introduced into Florida, California and Hawaii in the early 1800s and is now found worldwide where growing conditions are suitable. World avocado production grew at an average rate of nearly seven percent (7%) per year (Faris, 2016).

Mexico is the world's leading avocado producer. In 2012, it produced 1,300 metric tons (MT), equivalent to 30 percent of global production. This is nearly four times that of Indonesia. Production in Chile, the second largest producer in 2009, has dropped by 45 percent in the past 3 years as a result of poor weather and drought. Africa accounted for 16 percent of global production in 2012, a slight increase from 15 percent in 2008. Other major producers include Brazil, Colombia, Dominican Republic, and Peru.

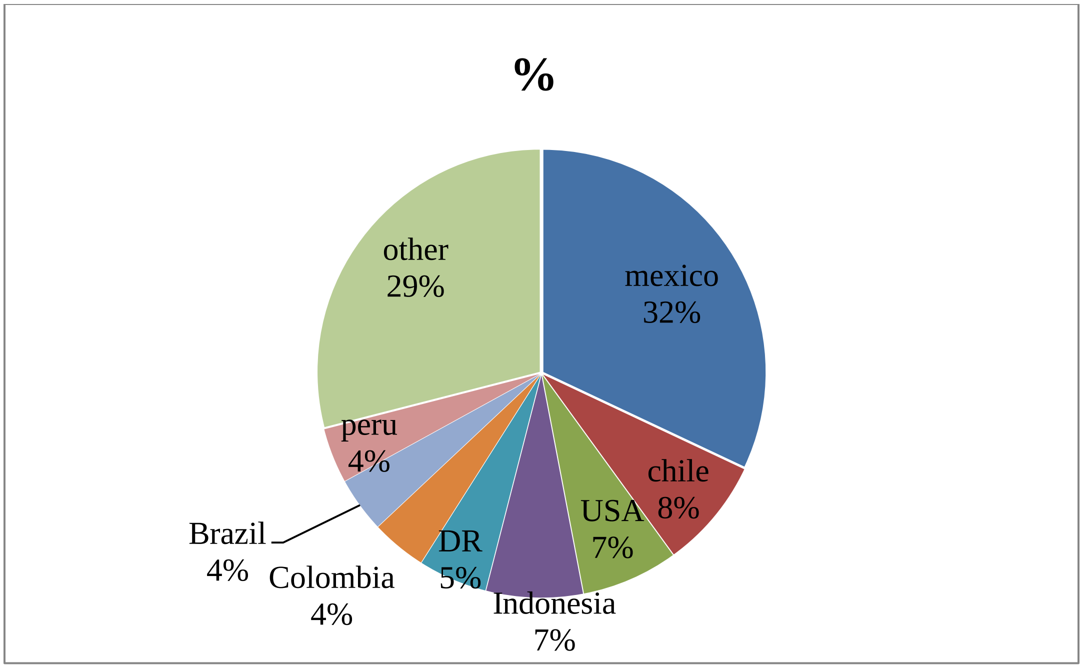


Fig 2.2: percentage of avocado production in the world

2.7.2. Review of avocado production in Ethiopia

The relatively early establishment of the avocado industry in Ethiopia is in its infancy and has not yet utilized the immense potential of this crop. In the context of increasing the high value production of agricultural commodities and fruit tree play an important role. Except table banana, tropical fruit trees like mango, avocado and the like were not well known and considered as diet by most Ethiopians (Yilma, 2009). According to CSA (2013) indicated avocado as one of the third potential fruit crop produced in Ethiopia.

Table 2.6: Summary of major fruit crops produced in Ethiopia in 2016/2017 cropping season

Crop	Area in Ha	Production in Quintal	Yield (Qt/Ha)
Fruits	107,890.6	7,923,665.02	
Avocados	17,834.58	649,821.04	36.44
Bananas	63,212.97	5,383,023.41	85.16
Guavas	3248.59	43,265.32	13.32
Lemons	1426.25	77,814.52	54.56
Mangoes	15,413.76	1,046,461.25	67.85

Oranges	2619.8	206,559.48	78.85
Papayas	3489.47	503,961.70	144.42
Pineapples	645.19	12,758.30	*

Source: CSA, 2016/2017, agricultural sample survey result.

2.7.3. Avocado Marketing in Ethiopia

Consumers are those purchasing the products for consumption. Most of the fruits produced in Ethiopia are consumed locally and are produced by smallholder (individual) farmers. After harvest, they are transported to rural market centers for local consumers or bought at the farm by neighbors. The Ethiopia avocado marketing in agricultural products consists primarily of moving products from production sites to points of final consumption. In this regard, the market performs exchange functions as well as physical and facilitating functions. The exchange function involves buying, selling and pricing. Transportation, product transformation and storage are physical functions, while financing, risk bearing and marketing information facilitating marketing (Branson and Norvell, 2002).

Market channel is a business structure of interdependent organizations from the point of product origin to the consumer with the purpose of moving products to their final consumption destination (Kotler and Armstong, 2003). Or it is the path one good follow from their source of original production to ultimate destination for final use. The analysis of marketing channels is intended to provide a systematic knowledge of the flow of goods and services from their origin (producer) to their final destination (consumer). This knowledge is acquired by studying the participants in the process, i.e. those who perform physical marketing functions in order to obtain economic benefits (Faris, 2016).

Avocado is channeled from producers to local collectors, Cafeteria and whole sellers and finally to Addis Ababa market through these channel middle men buys all avocado fruits from the farmers at a lower price and sells them in the market at higher price (Zekarias, 2010). Fruits for both fresh and processed have a huge domestic market in Ethiopia which is by far significant than that of the export volume.

2.7.4. Avocado and Avocado peels

Avocado peel (*persea Americana*) is a waste where so many people are throwing away after using the fruit flesh. It is one of the most popular fruit in Ethiopia as a result there is a significant increase in avocado fruit consumption and consequently an increase in the avocado peel waste generation. Therefore, alternative routes are needed for this waste management. This waste can be used for various applications. Avocado contain from 5 to 40% oil, the percentage varying with the variety, growing area and seasonal conditions. Only ripe olives have higher oil content (Faris, 2016).

Ethiopia has a potential agro-ecologically diverse and has a total area of 3.5 million km^2 with net irrigation area of about 1.61 million ha, of which currently only 4.6 % is utilized. The substantial areas in the southern and south-western parts of our country receive sufficient rainfall to support fruits adapted to the respective climatic conditions. In addition, there are also many rivers and streams which could be used to grow various fruits. The main fruits produced and exported are banana, citrus fruits, mango, avocado, papaya and grape fruits (Faris, 2016). As a result avocado is the second largest fruits produced next to banana. According to FAO the world production is around 4364.94 thousand tons per year where 76% of the total production is controlled by 10 countries (table 2.7). As it originated from Mexico, this country is the biggest producer with 1.9 million tons (32%) of world producer and Ethiopia is 20th in the world (a world share of 1.2%).

Table 2.7 World production of avocado in 2016

Country	**Production in 1000 tons**
Mexico	1889.35
Dominican Republic	601.35
Peru	455.39
Colombia	309.43
Indonesia	304.94
Brazil	195.49
Kenya	176.05
USA	172.63
Chile	137.37

China	122.94
World	4364.94

Source: - (Vazquez, 2014).

Avocados are one of the few fruit that contain significant quantities of oil. Oil content is a key part of the sensory quality. Oil quality is very similar to that of olive oil. However, avocado peel is one of the waste materials removed from avocado fruit. In some causes it is used for animals consumption and having all properties of avocado. The avocado fruit comprises a dark green peel, green oily pulp and a large seed which represents 10-22% of the total weight depending on the species. The peel (skin) is mainly composed of moisture, while the remaining 10% is lipids, proteins, ashes, fibre and others.

Table 2.8 Physicochemical parameters of the different fractions of the avocado

Parameter	**Pulp**	**Skin**	**Seeds**
Moisture (%)	70.83±3.53	69.13±2.58	54.45±2.33
Ash (%)	1.77±0.16	1.50±0.08	1.29±0.03
Proteins (%)	1.82±0.07	1.91±0.08	2.19±0.16
Fat (%)	43.5±4.62	2.20±1.65	14.7±0.32
Total soluble solids	43.5±4.62	3.01±2.03	3.54±1.97
Acidity	1.07±0.02	2.05±0.24	2.67±0.17

Source: (Vazquez, 2014).

The moisture content is one of the most important indices evaluated, especially in avocado fruits it contains (65%) of moisture or water and it is a good indicator of their economic value chain because it reflects solid contents. The results indicate in the above table has avocado skin has the second water content (69.13%) next to pulp (70.83%), and followed the seed (54.45%). The skin fat and ash quantified were significantly higher than to those found in the pulp. The yields of oil/ha in liters of the common crops used as feedstocks for biodiesel production are shown in table 2.9 and figure 2.3. Avocado produces 2638 liters of oil per ha and it is one of the third feedstocks for biodiesel production next to oil palm and coconut.

Table 2.9 Liters of oil per ha [Johnston, 2007]

Crop	**liters oil/ha**	**US gal/acre**
palm	5950	635
Coconut	2689	287
Avocado	2638	282
Calendula	305	33
castor vean	1413	151
cocoa (cacao)	1026	110
coffee	459	49
corn (maize)	172	18
cotton	325	35
jatropha	1892	202
jojoba	1818	194
macadamia nut	2246	240
mustard seed	572	61
oats	217	23
oil palm	5950	635
olive	1212	129
opium poppy	1163	124
peanut	1059	113
pecan nut	1791	191
pumpkin seed	534	57
rapeseed	1190	127
rice	828	88
sesame	696	74
soybean	446	48
sunflower	952	102

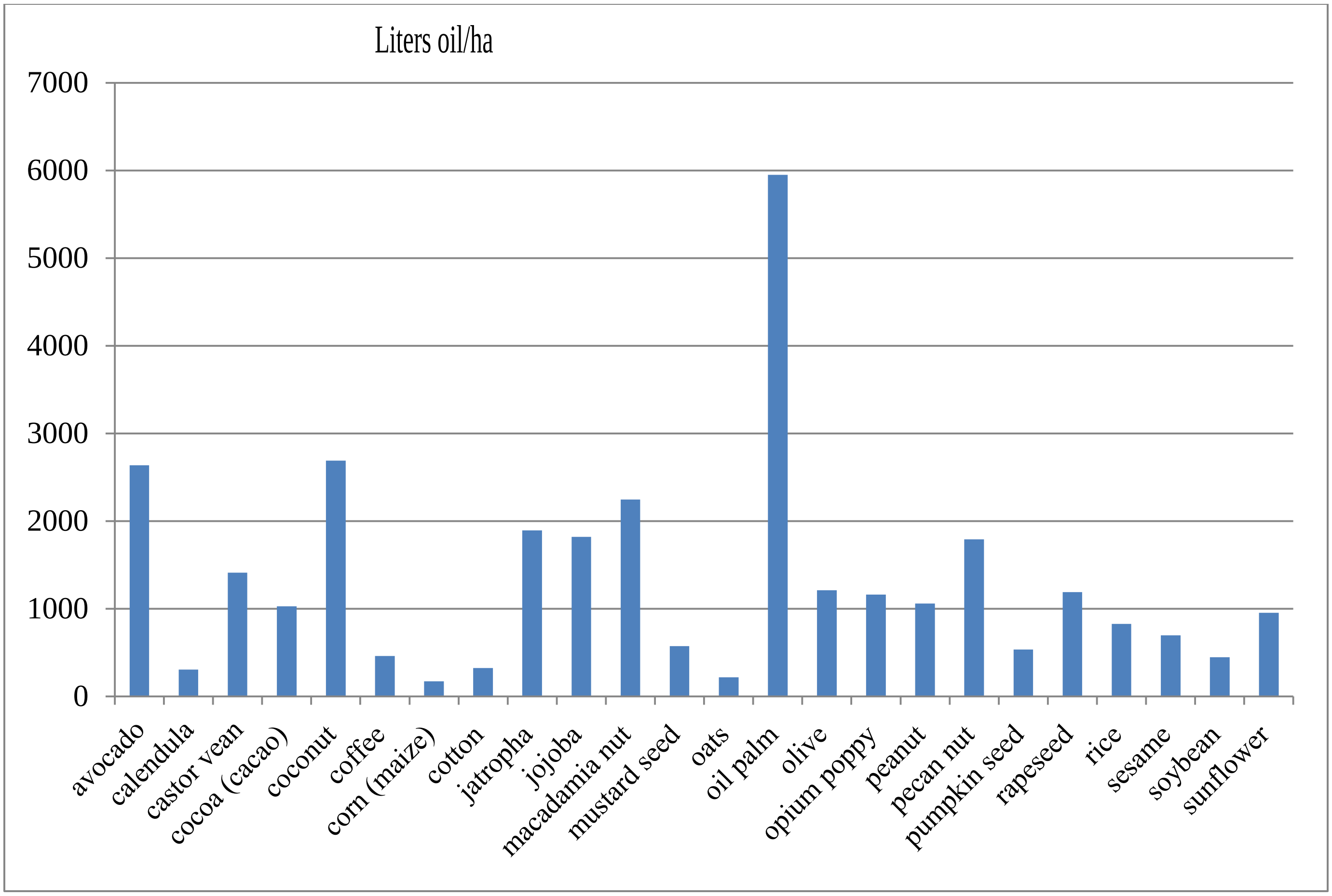


Figure 2.3 Yield of seeds (liters oil/ha)

2.8. Methods for extraction of oil

There are different extraction technique used to obtain high value oil from vegetables, fruits etc. The production process of oil involves the removal of oil from plant components, typically peels. This can be done via mechanical extraction using an oil mill or chemical extraction using a solvent. In general there are three different methods for extraction of oil: mechanical extraction, solvent extraction, and Soxhlet extraction method (Kittiphoom and Sutasinee, 2013).

2.8.1 Mechanical extraction method

Oils can be removed via mechanical extraction, termed "crushing" or "pressing." This method is typically used to produce the more traditional oils (e.g., olive, coconut etc.), and it is preferred by most "health-food" customers in the United States and in Europe. There are several different types of mechanical extraction. Expeller-pressing extraction is common, though the screw press and powered mortar and pestle are also used. Oil seed presses are commonly used in developing countries, among people for whom other extraction methods would be prohibitively expensive.

The mechanical extraction method is effective for peels or seeds contain 30-70% oil. This method has several advantages compared to the other methods, such as simple equipment and low investment, low operating cost, and the oil does not undergo solvent separation process. However, the oil produced with this method usually has a low price, since it’s turbid and contains a significant amount of water and metals contents. Due to low oil content of feedstocks it is not advisable to extract the oil using mechanical extraction.

2.8.2 Solvent extraction method

Solvent extraction is the transfer of solutes from a solid, usually in particulate form, to contiguous liquid, the extract (Henry, 1983). If the solute is uniformly dispersed in the solid, the material near the surface will be dissolved first, leaving a porous structure in the solid residue. The solvent will then have to penetrate this outer layer before it can reach further solute and the process will become progressively more difficult and the extraction rate will fall. If the solute forms a very high proportion of the solid, the porous structure may break down almost immediately to give a fine deposit of insoluble residue, and access of solvent to the solute will not be impeded (Richardson et al, 2002). Solvent extraction with peels containing only about (12 - 16) per cent of oil, solvent extraction is often used because mechanical methods are not very efficient.

The solvent extraction method recovers almost all the oils and leaves behind only 0.5% to 0.7% residual oil in the raw material. In the case of mechanical pressing the residual oil left in the oil cake may be anywhere from 6% to 14%. The solvent extraction method can be applied directly to any low oil content raw materials. Because of the high percentage of recovered oil, solvent extraction has become the most popular method of extraction of oils and fats.

The advantages of solvent extraction over other methods of oil expression include, higher oil yield (about 95% of the oil content could be obtained), larger processing capacity, solvent extraction also gave oil that many considered to be of superior bleaching quality, lower refining losses, reduced susceptibility to rancidity and better retention of fat - soluble vitamin (Lawson et al, 2010).

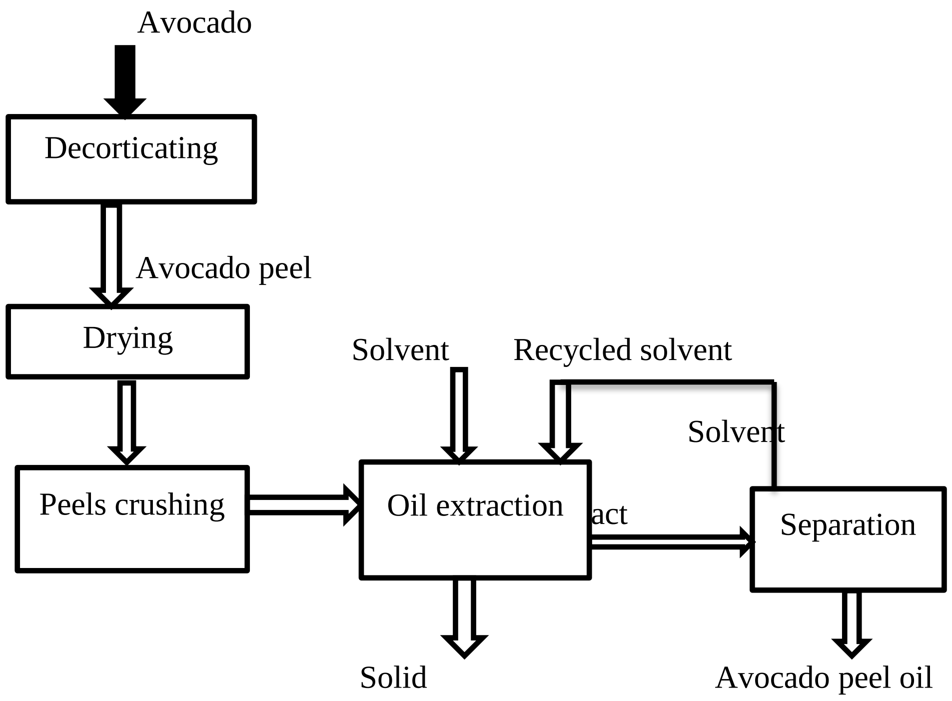


Figure 2.4 Solvent extraction

A certain gram of dried avocado peel was used in the process. The avocado firstly decorticated to obtain the peels. Then dried and milled to a certain particle size and then fed to an extractor. After waiting to a certain time, the separation process proceeds to separate the solvent from the product. The recycled solvent was used again by adding certain make up solvent.

2.8.3. Conventional solvent (liquid - solid) extraction

The most conventional solvent extraction methods include Soxhlet extraction (SXE), maceration, percolation, and sonication, while newer techniques comprise ultrasound and microwave-assisted extraction, as well as pressurized liquid extraction (PLE).

2.8.3.1. Soxhlet Extraction method

A Soxhlet extractor is a piece of laboratory designed equipment for processing certain kinds of solids invented in 1879 by Franz von Soxhlet. Soxhlet extraction is a process used for liquid-solid extractions, especially for compounds with limited solubility in a solvent (Meyer and Terry, 2008). According to the Soxhlet procedure, oil from solid material are extracted by repeated washing (percolation) with an organic solvent usually n-hexane under reflux in a special glassware. Because an avocado peel has low solubility in the solvent (n-hexane), the Soxhlet was the most suitable extraction technique. Specifically, the sample is dried and milled into small particles and placed in a porous thimble. If the desired compound has a significant solubility in a solvent then a simple filtration can be used to separate the compound from the insoluble substance. Avocado peel powder is placed inside a thimble made from thick filter paper, which is loaded into the main chamber of the Soxhlet extractor. The Soxhlet extractor is placed onto a flask containing the extraction solvent. The Soxhlet is then equipped with a condenser. The thimble is placed in an extraction chamber, which is suspended above a flask containing the solvent, and a condenser is placed on top of the extraction chamber (Chemat et al., 2008). After extraction the solvent is removed, typically by means of a rotary evaporator, yielding the extracted oil. The non–soluble portion of the extracted solid remains in the thimble, usually discard.

Table 2.10 Advantage and disadvantage of Soxhlet extractor

Advantage	**Disadvantage**
Long experience of use	Long extraction time (hours)
A displacement of transfer equilibrium occurs as the solid is continuously exposed to fresh solvent.	Considerable solvent consumption.
High extraction temperature enables exhaustive recovery of interest.	Non selective extraction
Simple to operate	Risk of thermal decompositions as the extraction is conducted at the boiling point of the solvent.
Economical	Only temperature, extracted time and solvent type can be Varied.

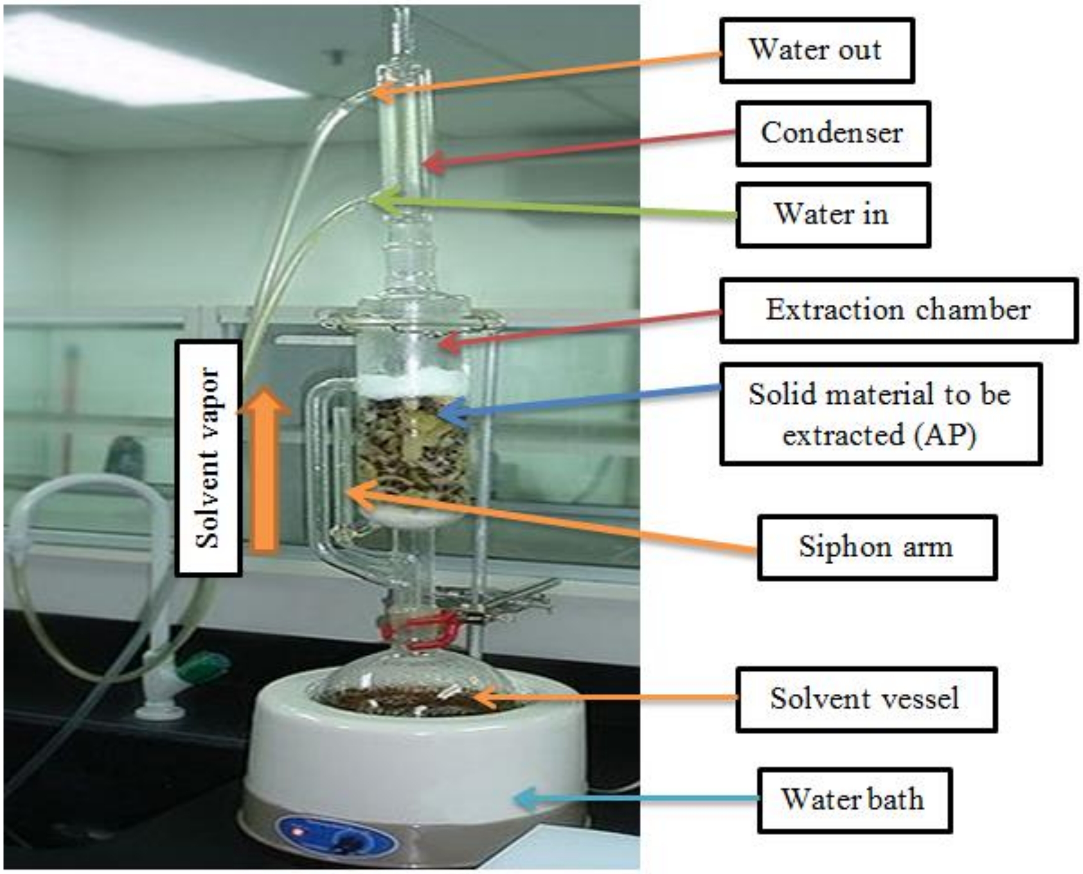


Figure 2.6 Soxhlet extractor set up

Note: From the three we use the Soxhlet extraction method because of it is simple to operate and uses. The solvent extraction used below the oil contents of avocado peels, we uses only about (12 - 16) per cent of oil content and the mechanical extraction method is used above the oil contents avocado peel, since the mechanical extraction used about (30-70) % oil content. Since the avocado peel oil contains (8-30) per cent of oil, therefore we use Soxhlet extractor.

2.9. Current Technologies in Biodiesel Production

There are many investigations on biodiesel production of nonconventional feedstock of oils and have reached a faster pace in the last few years. Oils used in engine lead to various problems like fuel filter clogging, poor atomization and incomplete combustion because of high viscosity, high density and poor non-volatility. The conversion of vegetable oils into biodiesel can be realized using four modern technologies: These are:-Pyrolysis, micro-emulsification, dilution; and trans-esterification.

2.9.1. Pyrolysis (cracking) method of Biodiesel production

The pyrolysis refers to a chemical change caused by the application of thermal energy in the absence of air or nitrogen. Or thermal cracking or pyrolysis is the process that causes the break of the molecules by heating at high temperatures that is, by heating of the substance in the absence of air or oxygen in temperature superior to 450^0C, forming a mixture of chemical compounds with properties very similar to those of petro diesel. In some situations that process is supported by a catalyst for the break of the chemical connections, in order to generate smaller molecules (Sonntag, 1979b). Typical catalysts to be used in pyrolysis are the silicon oxide SiO_2 and aluminum oxide Al_2O_3.

The equipment for Pyrolysis is expensive. However, the products are chemically similar to diesel oil. The removal of the oxygen of the process reduces the benefits of an oxygenated fuel, reducing its environmental benefits and usually producing a fuel closer to gasoline than diesel. Pyrolysis has great applicability in places that need smaller production volume and with smaller availability of qualified work. The liquid fractions of the thermally decomposed vegetable oils are likely to approach diesel fuels. The pyrolyzate has a lower viscosity, flash point, and pour point than diesel fuel and equivalent calorific values. The cetane number of the pyrolyzate is lower.

2.9.2. Micro-Emulsification Method of Biodiesel Production

The formation of micro emulsion is one of the potential solutions for solving the problem of vegetable oil viscosity. To solve the problem of the viscosity of vegetable oils, micro emulsion with solvents such as methanol, ethanol and 1-butanol have been used. A micro emulsion is defined as thermodynamically stable, isotropic liquid mixture of oil, water and surfactant (compounds that lower the surface tension of a liquid, the interfacial tension between two liquids) (Pryde, 1984b). Micro-emulsions are defined as transparent, thermodynamically stable colloidal dispersion. The droplet diameters in micro-emulsions range from 100 to 1000 Å. All micro-emulsions with butanol, hexanol and octanol met the maximum viscosity requirement for diesel fuel.

2.9.3. Dilution

The dilution of vegetable oils can be accomplished with such material as diesel fuels, solvent or methanol. Dilution results in the reduction of viscosity and density of vegetable oils. The addition of 4% methanol to diesel fuel increases the brake thermal efficiency, brake torque and brake power, while decreasing the brake specific fuel consumption. Since the boiling point of methanol is less than that of diesel fuel, it could assist the development of the combustion process through an unburned blend spray.

2.9.4. Transesterification Method of Biodiesel Production

The most common way and the accepted processes to biodiesel production are by transesterification process by which to catalyze chemical reaction involving vegetable oil and an alcohol in the presence of a catalyst, to produce fatty acid alkyl esters and glycerin. A byproduct of transesterification reaction is glycerin, also known as glycerol. The most common alcohol, which is used in biodiesel production is methanol, another name for biodiesel is fatty acid methyl esters (FAME) (Alimova, 2016).

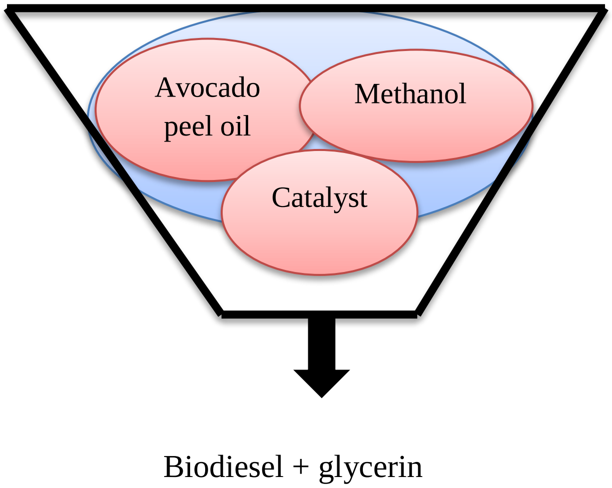
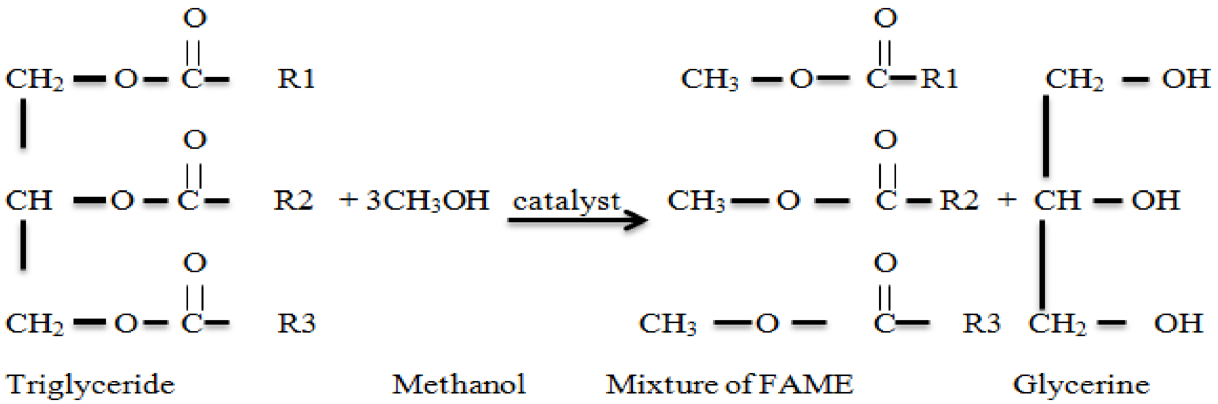


Figure 2.7 Catalytic transesterification

The mixture (NaOH + methanol) is then added to the pre-heated warm oil (normally to about (50-65^{0}C), also with stirring for (45-90min), to undergo the transesterification reaction. The reaction mixture is normally maintained above the boiling point of the alcohol, but in some systems for safety reasons it is recommended to maintain the temperature range from room temperature to 55^{0}C. To prevent evaporation of the alcohol the reaction should be carried out in a closed container, but it is important to avoid a sealed system (because of risk of explosion) (Alimova, 2016). According to stoichiometry, three moles of methanol reacts with one mole triglyceride to produce three moles of fatty acid methyl ester (FAME) and one mole of glycerine as shown in the following reaction.



Transesterification reaction significant reduces the viscosity of vegetable oils without affecting the heating value of the original fuel. Therefore, fuel combustion and emission characteristics will display better results than pure vegetable oils are used in engines. Alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol, and amyl alcohol. From these methanol is most commonly alcohol used for the transesterification reaction (Demirbas, 2009). Moreover, the catalyst NaOH quickly reacts with triglycerides and is easily dissolved in it. In this case, the reaction is referred to as methanolysis. In general the stoichiometry of methanolysis reaction requires 3mole of methanol and 1mole of triglyceride to give 3mole of FAME and 1mole of glycerol (Kiakalaiehn, 2013). This reaction, in turn, consists of three consecutive reversible reactions with intermediate formation of triglycerides and monoglycerides. After the reaction, the glycerol is separated by settling or density difference.

Transesterification reactions are basically of three types of catalysts used (i.e. alkali, acid and enzyme based), alkali based catalysts are most widely used in industrial processes because it is more cost effective and less corrosive to the industrial equipment [Alimova, 2016]. The third one is expensive and relatively slow than the first two (Marchetti et al, 2007). Sodium hydroxides are the commonly used alkali catalysts due to rapid reaction rate and produce high yields. By alkali catalyzed process, biodiesel production from avocado peel waste is challenging due to the presence of undesirable components such as free fatty acids (FFAs) and water. Water can be originated from the oils and formed during the saponification reaction and can hydrolyze the triglycerides to diglycerides resulting in the formation of FFA (Komintarachat & Chuepeng, 2010). Avocado peel waste typically contains 2–6 % FFAs and upon addition of an alkali catalyst to it, the FFAs react with the catalyst to form soap and water. Biodiesel is a safer alternative to diesel fuel because it is environmentally safe and has no known side effects on humans.

From all this techniques, transesterification is the most popular (commonly) used for biodiesel production and the most convenient and the most promising method because, it significantly reduces the viscosity of vegetable oils without affecting the heating value of the original (fuel reduction of viscosity), high yields and short reaction times, direct conversion process, simple in operation and environmentally friendly, density, low temperature and pressure and other properties of the vegetable oils. In transesterification, three consecutive reversible reactions convert triglycerides into a mixture of esters and glycerol, in the presence of a suitable catalyst and alcohol. The selection of biodiesel production method also depends on the level of free fatty acids (FFA) present in the feedstock (Abidin, 2012). A pre-treatment stage (transesterification process) is used to reduce the amount of FFA in the feedstock before base-catalyzed transesterification.

2.10. Feed material requirement for Biodiesel Production

40ml of treated oil was used for the maximum oil to alcohol ratio. The amount of methanol and catalyst required for the process parameters at central point was calculated as follows. The amount of methanol required when the molar ratio of oil to methanol ratio is 6:1;

The following data provides the basis for calculation of esters concentrations are:-

Volume of avocado peel oil = 40 mL

Based on above data, amount of methanol, total concentration of methanol is calculated in the following way.

$$\frac{nMeOH}{noil} = 6 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.1)}$$

$$\frac{\frac{(\rho\ MeOH \times VMeOH)}{MMeOH}}{\frac{(\rho 0il * Voil)}{Moil}} = 6 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.2)}$$

Where,

Molar mass of methanol = 32.04 g/mol

Density of methanol = 0.791 g/mL

Density of oil =0.91g/ml

Molar mass of oil =880 g/mol

Substituting the values in to the formula:

$$\frac{\frac{0.791 g/ml * VMeOH)}{32.04 g/mol}}{\frac{(0.91 g/ml * 40 ml)}{880 g/mol}} = 6$$, from this, Solving for V_{MeOH}

V_{MeOH} = 10.2 ml of methanol

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

$M_{oil} = \rho_{oil} * V_{oil}$

$M_{oil} = \frac{0.91 g}{ml} \times 40$ ml

M_{oil} = 36.4 g oil

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

$$\frac{MNaOH}{Moil} = 5\%$$

M_{NaOH} =5% $*$ M_{oil} = 1.8 g. Similarly for the minimum molar ratio of oil to methanol (3:1), the volume of methanol (V_{MeOH} =3.8 ml) and M_{NaOH}=0.68 g, therefore we use between in this gap for the design experiments run. The amount of methanol and NaOH for all design experiments runs used in the same manner.

2.11. Catalyst for biodiesel production

Generally catalysts are used to accelerate or speed up the reaction or it is usually used to improve their action rate and yield. Or a material it initiates and enhances the rate of a chemical reaction without being consumed by that reaction. While catalyst very much participates in the reaction, yet it does not itself appear in the overall reaction at the end, or on the other hand, it does not enter into the stoichiometry of the reaction. Since the reaction is reversible, excess alcohol is required to shift the equilibrium to the product side. Some advantages of catalyst are: changes the rate of reaction, does not affect the equilibrium, can only speed up a reaction that which is thermo-dynamically possible, Lowers the potential energy barriers i.e., lowering the free energy of activation (energy required to initiate the reaction) and has ability to alter yields and selectivity by speeding up some reactions more than others.

Currently there are three types of catalyst that used for the biodiesel production. These catalysts are: homogenous, heterogeneous and enzymatic. Different factors interact in choosing the catalyst, for instance: catalyst thermal stability, deactivation, speed of reaction and conversion rate.

2.11.1. Homogeneous Catalyst

The significant amounts of work have been carried out on homogeneous acid and base catalysis transesterification of vegetable oils. Most of the biodiesel produced today is obtained with the base catalyzed reaction for several reasons: It is a low temperature and low-pressure reaction. It yields high conversion with minimal side reactions and short reaction time. It is a direct conversion to biodiesel with no intermediate compounds. Biodiesel production from feed stocks with high FFA is extremely difficult using alkaline catalyzed transesterification. The alkaline catalysts react with FFAs to form soap that prevents the separation of the glycerine and ester. Sulphuric acid and hydrochloric acid are normally used as acid catalysts especially when the oil contains high amount of free fatty acids and water.

The desired products of the reaction are the methyl or ethyl esters of the fatty acids initially contained in the fat or oil. Glycerine and alkali salts (using alkaline transesterification) are also obtained as by-products, which may be used as raw materials in the chemical industry. One of the major disadvantages of homogeneous catalysts is that they cannot be reused or regenerated, because the catalyst is consumed in the reaction and separation of catalyst from products is difficult and requires more equipment which could result in higher production costs (Khurshid, 2014).

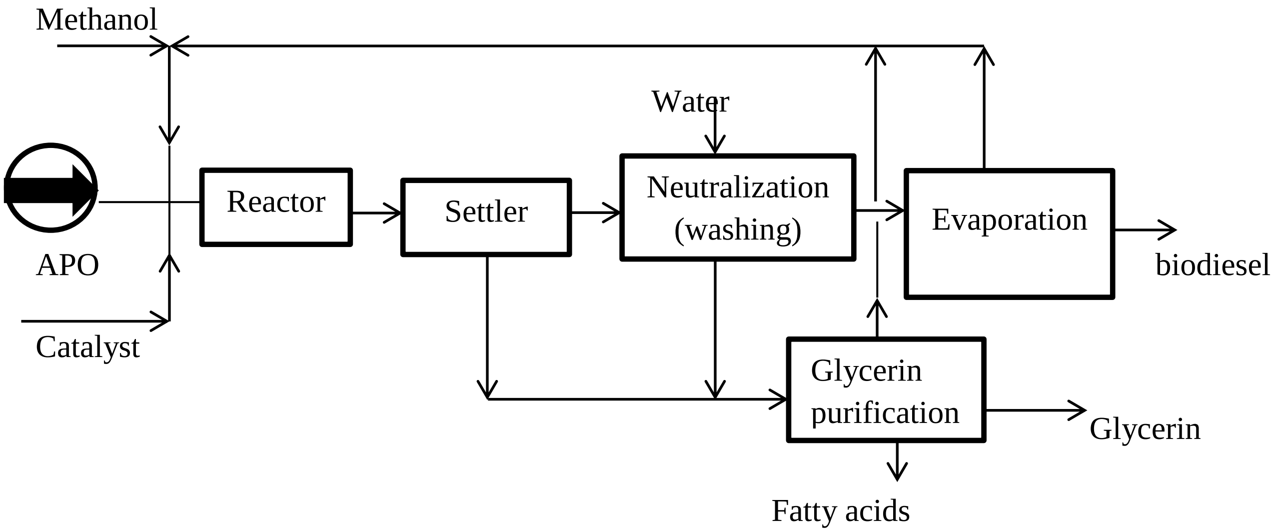


Figure 2.8: Flow chart for biodiesel production by homogenous catalyst.

2.11.2. Heterogeneous Catalyst

Heterogeneous catalysts can be separated from final product by filtration and reused. This causes less consumption of both chemicals and time of course. Heterogeneous catalysts are noncorrosive. They have a high selectivity and can be easily separated from the products. Both basic solids such as metal oxides (CaO) and zeolites as well acid solid such as sulphate tin oxide are used. The use of catalyst supports such as alumina, silica and zinc oxide in order to improve the mass transfer limitation of the three phase reaction will be included. Examples of heterogeneous catalyst are; BaO, KNO_3, KF, CaO, $CaCO_3$. Mass transfer limitations in heterogeneous catalyst are due to two phase zone (solid – liquid) requires well mixing efficiency in order to reduce the external limitations. It uses to be operated at high temperature and high alcohol to oil mole ratio. Heterogeneous catalyst can be used in batch or continues system. Acid catalysts are more expensive than alkali heterogeneous catalysts. They have also less active site, therefore, they are more affected by adsorption reactants rate, surface reaction rate, desorption product rate resulting in limiting biodiesel yield (Khurshid, 2014).

2.11.3. Enzyme Catalyst

In the past years research has been focused on use of an enzymatic catalyst for production of biodiesel. Lipases used in biotechnology are normally of microbial origin and produced by fermentation processes. The use of lipases makes the reaction less sensitive to high free fatty acid (FFA) content which is a problem with the standard biodiesel process. Enzyme catalysts have high selectivity and have approximately fixed running cost and reliable capital investment. It consumes low energy since it operates at low temperature and pressure with one or two steps of isolated enzymes and no side reactions (saponification) compared with alkali transterification. It is insensitive to water content. Enzymatic reaction has low reaction rate and the enzyme has high cost and less activity which is considered as drawback affecting the economic benefit of the process. The produced glycerol covers the enzyme and reduces its efficiency, therefore, it is required additives to observe and remove the glycerol such as silica gel (Khurshid, 2014).

From the three we use the homogeneous catalysts. Because of homogeneous catalysts are favorable due to their capability to produce a high yield of biodiesel under optimum reaction conditions, their simplicity, the process proves faster and the reaction conditions are moderated and short reaction times. However, Sodium hydroxide is very well accepted and widely used because of its low cost and high product yield.

2.12. Alcohols for biodiesel production

Alcohol is one of the most important materials for the production of biodiesel. A number of alcohols have been explored for biodiesel production, the most widely used alcohol are methanol and to a slight extent, ethanol. Other alcohols utilized in producing biodiesel are the short-chain alcohols such as propanol, butanol, isopropanol, tert-butanol, branched alcohols and octanol; however these alcohols are costly.

The selection of alcohol usually depends on the reaction performance and cost. Methanol is commonly preferred because of it is considerably easier to recover physical and chemical advantages, it has a good reactivity with triglycerides, good physico-chemical properties, low cost, the short-chain alcohols provide better conversions under the same reaction time and is easily available. Additionally the reaction with triglycerides was quickly and it can be easily dissolved in NaOH, Ethanol forms an azeotrope with water so it is expensive to purify the ethanol during recovery. If the water is not removed it will interfere with the reactions. Methanol recycles easier because it does not form an azeotrope. These crucial factors are the reason that evens though methanol is more toxic, it is the preferred alcohol for producing biodiesel.

2.13. Mixing and neutralization

The purpose of mixing methanol with the catalyst is to produce methoxide which reacts with the base oils. Most of the catalysts (NaOH and KOH) are in solid form and do not readily dissolve into methanol, it is best to start agitating the methanol in a mixer and add the catalyst slowly and carefully mixed together (Istc, 2006). Once the catalyst completely dissolves in the methanol, the methoxide is ready to be added to the warm oil. Once the methoxide is added into the oil, a neutralization reaction will immediately start. Some alkali catalysts will react with acids during the pretreatment step or will react with the free fatty acids from the oil. Therefore, more catalyst needs to be added to complete the reaction.

2.14. Biodiesel Production Process through Transterification reaction

Transesterification is the process of using an alcohol (e.g. methanol, ethanol or butanol), in the presence of a catalyst, such as sodium hydroxide or potassium hydroxide, to break the molecule of the raw renewable oil chemically into methyl or ethyl esters, with glycerol as a byproduct. Glycerol is the major value-added byproduct produced from oil and fat from trans-esterification reactions performed during biodiesel manufacturing processes. When the catalyst, alcohol, and oil are mixed and agitated in a reaction vessel, a transesterification reaction will start. A stirred reactor is usually used as the reaction vessel for continuous alkali-catalyzed biodiesel production. The two reactants fluids fed were into the designed experimental setup; the first is the preheated oil at 50 ^{0}c, and the second is the well proper mixture of methanol and sodium hydroxide in the well proper flask. The proper amount of catalyst (sodium hydroxide) was dissolved completely in methanol to avoid clogging. The reactants molar ratio was optimized to determine the most proper mixing ratio. The mixer that includes the process reactants was maintained at specific water bath temperature (50-65)^{0}C (Jagadale S.S, 2012). The production processes of biodiesel from the extracted avocado peel oil are in general consists of the following steps.

Table 2.11 the production process of biodiesel

N0.	Operation	Description
1	Avocado peel pre-treatment	Avocado peels are removed by hand from avocado fruits. After removing the peels, avocado peels destined for oil production must be firstly inspected for physical damage and other abnormalities like reducing the size of peels by knife cutting. Then the peels drying in oven at temperature 50^0c for 18 hours (at constant mass). Then the dried avocado peels milled. The powder is prepared to extract oil by Soxhlet extraction method. The oil feedstock is pre-heated to remove any free fatty acids. Some biodiesel producers are etherifying the fatty acids with strong base, and then feeding the mixture to the transesterification process.
2	Catalyst Preparation	First the catalyst is weight, then the catalyst sodium hydroxide reacting with methanol. The catalyst sodium hydroxide is dissolved in the methanol using a simple mixing process. The proportion of sodium hydroxide to methanol is based on the ratio of transterification reaction.
3.	Reaction	Excess methanol is normally added to ensure high levels of conversion of the fat to methyl esters. The catalyst (NaOH) will first react with methanol which can form emulsions and hamper separation and catalyze the reaction. After the (NaOH) react with methanol, oil is added to the reactor and mix in the temperature and time limits.
4.	Methanol Recovery	After the well mixed reaction, the excess methanol is removed (recovered) at this stage via a simple vacuum distillation. In other processes, the methanol is removed after the glycerine and esters have been separated. In either case, the excess methanol is recovered and distilled using a conventional distillation equipment to remove any water. Some care must be taken to ensure no water accumulates in the recovered methanol stream.
5.	Product Separation	Once the reaction is complete, and the methanol has been removed, two major products exist: methyl esters and glycerine. Product Separation due to the density difference between glycerine and methyl esters, it is easy to separate both in a gravity separator. The crude glycerine is simply drawn off the bottom and the bio-

		diesel (methyl esters) at the top layer.
6.	Biodiesel Washing	Once separated from the glycerol, the biodiesel are gently washed with warm water to remove the residual, like catalyst and soaps or any impurities. The esters are dried by oven and sent to storage. In some cases, the esters are distilled under vacuum to achieve even higher purity.
7.	Glycerine Recovery	The co-product, crude glycerine, contains water, residual base catalyst and fatty acid base soaps. The fatty acids usually are separated from the crude glycerine by gravity separation and each phase is sent to storage. Any catalyst remaining in the glycerine (sodium hydroxide) is neutralized by the acid creating a sodium salt, which is simply left in the glycerine.

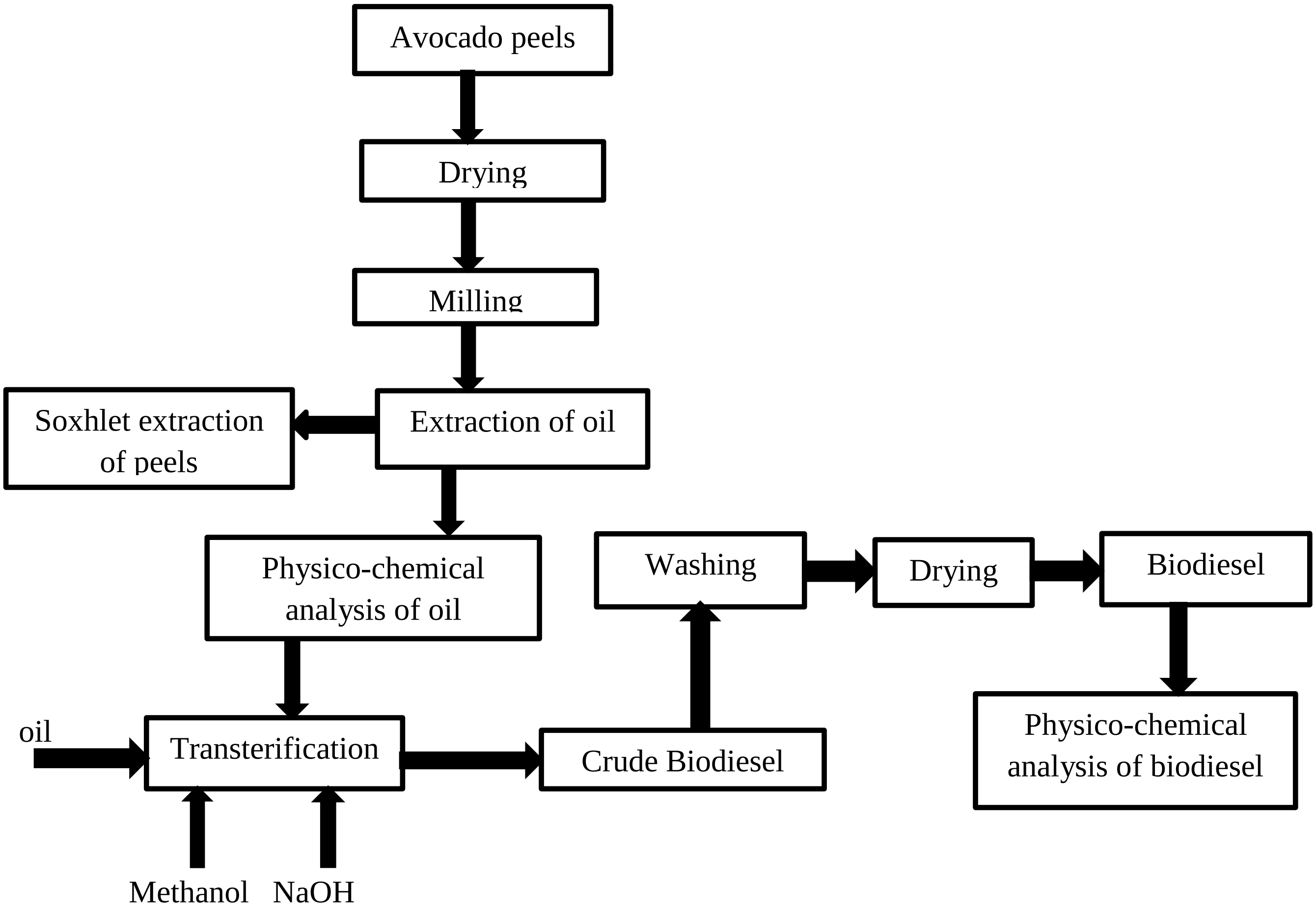


Figure 2.9.The production process of biodiesel.

2.15. Biodiesel compared with other transport fuels

In this section, the comparison of biodiesel with other transport fuels, especially with diesel, in terms of energy, properties and emissions are discussed below:-

2.15.1. Energy comparison

There are different ways in which a comparison between conventional road fuels and bio-road fuels can be made. One valuable way is set on the basis of an energy balance, which is the difference between how much energy is created when producing the fuel, and how much is obtained when using the fuel. The approximation considers the energy used to make the plant grow, to produce biodiesel and to distribute it. According to figures of the US dept. of energy (DOE), the quantity of energy yield by biodiesel is higher than that used on its production. Biodiesel is much higher energy output than the other energy use. On the table below, the energy balance of biodiesel production by transesterification process is much different when we compare each other.

Table 2.12- Energy comparison of biodiesel production from soybean seeds

Fuel	Energy in	Energy out	%
Biodiesel	1	3.2	320
Ethanol	1	1.34	134
Petro-diesel	1	0.84	84
Gasoline	1	0.81	81

Source U.S. Dept of energy (DOE).

The energy efficiency on the above table shows different studies show different values depending on the type of raw material used, and the process carried out, thus it is widely accepted that this will be about 220% higher than other fuel used (Méndez, 2006).

2.15.2 Emissions

According to the environmental protection agencies, using biodiesel are a great contribution instead of petroleum diesel, to nearly 80 per cent reduce greenhouse gas emissions can be made:

- Biodiesel also substantially reduces particle emissions which are hazardous to human health.

- The use and the production of biodiesel exhibit a closed-loop carbon cycle. Greenhouse gases releases to the earth, the emissions released by using biodiesel is equivalent to the amount absorbed by the plant while growing.

Although emissions vary with engine design with the exception of NOx, vehicle condition, and fuel quality the US EPA found the potential emissions reductions from biodiesel blends are considerable relative to conventional diesel, and they increase nearly linearly with increasing blend levels. Toxic emissions reductions are focused in similarly potential emissions reductions (Nerl, 2000), next figure will show it.

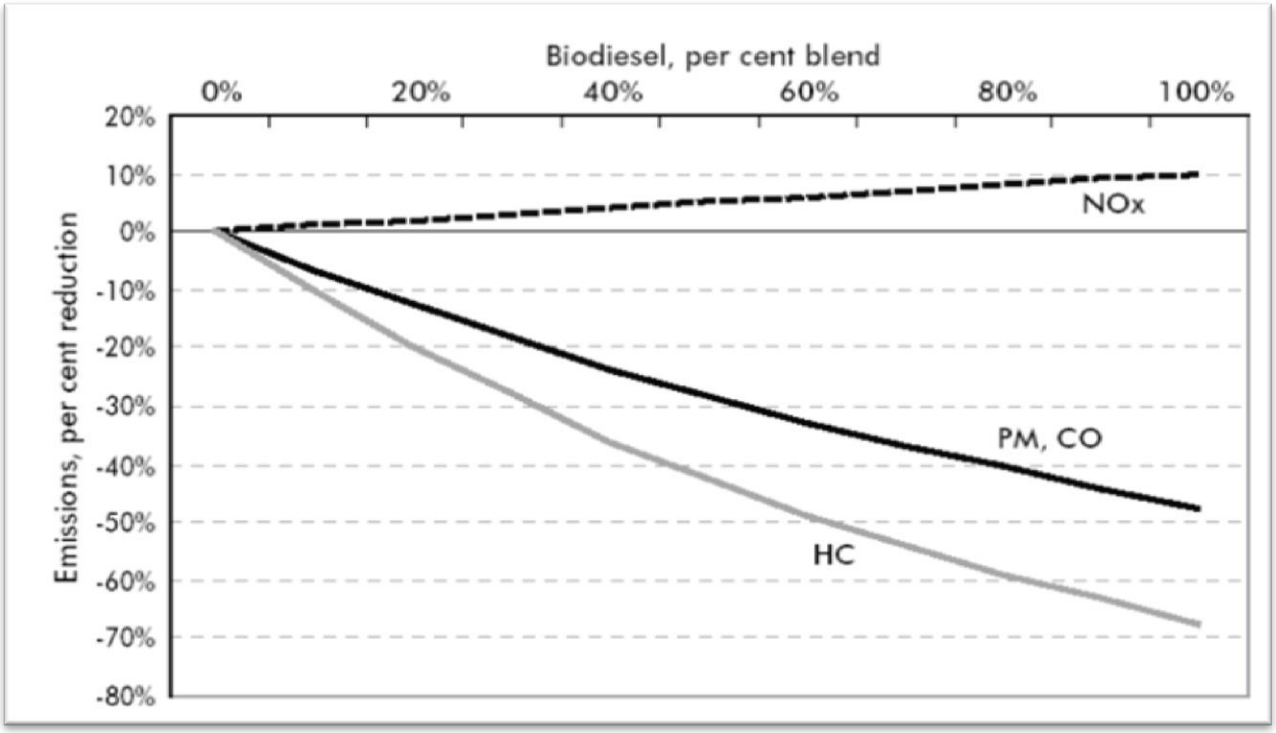


Figure 2.10- Potential emissions reductions from biodiesel. Source: EPA (2002b).

In the above figure as show, by using biodiesel B20, carbon monoxide can be decreased on 13%, hydrocarbons on 11%, particles on 18%. By using biodiesel B100 according to the figure, carbon monoxide can be reduced on 43%, hydrocarbons on 56%, particles on 55%. In general it was considered that total air toxics can be reduced 1.5% by using B100 or 0.3% by using B20.

2.16. Benefits of biodiesel

Biodiesel is a renewable source or an ecological fuel which has the following characteristics has many major advantages, and some minor disadvantages:

2.16.1. Advantages of biodiesel

Important properties of the biodiesel are:

- Biodiesel is renewable. As biodiesel is produced from renewable sources, biodiesel fuel is a renewable energy source.
- It can be used in the diesel engine without little or any modifications.
- It improves combustion process. The biodiesel contains at least 11% oxygen. Biodiesel burns better (more completely with few fuel unburned emissions) than petroleum diesel. Less smoke is produced. The use of biodiesel can reduce the emissions of unburned hydrocarbons.
- It does not contain sulfur. No sulfur emissions are emitted during the combustion
- Biodiesel reduces the health risks associated with petroleum diesel. The use of biodiesel decreases emission and it is non-toxic.
- Greenhouse gas benefit. Moreover, the use of biodiesel can reduced the CO_2 emissions up to 50% in comparison to the use of petroleum diesel.
- Biodiesel is biodegradable. The absence of a chemical and synthetic compound makes it innocuous with our environment.

2.16.2. Disadvantages

There are few disadvantages of using biodiesel as a replacement for diesel fuel that must be taken into consideration:

- Slightly higher fuel consumption due to the lower calorific value of biodiesel.
- Production costs still can be higher than the cost of diesel itself. It all basically depends on the oil source which has been used.
- The biodiesel needs more additives, mainly in cold countries, due to its high cloud point.

- The biodiesel produces more NOx emissions than petrodiesel. It can cause acid rain

2.17. Environmental Impacts of Biodiesels

Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the clean air act. Biodiesel is safer fuel as it has high flash point. It is regarded as clean fuel since it does not contain carcinogenic substances and its sulphur content level is also lower than its content in petrodiesel (Akhtar, 2011). It has many environmental benefits, such as it is biodegradable, non-toxic, is less pollutant to both water and soil and has low emission profile (including potential carcinogens). Moreover since the primary feedstock for biodiesel is a biologically-based material that can be grown season after season, it is renewable.

In contrast to diesel engine, biodiesel creates significant reduction in emission of unburned hydrocarbons, carbon monoxide and particulate matter compared to emissions from diesel fuel. In addition, the exhaust emissions of sulfur oxides and sulfates (major components of acid rain) from biodiesel are essentially eliminated compared to diesel.

2.18. Experimental design

Experiment can be defined as a test or series of tests in which purposeful changes are made to the input variables of a process or system so that we may observe and identify the reasons for changes that may be observed in the output response.

2.18.1. Central composite design

RSM is a collection of mathematical and statistical techniques that are useful for analysis in applications where a response of interest is influenced by several variables. These independent variables for production of biodiesel from avocado peel oil are; the molar ratio of oil to alcohol, reaction temperature, reaction time, and amount of catalyst concentration that used during the reaction mixture at different molar ratio.

A central composite design (CCD) of experiments, originally developed by Box and Wilson (1951), is one the most efficient class of designs capable of generating a response surface. Several factors at several levels can generate a response surface. Systematic errors were avoided by randomized order of experimental runs. For each categorical variable, a 26 factorial CCD for the four variables, consisting of 16 factorial points, 8 axial points and 2 center points are used to reduce the experimental error and the reproducibility of the data, indicating that altogether 26 experiments were required, as calculated from the following equation:

$N=2^4+2n+c$ ……………………………………………………2.3

Where, N= the total number of experiments run

n= the number of factors

c=center points

- $N=2^4+2*4+2=26$

The experimental plan was made using the CCD and the responses measured were the methanol-to-oil molar ratio, amount of catalyst concentration, reaction time and reaction temperature were the independent variables selected to optimize the conditions for production of the biodiesel production from waste avocado peel oil. The experiments were carried out in randomized order and data was statistically analyzed by the design expert software version 6.8.0.Portable (Stat-Ease Inc., USA).

Table 2.13 below shows the specification of, the reaction temperature, reaction time, molar ratio oil to methanol and amount of catalyst (Hiwot, 2017). The independent variables are coded to the (−1, 1) interval where the low and high levels are coded as −1 and +1, respectively.

Table 2.13: Experimental variables and levels

Factor Code	Variable	Low Level (–1)	High Level (+1)
A	Molar ratio of oil to methanol (ml)	3:1	8:1
B	Reaction temperature (^{0}C)	50	65
C	Reaction time (min)	45	90
D	Amount of catalyst (g)	0.6	1.82

CHAPTER - 3

3.1. Materials and Methods

The experimental work has been done in laboratory of Addis Ababa institute of technology school of chemical and bio Chemical Engineering and Science faculty Center of food science and nutrition of Addis Ababa University.

3.1.1 Materials and equipment

Materials that were used in the production of the biodiesel during the experiment work are as follows: avocado peel oil, filter paper ,heater mantle, knife, pipette, measuring cylinder, hydrometer, conical flask, plastic bags, hot plate, condenser, pH meter, measuring cylinder and Piece of cloth.

3.1.2. Equipments

The equipment's used during this experimental work are: Soxhlet extractor, vacuum pump, chiller, water bath, oven was used for drying avocado peel and used to evaporate the excess alcohol from oil, vibro viscometer, conical flasks, three neck flasks, sample bottles, weighing balance, magnetic stirrer, test tubes, milling machine, FT-IR, sieve, beaker, density bottle, measuring cylinder, extraction glass column, heating device, refractometer, thermometer and separation funnel.

3.1.3. Chemicals (Reagent)

The most commonly (primary) used alcohol in production of biodiesel are methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol was the most commonly used alcohol. N-hexane (99%) was used as a solvent for oil extraction from avocado peel powdered. The most commonly used catalyst was alcoholic sodium hydroxide (NaOH) (97%), hydrochloric acid (HCl), distilled water and phenolphthalein indicator.

All the chemicals and reagents were purchased and obtain from Wise team PLC, school of chemical and bio Chemical Engineering of Addis Ababa institute of technology, center of food science and nutrition of science faculty of Addis Ababa University.

3.2. Raw material preparation

The avocado was cut into two pieces and the peels were removed from avocado fruits by hand. The waste avocado peels collected from hotels, cafeteria and juice processing house. The raw material (sample) preparation process include: - manual size reduction (Knife cutting), drying and grinding. Waste peel of avocado 10 kg was used for the sample preparation.

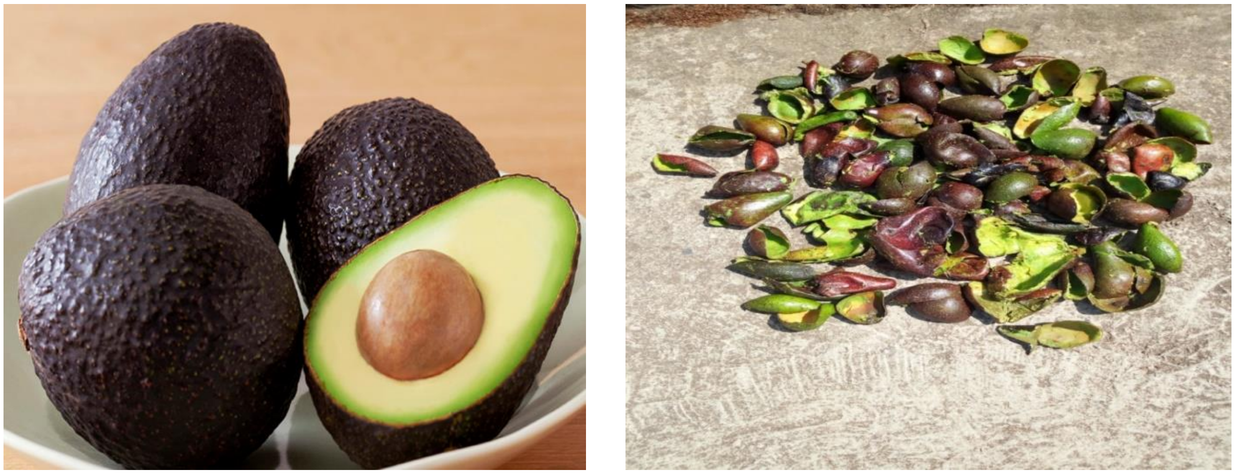


Fig 3.1: Avocado and avocado peel.

3.3. Drying process

Drying process is important in removing water contents from avocado peel. Lipids are impervious to water; therefore any water in the sample will hinder the isolation of triglycerides, which are the precursors needed to generate biodiesel. To determine the most appropriate moisture content of avocado peels, avocado peels were manually crushed with a knife and drying the peel until all of its moisture content was removed. The peel was dried by sun for five days.

Figure 3.2: avocado crushed with knife and drying the peel.

3.4. Determination of moisture content of the Avocado peel

10 kg sample of the avocado peel were weighed and dried by sun for five days and the weight was measured every two hours. The procedure was repeated until a constant weight was obtained and the percentage moisture content of the peel was determined. After a constant weight the moisture content of the sample was obtained by calculating for the water lost upon the drying process.

Moisture content (%): $W = 100 \times \frac{(M0-M)}{M0}$…………………………. (3.1)

Where: M = the final weight of the dried sample (peel).

Mo = initial weight of the fresh sample (peel).

3.5. Milling process (Size reduction and sieve analysis)

After the moisture was removed by placing in sun for five days the dried avocado peel was milled in centrifugal miller. The purpose of milling is to size reduction by cutting action is carried out by feeding dried avocado peels against the rotating cutter. Thus, the spindle, speed, the table feed, the depth of cut, and the rotating direction of the cutter become the main parameter of the process. The particle size was standardized with 2.6 mm sieve. This particular size was selected because literature reveled that to have a higher yield of oil the particle size should be less than 5mm and higher than 0.2mm (Henry, 1983), we use the mean of the two. Finally, the powder was stored in a dark bottle until we use.

(a) (b)

Figure 3.3: (a) Milling machine and (b) powder of avocado peel.

3.6. Oil Extraction process

3.6.1. Method for extraction of avocado peel oil by Soxhlet extraction

A Soxhlet extraction was one of the most used for extraction of the oil. A ratio of crushed avocado peels (powder) to solvent of 1:5 (m/v) was used.100 g of avocado peel powder with the average size of 2.6 mm sieve was placed into the thimble and placed in the Soxhlet chamber. The solvent used for oil extraction was n-hexane.

The extraction was carried out using 500 ml with n-hexane at 69^{0}C (below the boiling temperature) of hexane with purity 99.0 % for 3-5 hr were placed in a round bottom in1000 ml flask and assembled for Soxhlet extractor. Then solvent evaporates and moves up into the condenser, where it is converted into a liquid that trickles into the extraction chamber containing the sample. Eventually, the solvent builds up in the extraction chamber and completely surrounds the sample. The extraction chamber is designed so that when the solvent surrounding the sample exceeds a certain level, it overflows and trickles back down into the boiling flask (Chemat et al., 2008). As the solvent passes through the sample it extracts the oil and carries them into the flask. Finally the oil obtained from 100 g of avocado peel powder was 70 ml (52.2 g) for 3 hr at 60^{0} C and at 4 and 5 hrs 74.74 ml (55.74 g) and 80.3 ml (59.9 g) at 65 & 69 ^{0}C respectively.

Figure 3.4 Extraction of oil by Soxhlet extraction

3.7. Evaporation Process

After completed the extraction process, the flask containing the solvent and lipid is removed and the distillation (recovered) process of oil was begun. The solvent and extractor were placed on water bath to evaporate the solvent. The solvent was evaporated at 70^0c and the oil remains in the flask because of its low volatility (Chemat et al., 2008) and the solvent (n-hexane) evaporates through condenser and we use this solvent for other extraction.

3.8. Degumming process

In degumming process, distilled water was heated to 100^0C and left to boil for several minutes. Then crude avocado peels oil was poured into a beaker and equal volume of hot distilled water was added and stirred vigorously to remove the gums. The mixture was allowed to settle for 5 minutes the oil -water mixture separated into layers with the oil layer on top. The oil was decanted and the process repeated again.

Figure 3.5 Degumming process

3.9. Characterization (Physicochemical) properties of oil

The oil extracted by Soxhlet extraction was used after analyzing the physicochemical properties oil. Physical properties such as density, kinematic viscosity, pH value and chemical properties like acid value, free fatty acid value, saponification value, and iodine value, were determined for oil physicochemical properties using optimum operating parameters.

3.9.1. Determination of density

A clean and dry density bottle of 50ml capacity was weighed in gm. Then, the bottle was filled with water and reweighed. The water was substituted with oil and weighed again and the specific gravity of oil was determined. The density of the sample was calculated from the specific gravity by equation 4.3.

3.9.2. Determination of kinematic viscosity of oil

A kinematic viscosity of the oil was measured indirectly using vibro viscometer which was available in laboratory of school of chemical and bio engineering. The sample was kept in the water bath heated by thermostat until it reaches the equilibrium temperature. A sample of 35 ml oil was measured and fed to a sample holder of the vibro viscometer. A sensor of the viscometer was immersed to the oil and then a dynamic viscosity of oil was displayed on the vibro viscometer screen at a temperature of 30^0C. This was done in triplicate and the average dynamic viscosity was recorded and calculated. The kinematic viscosity (μ) of the oil was calculated from equation 4.4.

3.9.3. Determination of Saponification Value

Saponification Value is defined as the numbers of milligrams of sodium hydroxide require saponified. The saponification value gives on idea of the molecular weight of the fatty acid and the higher the saponification value, the higher the molecular weight.

2 gm of the sample was taken and added in to a 250 ml conical flask followed by the addition of 25ml of 0.5M alcoholic sodium hydroxide solution was added in to the flask. The flask was connected to reflux condenser and kept on the water bath and boiled gently for 1 hour. After the flask and the condenser were cooled, the inside of the condenser was washed with 10 ml of hot ethyl alcohol. Then few drops of phenolphthalein indictor were added and the excess sodium hydroxide was titrated with 0.5 N hydrochloric acid to the end point, until the pink color of the indicator just removed. The same procedure was conducted for the blank and the saponification value (SV) expressed as the number of milligrams of NaOH required to saponified 1 gm of fat or oil was (Nguamo, 2008). Blank determination was also conducted along with that of sample, using the same reagents minus sample (and volume V_b was recorded).

The saponification value (SV) expressed as the number of milligram of NaOH required to saponified 1g oil) was calculated using equation 4.5.

3.9.4. Determination of acid value

Acid value measure the free fatty acids present in oils. Or the number of milligram of sodium hydroxide that is required to neutralize free fatty acids in 1 g of fat or oil. A good quality of oil generally has low acid value (Otieno, 2011). 5 gm of the sample was weighed and poured in to 250 ml conical flask and 50 ml of hot ethyl alcohol was added to the flask. After few drops of phenolphthalein added, the mixture was boiled for about five minutes and while it was hot titrated with 0.5N sodium hydroxide solution and then the acid value was determined.

The total acidity (acid number) in mg NaOH/g oil was calculated using equation 4.6(i). Since the acidity is frequently expressed as free fatty acid from acid value free fatty acid was calculated and FFA of oil was calculated from the acid value using equation 4.6(ii).

3.9.5. Determination of iodine value

Iodine value is a measure of the proportion of unsaturated acids present. Iodine value is measure as the number of grams of iodine taken up by l00gm of fat or oil (Otieno, 2011). Generally, biodiesel made from low iodine value oils have a higher melting point and high iodine value oils have lower melting points and make better cold weather biodiesel.

3.9.6. Determination of high heating value

Energy content or heat of combustion of a fuel was determined using bomb calorimeter. 1 g of sample was taken in a crucible and made into a pellet and the initial weight was noted. It was placed in the bomb, which was pressurized to 18atm of oxygen. The bomb was placed in a vessel containing 2kg of water. The ignition circuit was connected and the water temperature noted. After ignition a temperature rise was noted every minute till a constant temperature was reached. The pressure was released and the length of unburned fuse wire was measured. The determination of the oils calorific value was conducted following the same procedure as that for standardization, except that the sample was solid fat. Including the corrections for heat transfer between the surrounding and the apparatus, heat liberated by the glowing wire etc, the heat value of the oil was calculated according to equation 4.7(**i**).

3.9.7. Determination of melting point

The melted oil was poured into a small heat resistant glass capillary and then let to solidify. After this, the solidified glass capillary was inserted into the $B\breve{U}$CHI apparatus. The melting temperature set point was assigned on the apparatus. When the first melting was observed on the watching screen, the corresponding temperature was recorded.

3.9.8. Determination of pH

The determination of pH value of avocado peel oil was determined to be 5.7; this shows the slightly acidic nature of the oil, it meets the standard value of (5-6.7).

3.10. Transesterification Reaction

Transesterification reaction is the most commonly used method of producing biodiesel. Transesterification is the reaction of oil with an alcohol to separating the fatty acids from their glycerol backbone to form fatty acid methyl esters (FAME) and free glycerol [Abhullah et al, 2007]. Biodiesel can be produced in batch reactor by transesterifying triglycerides APO with lower molecular weight alcohols in the presence of a base catalyst. Biodiesel is biodegradable, non-toxic and essentially free from sulfur, which has a correlation with sustainable development, energy conservation, management, efficiency and environmental preservation.

3.10.1. The Transterification procedure (making biodiesel)

Biodiesel production process by transterification reaction is made using three main components are: avocado peel oil, alcohol, and a base catalyst have been studied in laboratory experiments. A 500ml glass three neck flask reactor equipped with magnetic stirrer, electric thermostat, and condenser was used in all experiments. The reactor was connected to a water bath heated with thermostat, which was capable of controlling the temperature within deviation of 1^0C. The procedures for the biodiesel production by transterification reaction are:

(i). Mixing of the methanol and the catalyst in a 200 ml beaker using the mixing ratio of methanol and catalyst concentration respectively. A quantity of methanol was poured in a beaker and the sodium hydroxide pellet was placed in the weighing balance to get exactly weight and mix with methanol to 50^0C (in a water bath) and stirred by manually until the catalyst is completely dissolved in methanol. The moisture level should be kept as low as possible. Water causes the formation of soap by saponification. It is necessary to reduce the formation of soap. Formation of soap consumes the catalyst is consumed and complicates the separation and purification process. Formation of soap also decreases the biodiesel yield.

(ii).The methanol and sodium hydroxide solution was poured in the warm avocado peel oil in a 500 ml three neck flask and stirred vigorously for (45-90) minutes using a magnetic stirrer at 500 rpm. The mixture was then allowed to settle for 24 hours in a separating funnel. After settling, the upper layer which was biodiesel was poured into a separate beaker, while the lower layer (i.e. glycerol, soap and other residual) was collected from the bottom of the funnel. The quantity of biodiesel collected was measured and recorded in each run.

(iii). Washing biodiesel. Warm distilled water was used to wash the biodiesel to remove any impurities like, excess methanol, glycerol and soap that remain in the funnel. This was repeated until a clear biodiesel in the separating funnel was obtained (clear water was seen below in the separating funnel).

(iv).The washed sample was dried by placing it on a hot plate (oven) to evaporate the excess water in the biodiesel.

(v).The quantity of biodiesel was measured and collected in the sample holder and recorded in each sample run.

Note: The above procedures were repeated by varying the mole ratio of avocado peel oil to methanol, catalyst concentration, stirring time, and reaction temperature by design experimental run.

Figure3.6 Mixing of NaOH and methanol and experimental transesterification reaction process

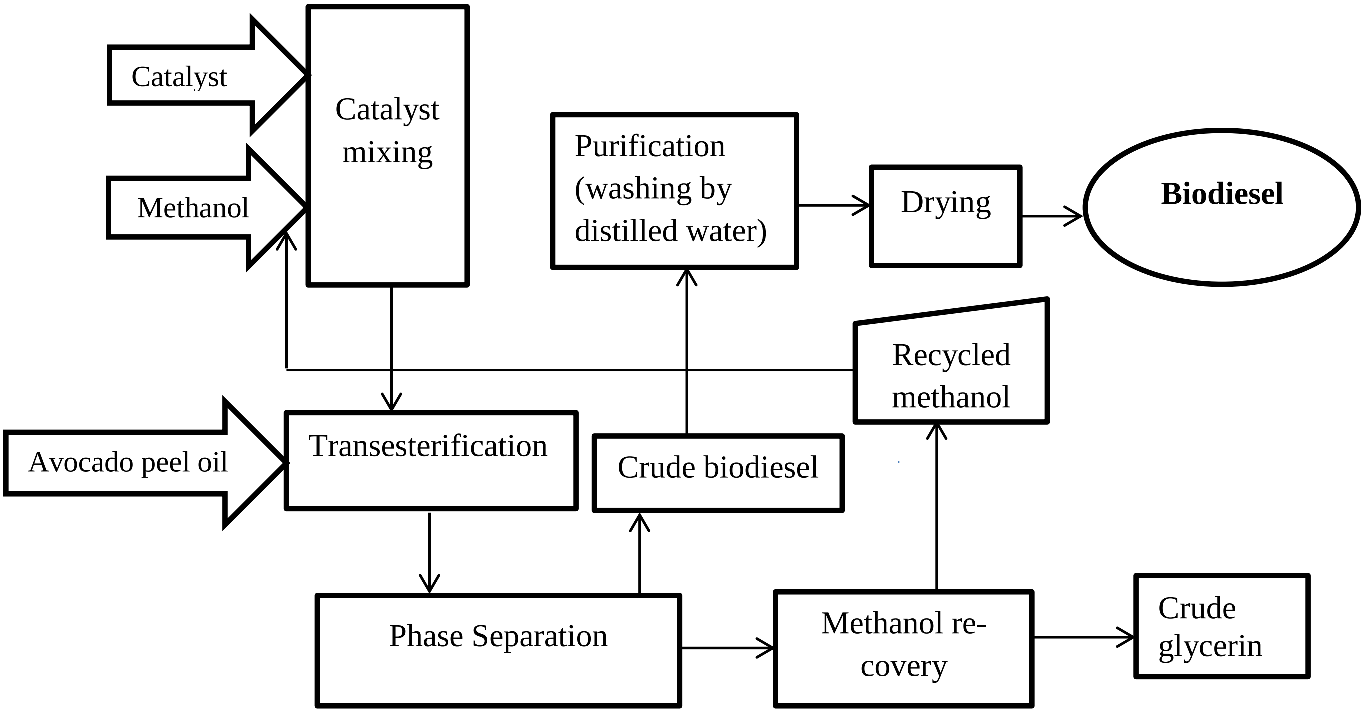


Figure 3.7: The production process of the biodiesel by transterification reaction.

3.11. Separation process

After the reaction was completed the separation process is one of the most crucial parts of biodiesel production. The product from the transesterification process is normally composed of biodiesel, glycerine, alcohol, catalyst and unreacted glycerides. The properties of the fuel are strongly influence by the purity of the biodiesel product. Normally, the biodiesel is separated from by-product glycerine using a simple gravitational settling (density difference) method and left for 24 hours. The separation process using the separation funnel was considered to be cost effective. After 24 hours two different layers were seen in the separating funnel. The above biodiesel layer was separated for further purified and the lower glycerol layer was decanted off. The glycerol phase is much denser than the biodiesel phase.

Figure 3.8 separation processes.

3.12. Washing and Drying

3.12.1. Washing (Purification) of crude biodiesel

Once phase separation has been achieved, the purification of the ester phase is necessary to ensure that the biodiesel meet specifications (ASTM). After the phase separation of glycerol, the biodiesel still has an excessive amount of soaps, aggressive pH, catalyst, FFAs, water, methanol, glycerides and other impurities. These substances, if not reduced to their limits value, this will have effects on the biodiesel and it may not meet the ASTM. The biodiesel is washed with warm distilled water to remove any residue, insoluble impurities left in biodiesel after the reaction and initial settling is complete. The contaminants include (primarily) excess alcohol, excess catalyst, soap formation glycerine and a small amount of left over lye. Water used is warmed to about 50^0C for the washing process, 50% (related the biodiesel volume) of water was added to the biodiesel in order to extract contaminants passed through the esters to allow soluble material, excess catalyst and other impurities to stick to the water and be settled to the bottom of the vessel. The mix was allowed to separate, forming a top biodiesel layer and a bottom aqueous layer, due to difference in densities and immiscibility. After complete separation, the aqueous layer is removed and the washing process is repeated until the aqueous layer shows no contamination and the pH of the biodiesel becomes relatively neutral. When biodiesel is first made, it is quite with a pH of between 8 and 9. Washing with distilled water it is sufficient to improve impurities bringing the pH down biodiesel becomes relatively neutral.

Table 3.1 Effects of Impurities in biodiesel on diesel engine performance (Prah, 2010)

Impurity	**Effects**
FFAs	Corrosion and low oxidation stability.
Water	Hydrolysis (free fatty acid and alcohols formation), corrosion, bacteriological growth (filter blockage).
Methanol	Low values of density, viscosity and low flash point.
soap, catalyst	Deposit in the injectors, filter blockage (sulphate ashes), and engine weakening.
Glycerol	Settling problems.

3.12.2. Drying (Evaporation) process

The last step was drying process. The biodiesel washing process sometimes leaves the biodiesel looking a bit cloudy. This means there's still a little water in it. Drying biodiesel requires a little more than heating up the final biodiesel at 65 ^{0}C, for 15 - 20 minutes until all any remaining moisture (water) evaporate and removed from the sample. After the biodiesel washed and dried, the yield of biodiesel production must be analyzed to ensure it meets any required specifications and product was then characterized using empirical formula to confirm the biodiesel production yield and consider the biodiesel yield with its standard.

3.13. Physicochemical Properties of Biodiesel

The production of biodiesels from avocado peel oil by the transesterification reaction was characterized by their physical and chemical properties by empirical formula and gas chromatography analysis. The extensively characterized physical properties were specific gravity, kinematic viscosity, pH, higher heating value, and cloud point. The biodiesels were, also characterized for their chemical properties such as acid value, free fatty acid value, iodine value, saponification value, cetane number and flash point (U.S, 2014).

3.13.1. Determination of Specific Gravity

The density of the oil (biodiesel) was determined by using density beaker. A clean and dry bottle of 100ml capacity was weighed (W_0) and then the beaker was filled with the oil (biodiesel) and reweighed to give (W_1). The oil (biodiesel) was substituted with water after washing and drying the bottle and weighed to give (W_2). The expression for specific gravity (Sp.gr) is:

Specific gravity= $\frac{(w1-W0)}{W2-w0}$ ……………………………………………………………….3.2

Where, $W_1 = M_{oil\ (biodiesel)} + M_{beaker}$

$W_o = M_{beaker}$

$W_2 = M_{water} + M_{beaker}$

Sp.gr = $\frac{87.8-35.6}{94.6-35.6}$ =0.88, it meets the standard Limits of ASTM (0.86-0.9) of the specific gravity of biodiesel.

3.13.2. Determination of density

Density influences the efficiency of the fuel for airless combustion system. It has some effect on the break-up of fuel injected into the cylinder. Since density is strongly influenced by temperature, the quality standards state the determination of density at 15 ^{0}C. The air fuel ratio and energy content within the combustion chamber are influenced by fuel density. The denser the oil the higher the energy content per liter. The density of oil or biodiesel was determined from specific gravity of oil (biodiesel).

Density=specific gravity *density of water……………………….………..……..3.3

Density =0.88 × 1000 kg/m^3 = 880 kg/m^3. From this result the density of avocado peel methyl ester is 880 kg/m^3 which meet the ASTM Standards.

3.13.3. Determination of API Gravity of Biodiesel

API Gravity of biodiesel test is actually determined using specific gravity of biodiesel. The API gravity is a widely used measure of fuels density. API Gravity is inversely proportional to specific gravity. As API gravity goes up, specific gravity goes down.

The formula that relates API to SG is:

API = $\frac{(141.5)}{SG} - 131.5$………………………………………………………….. (3.4)

API = $\frac{(141.5)}{0.88} - 131.5$ =31.14

As API gravity increases energy content decreases. Since specific gravity is the inverse of API gravity, a higher specific gravity means a higher energy content fuel. As specific gravity increases, power output increase. The API limits for biodiesel are 30 to 45. This value translates to specific gravities of 0.879 to 0.802.

3.13.4. Kinematic Viscosity

Viscosity is the most important factor of fuels that affects the flow of the fuels i.e. its fluidity. The kinematic viscosity is defined as the resistance to flow of a liquid against gravity (viscosity is the reverse of fluidity). To define kinematic viscosity, it is useful to begin with the definition of viscosity. Simply stated, viscosity, which is also called dynamic viscosity (η), is the ease with which a fluid will flow and technically, it is the ratio of the shear stress to the ratio of a fluid. In contrast, the kinematic viscosity *(V)* is the resistance to flow of a fluid under gravity. Therefore, the kinematic viscosity of a fluid is related to the dynamic viscosity through the density (ρ) i.e.

$$V = \frac{\eta}{\rho} \text{……………………………………………….. (3.5)}$$

Where, μ= dynamic viscosity, mpa.sec

ν= kinematic viscosity, mm^2/s

ρ=density, Kg/m^3

Dynamic viscosity of oil, which was red from vibro viscometer was 37.2mpa.s at a temperature of 40 ^{0}C. Substituting the dynamic viscosity = 37.2mpa.s = 3.72×10^{-2}kg/m.s and density of biodiesel (BD) is 880kg/m^3.

V = $\frac{3.72*10-2kg/m.s}{880kg/m3}$ = $4.22\times10^{-5}m^2/s$, Therefore kinematic viscosity of avocado peel methyl ester is 4.22cSt which meets ASTM Standards.

3.13.5. Determination of pH Value

The pH electrode was standardized with distilled solution and the electrode immersed into the sample and the pH value was read and recorded. Therefore the pH values read from the standardize electrode is 7.8, this satisfy the ASTM which is from (7-9).

3.13.6. Cloud point (CP)

The cloud point (CP) is a measure of the temperature at which components in the biodiesel begin to solidify out of the solution. The cloud point is reached when the temperature of the biodiesel is low enough to cause wax crystals to precipitate. Initially, cooling temperatures cause the formation of the solid wax crystal. Further decrease of temperature causes these crystals to grow. The CP is the most commonly used measure of low-temperature operability of the fuel. The biodiesel cloud point is typically higher than the cloud point of conventional diesel.

3.13.7. Pour point (PP)

The pour point is the temperature at which the fuel contains so many agglomerated crystals that it is essentially a gel and will no longer flow. This occurs if the temperature of the biodiesel drops below CP. Similarly to the cloud point, the pour point values also depend on the feedstock. Although CP and PP are relatively easily determined, they only provide indicative values for the minimum temperature at which the fuel can be used.

3.13.8. Flash point (FP)

A key property determining the flammability of fuel is the flash point. It measures the tendency of fuel to form flammable mixture with air. The flash point is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source under specified conditions. The flash point does not affect the combustion directly; higher values make fuels safer with regard to storage and transportation. Minimum flash point temperatures are required for proper safety and handling of diesel fuel. FP varies inversely with the fuel’s volatility. If the temperature is at or above the flash point, the vapours will ignite and an easily detectable flash can be observed. (Surma, 2008)

3.13.9. Determination of Acid Value (Number)

Free fatty acids occur naturally in vegetable oils and thus are carried over into the final product after transesterification. The amount of free fatty acids in the biodiesel is indicated by the acid number which is an expression of the milligrams of NaOH per gram of sample required to titrate a sample to a specified end point. The standard established by the ASTM is a maximum of 25ml of toluene and 25ml of methanol was mixed in beaker. The resulting mixture was added to 2g of biodiesel in a 250ml conical flask and few drops of phenolphthalein were added to the mixture. The mixture was titrated with 0.1M NaOH to the end point with consistent shaking for which a dark pink color was observed and the volume of 0.1M NaOH (V) was noted.

The Acid value was calculated as:

Acid Value = $\frac{(v * c * 40)}{M}$……………………………………………………….3.6

Where,

C=concentration of NaOH

V=Volume of titrated solution

M=Mass of sample

40=Molecular weight of NaOH

Acid Value = $\frac{(0.1 * 0.1 * 40)}{2}$ = 0.4

3. 13.10. Determination of free fatty acid value

Determination of the free fatty acid has from acid value. Therefore the free acid value was calculated using the following formula.

Free fatty acid value = $\frac{(AcidValue)}{2}$………………………………………………3.7

Free fatty acid value = $\frac{(0.4)}{2}$ = 0.2, this value satisfy the ASTM.

3. 13.11. Determination of refractive index

Refractive index was determined by using refract meter and three drops of oil (biodiesel) onto refract meter and reading the value at specified temperature. Refractive index implies the purity of oil. The lower the refractive index is the higher the quality of oil (Anhwange et al, 2010). A refractive index of 1.54 at a temperature of 40 ^{0}c was obtained. The result obtained indicated that the oil is of high quality.

3. 13.12. Cetane Number (Index)

Cetane number is a relative measure of the interval between the beginning of injection and auto ignition of the fuel. Fuels with low cetane numbers will result in difficult starting, noise and exhaust smoke. Theoretically, the cetane number is defined in the range of 15-100. In general, biodiesel engines will operate better on fuels with cetane numbers above 51. Higher cetane numbers indicate shorter times between the injection of the fuel and its ignition.

3. 13.13. Determination of Iodine Value

Iodine Value (IV) is the amount of iodine, measured in grams, absorbed by 100 grams of given oil. 0.2g of avocado peel oil in each case was weighed out and placed in a dry flask. The oil was dissolved in 20ml of carbon tetrachloride. The stoppered flask was swirled to mix the contents and in a dark cupboard for 1 hour at normal temperature (Approx. 25^0C). It was removed and 20ml of a 15% potassium iodine solution was added followed by l00ml of distilled water. The liberated iodine was slowly titrated with 0.1M thiosulphate solution until the yellow colour almost disappeared. At this stage 2ml of indicator was added and the blue colour which appeared was added discharged by further slow additions of thiosulphate. The iodine value was calculated by this formula:

$$\text{Iodine value} = \frac{(B-S)\times M\times 12.69}{Weight\ of\ sample} \qquad 3.8$$

Where, B = blank titration

S = Sample titration

M = Molarity of sodium thiosulphate solution

12.69 = atomic weight of iodine

IV = $\frac{(20-2)\times 0.1\times 12.69}{0.2}$ =114.21, this satisfy the ASTM, since higher iodine value indicates a higher quantity of double bonds in the sample and greater potential to polymerize in engine and hence lesser stability.

3.14. Factor affecting on the Extraction of Avocado peel oil by Soxhlet extraction

The efficiency of oil extraction by Soxhlet extraction from avocado peel oil can be influced by different factors such as particle size, solvent type used, extraction temperature, extraction time, moisture content of the peel and solid to solvent ratio (avocado peel powder to n-hexane).

3. 14.1. Effect of Time on the extraction

In the above result obtained the oil yield (expressed in percent) was extraction time reliant. In general, the oil yield increased with increase in extraction time and there was no considerable increase after 5hour (Tesfaye and Tefera, 2017). Results shown from table *4.1 and figure 4.1*, Soxhlet extraction using n-hexane the time changed from 3hr to 5hrs the percent oil yield changed from 35.6% to 40.5%. This percent indicates as the extraction time increases the percent oil yield also increases.

3. 14.2. Effect of Temperature on the extraction of oil

From the above results (*table.4.1, figure 4.1)* the obtained value analysis showed that an increase in temperature generally favors an increase in percent oil yield. This phenomenon is due to the fact that oils are generally more soluble at elevated temperatures. At higher temperatures, the viscosity of the solvent is reduced while the diffusivity, as well as evaporation rate is increased. This increases the contact time between the solvent and the oil bearing material (Tesfaye and Tefera, 2017). Temperature generally affects both the equilibrium and mass transfer rate of the extraction process. Soxhlet extraction using n-hexane the temperature changed from 65 to 69^0c the percent oil yield changed from 35.6% to 40.5%. This percent indicates as the extraction temperature increases the percent oil yield also increases.

3. 14.3. Particle size

The Particle size influences oil extraction by the Soxhlet extraction rate in many ways. The smaller the particle size, the greater is the interfacial area between the solid and liquid, and therefore the higher is the rate of transfer of material and the smaller is the distance the solute must diffuse within the solid as already indicated. On the other hand, the surface may not be so effectively used with a very fine material if circulation of the liquid is impeded and separation of the particles from the liquid and drainage of the solid residue are made more difficult (Richardson et al., 2002).

To obtain adequate oil release, particle diameters or thicknesses in the 0.2 - 5 mm range usually represent a good choice for scale up extractions (Henry, 1983). For our cause we use the mean of the two sizes, i.e. [(0.2+ 5)] / 2 =2.6 mm.

3. 14.4. Solvent Type

The liquid chosen should be a good selective solvent and its viscosity should be sufficiently low for it to circulate freely. Generally, a relatively pure solvent will be used initially, although as the extraction proceeds the concentration of solute will increase and the rate of extraction will progressively decrease, first because the concentration gradient will be reduced, and secondly because the solution will generally become more viscous (Richardson et al., 2002). The most solvent extraction methods that we use during extraction are a trial and error approach. The most commonly used solvents for avocado peel are commercial n-hexane. N-hexane is solvents desirable to be cheap, noncorrosive, nonflammable, non-explosive, nontoxic, easily removable, and easily recoverable. It obviously may be impossible to meet all these objectives (Henry, 1983). `

3.15. Factor affecting on the production of biodiesel

3. 15.1. Purity of reactants

The impurities present in the vegetable oil affect ester conversion significantly. The vegetable oil (crude oil) is filtered before the transesterification reaction. The oil settled at the bottom of the flask during storage would give lower yield because of deposition of impurities such as wax.

3. 15.2. Water Content

Water content is one of the variables that significantly affect the performance of the transesterification reaction when present in the feed stock oil and also the final biodiesel product. All materials involved in the transesterification process should be waterless because it decreases the biodiesel yield in the transesterification reaction, can lead to corrosion and also promotes bacteria growth in biodiesel and simultaneously contributes to the formation of soap. The produced soap increases the viscosity of the reaction mixture leads to difficulty in the separation process. A limit of water in the product is a maximum of 0.05 volume % is set as a standard in ASTM (Prah, 2010).

3. 15.3. The kinetics and mechanism of transesterification reaction

Kinetic of the transesterification reaction of oils provide the extent of reaction by predicting parameters at any given time under particular reaction conditions. Kinetics usually includes the determination of rate constant and reaction rate equation as well as activation energy. The overall transesterification reaction consists of a number series, of three equivalents, consecutive and reversible reactions, in which mono and diglycerides are formed as intermediates. Transesterification is, in principle, the action of one alcohol displacing another from an ester, referred to as alcoholysis. In transesterification reaction oils, triacylglycerol react with an alcohol, to produce esters and glycerin. Transesterification is conducted to produce biodiesel with the objective to reduce the viscosity of the parent vegetable oil fat, since it is an order of magnitude greater than that of the biodiesel. The kinematic viscosity of avocado peel oil significantly reduces after transesterification.

A mole of ester is liberated at each step. The triglyceride is converted stepwise to di-glyceride, mono-glyceride and finally to the by-product which is called glycerol. The reactions are reversible, although the equilibrium lies toward the production of fatty acid esters glycerol (Ecky, 1956).

CHAPTER FOUR

4. RESULTS AND DISCUSSIONS

4.1.1 Determination of moisture (water) content of the avocado peels

The total weight of the avocado peel we use (weight of sample before dry) was 10 Kg, but weight of sample after dry from this mass of peel was 2.9 Kg. The percent moisture content of the peel was calculated by substituting these values in to equation 4.1.

% Moisture content = $\frac{W1 - W2}{W2} \times 100$ 4.1

Where, W_1 = Original weight of the sample before drying.

W_2 = Weight of the sample after drying.

% Moisture content = $\frac{10\ kg - 2.9\ kg}{10\ kg} \times 100$ =71 %.

This meets the physicochemical properties of avocado skin. Therefore, 71 % of the avocado peel was moisture and drying by oven or sun drying for five days used for oil extraction using n-hexane.

4.1.2. Determination of the percentage of oil yield extracted from avocado peel

100 g (W_1) of the sample was placed in the thimble and about 500ml of n-hexane was poured into the round bottom flask. The apparatus was heated at 70 ^{0}C and allowed for 5hrs for extraction process. After the extraction, the solid avocado powdered was dried in the oven at 105 ^{0}C and weighed until the constant weight (W_2) is attained and the percentage of oil extracted was determined as:

% crude oil yield = $\frac{(w1 - W2)}{w1} \times 100$ ……………………………………………………4.2

Where, W_1 =weight of sample before extraction

W_2 = weight of sample after extraction

Table.4.1: show result of Soxhlet extraction with particle size 2.6mm at different temperature and time with the above formula.

Trial	*Temperature (0c)*	Time (hr)	weight of sample before extraction(g)	weight of sample after extraction(g)	Oil yield (%)	Average (%)
1	60	3	100	64.6	35.6	38
2	65	4	100	62.8	37.8	
3	69	5	100	59.4	40.6	

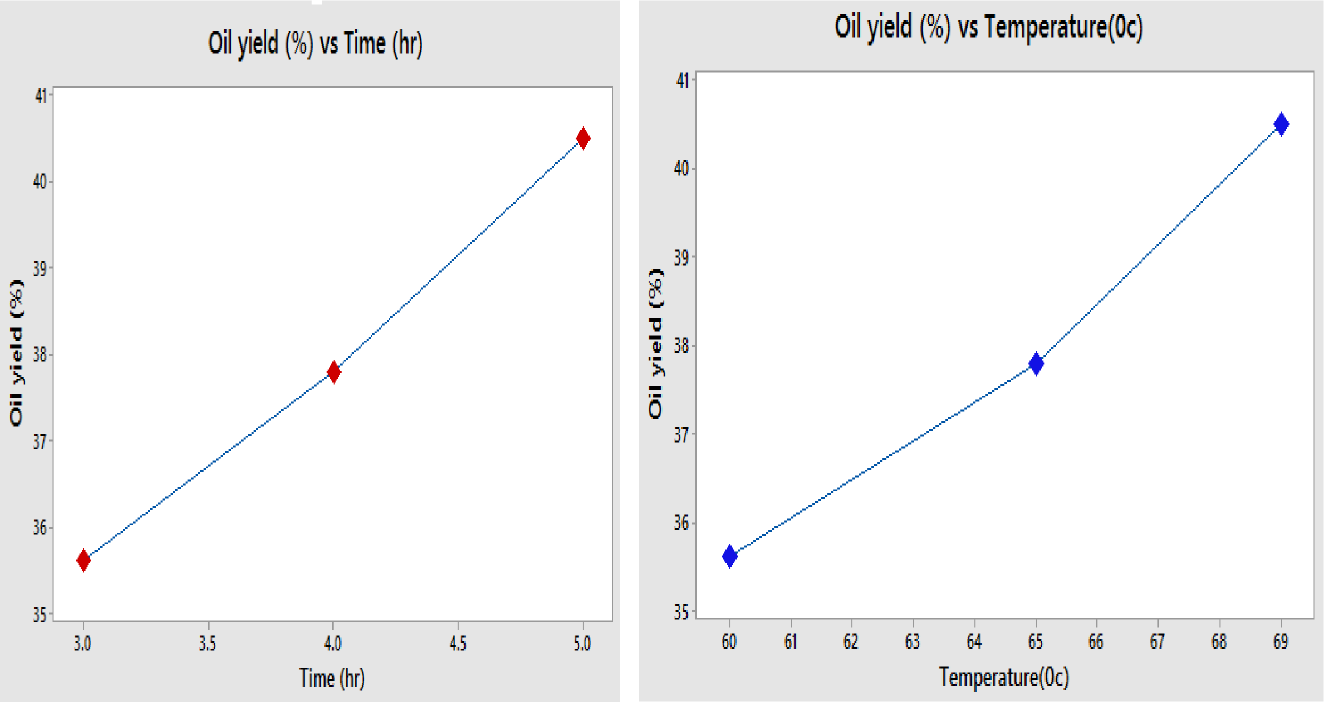


Figure 4.1 oil yield (%) of oil extraction by Soxhlet extraction at different temperature and time.

4.1.3. Physicochemical properties of avocado peel oil

Avocado peel oil was first characterized before produce biodiesel. The details of the properties are discussed below as follows:

4.1.4. Specific gravity

The oil sample was brought to a test portion was transferred to the measuring cylinder. Densimeter was inserted in to the cylinder. Then, the reading was taken.

The specific gravity observed was 0.91. Hence, the density of the oil is determined using the specific gravity.

$$SG = \frac{\rho oil}{\rho w} = \rho_{oil} \qquad 4.3$$

Where, ρ_{oil} = Density of avocado peel oil

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

Therefore, the density of the oil was 0.91g/ml or 910kg/m^3.

4.1.5. Kinematic viscosity

Viscosity refers to the thickness of the oil, and is determined by measuring the amount of time taken for a given measure of oil. The viscosity of oil was measured using Vibro viscometer. The device detects the dynamic viscosity, which is resistance to flow with vibration. The observed dynamic viscosity was at 40 ^{0}c was 47.2mpa.s

$$V = \frac{\eta}{\rho} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (4.4)$$

Where, μ= dynamic viscosity, mm^2/s

ν= kinematic viscosity, mpa.sec

ρ=density, Kg/m^3

$V = \frac{\eta}{\rho} = \frac{4.72\times10-2\,\frac{kg}{m}.sec}{910kg/m3}$ = 5.2 *$10^{-5}$$m^2$/s, which is in agreement with literature data.

4.1.6. Saponification value

Generally the SV is inversely proportional to the mean molecular weight of the fatty acid in oil. The saponification number was determined by using titration. Solutions were prepared with the required concentration. In order to know the exact concentration, the solution was standardized. Hence, primary and secondary standardization was used.

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

= 0.5mol/l *40g/mol*1 lit = 20 g

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

=0.5*36.5*1l =18.25g

V_{HCl}= m/ρ=18.25/1.16 =15.73ml

2g of oil was dissolved in ethanolic NaOH and titrated with HCl. Similarly blank titration was done. In both cases, the volume of HCl was recorded. The saponification value was then calculated using equation 4.5.

$$SV = \frac{40*N*(Vb-Va)}{W} \qquad 4.5$$

Where, w = weight of oil used, 2g

N= normality of HCL solution, 0.562N

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

V_b= volume of HCl solution used in blank, 47.2 ml

Values for unknowns in equation 4.5 were substituted; hence the SV was calculated. The observed value was 200 mg of NaOH/g of oil, which is satisfy the literature data. The ranges of SV of avocado peel oil are 170-200 mg/NaOH/g in AOCS. (1998).The experimental result was attached in Appendix C.

4.1.7. Acid value

Acid value is the measure of total acidity of the lipid involving from all the constituent fatty acids that make up the glyceride molecule (Indhumathi P et al, 2014). Titration method was used to determine the acid value. The required solutions were prepared with the required concentration as follows. The titrant volume was observed to be 11ml. The acid value of the oil was calculated as:

$$\text{Acid Value} = \frac{(v * c * 40)}{M} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.6(i)$$

Where,

C=concentration of NaOH

V=Volume of Titrated Solution

M=Mass of Sample

40=Molecular Weight of NaOH

Acid Value = $\frac{(11 * 0.1 * 40)}{5}$ = 8.8 mg NaOH/g of oil

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

$$AV = FFA * 2 \qquad 4.6(ii)$$

Therefore, % FFA = AV/2= 8.8/2 = 4.4 %, the % FFA value was far beyond the required limit for biodiesel transesterification.

4.1.8. Higher heating value

Heating Value or Heat of combustion is the amount of heating energy released by the combustion of a unit value of fuels. It was determined by using bomb calorimeter. 1g of benzoic acid was used as a calibrating substance (Tesfaye, July, 2011). The amount of water used to fill the calorimetric container was 2000g. Equation 4.8(**i**) was used to calculate the HHV of the oil.

$$HHV = \frac{[mw + Cw + (mc)app]\ (tm + c - to) - \sum b}{m} \qquad 4.7\ (i)$$

Where: HHV= Higher heating value, cal/g

m =Mass of the fuel, g

m_w = Mass of the calorimeter water, g

C_w=Specific heat of the calorimeter water, C_w = 1cal/g^{0}C

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

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

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

Σb=Correction for heat exchange between calorimeter and the surrounding, cal

The correction, c was calculated from the formula in equation 4.7 (ii).

$$c = m'\Delta n - (\Delta n + \Delta \nu)\ F \qquad 4.7\ (ii).$$

Where, m′= duration of main test, min

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

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

The factor F can be approximated to: F = 1.0, 1.25 and 1.5, and if the temperature rise in 1st minute of the main test is higher than in the 2nd, temperature rise in the 1st minute and 2nd minutes of the main test are about the same, and temperature rise in the 1st minute of the main test is less than in the 2nd minute respectively.

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

The HHV of benzoic acid was known with a guaranteed heat of combustion of 6324 Cal/g. The recorded higher heating value of the oil is 40MJ/kg. The result is in agreement with literature data. See Appendix C for more experimental calculations.

4.1.9. Iodine Value

Iodine value is the measure of the degree of unsaturation of a particular oil or fat. It was determined using empirical equations given in equation 4.9.

$$HHV = 49.43 - [0.041(SV) + 0.015(IV)] \qquad 4.8(i)$$

$$IV = \frac{-HHV + 49.43 - 0.041(SV)}{0.015} \qquad 4.8(ii)$$

The iodine value of the oil was calculated equal to 82 g I_2/100g.

4.1.10. Melting point

The melting point of the solidified oil was determined by BUCHЇ Melting Point B-540. 1 g of APO was introduced into the capillary tube. Then the temperature set of the apparatus was adjusted to heat to 45 ^{0}C. The first melting was observed on the watching screen and the temperature was recorded, and it was 38.5 ^{0}C.

4.1.11. Molecular Weight Determination

To determined molecular weight of oil the saponification value and acid value of avocado peel oil was used (Indhumathi P, 2014). The molecular weight of the oil was calculated as:

$$M_W = \frac{168300}{SV-AV} \qquad 4.9$$

Where, M_W-molecular weight of oil

SV- Saponification value of oil

AV- acid value of oil

- ❖ $M_W = \frac{168300}{200-8.8}$ = 880 g / mol

Table 4.2: Physico-chemical of Properties of the obtained biodiesel and avocado peel oil and the standards of biodiesel in the United States and Europe

Property	**Avocado peel oil**	**Biodiesel Yields**	**EN 14214**	**ASTM D-6751**
Density at 15 ^{0}C, kg/m^3	910	880	860-900	
Flash point, (^{0}C)		161	>120	>130
PH	6.2	7.8	5- 6.7	7-9
API		31.14		30-45
Specific gravity	0.91	0.88	0.86-0.9	
kinematic viscosity at 40 ^{0}C, cSt	5.1	4.22	3.5-5.0	1.9-6.0
Esters content %	38	95.2		
HHV (MJ/kg)	40	41.25	36– 40	40-42
Melting point (0C)	38.5			
Fire Point (0C)	250	190		-
Iodine value , g I_2/100 g	82	114.21	< 120	
Cetane number		54	>51	>47
Acid value , mg NaOH/g	8.8	0.4		<0.5
Free fatty acids	4.4	0.2		< 0.24
Refractive index @40^{0}c		1.54		1.4-1.7
Saponification value (mgKOH/g)	200			

4.2. Statistical Analysis of the Experimental Results

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). The analysis of variance will be used as one of the primary tools for statistical data analysis. The Design Expert 6.8.0 program was used in the regression analysis and analysis of variance. The Statistical software program was used to generate surface plots, using the fitted equation obtained from the regression analysis, holding one of the independent constant variables.

The predicted values of percentage conversion of the oil to biodiesel at the design points are shown in table 4.5. All 26 run were conducted by the experimental design expert 6.8.0 software. The actual yield of biodiesel produced at different process parameters was calculated. The yield of the transesterification processes were calculated as final weight of FAME produced to weight of total feed used, multiplied by 100.The formula is given as:

Yield of FAME (biodiesel %) = $\frac{weight\ of\ BD\ produced}{weight\ of\ oil\ used} \times 100$ ……………………………4.9

Table 4.3 Result using Experimental design expert 6.8.0 software

Run NO.	Factor 1 A:molar ratio of oil: methanol (ml)	Factor 2 B:reaction temperature(^{0}c)	Factor 3 C:reaction time(min)	Factor 4 D:amount of catalyst(g)	Biodiesel yield (%)
1	1 : 3	50	45	0.6	67.6
2	1 : 8	50	45	0.6	72.9
3	1 : 3	65	45	0.6	69.5
4	1 : 8	65	45	0.6	73.7
5	1 : 3	50	90	0.6	69.5
6	1 : 8	50	90	0.6	73.3
7	1 : 3	65	90	0.6	78.4
8	1 : 8	65	90	0.6	79.6
9	1 : 3	50	45	1.82	68.7
10	1 : 8	50	45	1.82	70.9
11	1 : 3	65	45	1.82	72.9
12	1 : 8	65	45	1.82	74.2

13	1 : 3	50	90	1.82	68.5
14	1 : 8	50	90	1.82	69.3
15	1 : 3	65	90	1.82	71.6
16	1 : 8	65	90	1.82	77.6
17	1 : 5.25	57.5	67.5	1.21	87.1
18	1 : 6	60	67.5	1.21	95.2
19	1 : 5.5	56.75	67.5	1.21	90.7
20	1 : 5.5	58.25	67.5	1.21	92.9
21	1 : 5.5	57.5	65.25	1.21	92.7
22	1 : 5.5	57.5	67.5	1.21	93.2
23	1 : 5.5	57.5	69.75	1.21	93.8
24	1 : 5.5	57.5	67.5	1.15	91.5
25	1 : 5.5	57.5	67.5	1.27	92.9
26	1 : 5.5	57.5	67.5	1.21	93.2

Table 4.4 Design Summary of factorial designs.

Design Summary of Design expert® 6.8.0 software	
Study type	Response surface
Initial design	CCD
Design model	Quadratic, polynomial
Run	26

Table 4.5 Actual versus Predicted model of biodiesel yield

Standard Order	Residual	Leverage	Student Residual	Cook's Distance	Outlier T	Run Order	Actual Value	Predicted Value
1	-0.22	0.687	-0.244	0.009	-0.233	3	67.60	67.82
2	1.36	0.687	1.484	0.323	1.582	10	72.90	71.54
3	-0.70	0.687	-0.767	0.086	-0.752	18	69.50	70.20
4	-0.37	0.687	-0.407	0.024	-0.391	7	73.70	74.07
5	-0.71	0.687	-0.774	0.088	-0.758	21	69.50	70.21
6	-0.32	0.687	-0.354	0.018	-0.340	20	73.30	73.62
7	1.71	0.687	1.864	0.509	2.149	4	78.40	76.69
8	-0.66	0.687	-0.719	0.076	-0.702	25	79.60	80.26
9	-0.29	0.687	-0.319	0.015	-0.306	22	68.70	68.99
10	-0.76	0.687	-0.826	0.100	-0.814	2	70.90	71.66
11	1.28	0.687	1.392	0.284	1.462	9	72.90	71.62
12	-0.24	0.687	-0.265	0.010	-0.253	16	74.20	74.44
13	1.32	0.687	1.440	0.304	1.525	12	68.50	67.18
14	-0.24	0.687	-0.266	0.010	-0.254	26	69.30	69.54
15	-2.31	0.687	-2.517	0.928	-3.687 *	13	71.60	73.91
16	1.17	0.687	1.277	0.239	1.319	1	77.60	76.43
17	-0.88	0.901	-1.696	1.740	-1.882	23	87.10	87.98
18	0.26	0.976	1.040	2.981	1.044	6	95.20	94.94
19	-2.24	0.145	-1.475	0.025	-1.571	11	90.70	92.94
20	-0.50	0.144	-0.330	0.001	-0.317	8	92.90	93.40
21	-0.36	0.400	-0.279	0.003	-0.267	17	92.70	93.06
22	0.53	0.400	0.414	0.008	0.398	15	93.80	93.27
23	-0.68	0.400	-0.536	0.013	-0.518	5	91.50	92.18
24	0.85	0.400	0.671	0.020	0.653	14	92.90	92.05
25	1.51	0.119	0.979	0.009	0.977	19	93.20	91.69
26	1.51	0.119	0.979	0.009	0.977	24	93.20	91.69
* exceeds limits								

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 model for percentage of biodiesel % final equation in terms of Coded factors is shown in equation 4.10 below:

$$\text{biodiesel yield} = +91.69 + 1.56 * A + 2.32 * B + 1.09 * C - 0.67 * D - 356.10 * A^2 + 147.62 * B^2 + 147.09 * C^2 + 42.09 * D^2 + 0.039 * A * B - 0.075 * A * C - 0.26 * A * D + 1.03 * B * C + 0.063 * B * D - 1.05 * C * D \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.10$$

Where, A – molar ratio of oil to methanol

B – Reaction temperature

C- Reaction time

D-amount of catalyst

The coefficients of the response surface model, as provided by the above quadratic model equation, were also evaluated. From ANOVA for the quadratic model for esterification is listed in table 4.6 below. From the ANOVA for response surface quadratic model for transterification reaction, the Model F-value of 70.65 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, B, C, A^2, B^2 and the interaction BC and CD are significant model terms. From this Prob > F Values greater than 0.1000 indicate the model terms are not significant.

Table 4.6 Analysis of variance (ANOVA) for the quadratic model of esterification

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	2661.13	14	190.08	70.65	< 0.0001	Significant
A	38.88	1	38.88	14.45	0.0029	
B	85.97	1	85.97	31.95	0.0001	
C	19.14	1	19.14	7.11	0.0219	
D	7.09	1	7.09	2.64	0.1327	

A^2	19.78	1	19.78	7.35	0.0202	
B^2	22.65	1	22.65	8.42	0.0144	
C^2	6.84	1	6.84	2.54	0.1391	
D^2	0.56	1	0.56	0.21	0.6570	
AB	0.024	1	0.024	8.857E-003	0.9267	
AC	0.090	1	0.090	0.033	0.8582	
AD	1.10	1	1.10	0.41	0.5352	
BC	16.81	1	16.81	6.25	0.0295	
BD	0.063	1	0.063	0.023	0.8816	
CD	17.64	1	17.64	6.56	0.0265	
Residual	29.59	11	2.69			
Lack of Fit	29.59	10	2.96			
Pure Error	0.000	1	0.000			
Cor Total	2690.72	25				

As can be seen from the above table 4.6, F-values of the model coefficients, the value of the reaction temperature in both linear and quadratic is less than 0.0001. This indicated that reaction temperature is the most significant in determining the model than rest and the value of the methanol to oil molar ratio is the second. However, in order to minimize error, all of the coefficients were considered in the design. The Lack of Fit F-value of 2.96 implies its insignificance relative to the pure error. Non-significant lack of fit is good because we want the model to fit.

Table 4.7 Model adequacy measures

Std. Dev.	1.64	R-Squared	0.9890
Mean	80.05	Adj R-Squared	0.9750
C.V. %	2.05	Pred R-Squared	0.8528
Press	396.15	Adeq Precision	22.281

The "Pred R-Squared" of 0.8528 is in reasonable agreement with the "Adj R-Squared" of 0.9750 in less than 0.15 difference as one might expect. "Adeq Precision" measures the signal to noise ratio due to random error. A ratio of 22.281 indicates an adequate signal. Therefore, this model can be used to navigate the design space.

The regression coefficients and the corresponding 95% CI (Confidence Interval) Low and High were presented in table 4.8 below. If zero was in the range high and low 95% Confidence interval, the factors has no effect. From the 95% CI High and Low values of each model term, it could be concluded that the regression coefficients of catalyst concentration and the interaction terms of molar ratio of oil to methanol and reaction time have highly significant effect in biodiesel production.

Table 4.8: Regression coefficients and significance of response surface quadratic model for transterification.

Factor	Coefficient Estimate	DF	Standard Error	95% CI		VIF
				Low	High	
Intercept	91.69	1	0.57	90.45	92.94	
A	1.56	1	0.41	0.66	2.46	1.00
B	2.32	1	0.41	1.41	3.22	1.01
C	1.09	1	0.41	0.19	1.99	1.00
D	-0.67	1	0.41	-1.57	0.24	1.00
AB	0.039	1	0.41	-0.86	0.94	1.00
AC	-0.075	1	0.41	-0.98	0.83	1.00
AD	-0.26	1	0.41	-1.17	0.64	1.00
BC	1.03	1	0.41	0.12	1.93	1.00
BD	0.063	1	0.41	-0.84	0.97	1.00
CD	-1.05	1	0.41	-1.95	-0.15	1.00

Table 4.9 Sequential model sum of squares and model summary statistics of the response quadratic model for transesterification reaction

Source	Sum of Squares	DF	Mean Square	F Value	P-value Prob > F	Std. Dev.	R^2	Adj. R^2	Pred. R^2	press
Mean	1.666E+005	1	1.666 E+005							
Linear	181.24	4	45.31	0.38	0.8209	10.93	0.0674	-0.1103	-0.3360	3594.85
2FI	35.85	6	5.98	0.036	0.9997	12.84	0.0807	-0.5322	-2.7127	9989.75
Quadratic	2444.04	4	611.01	227.11	< 0.0001	1.64	0.9890	0.9750	0.8528	396.15
Cubic	25.98	9	2.89	1.60	0.4431	1.34	0.9987	0.9832		+
Residual	3.61	2	1.81							
Total	1.693E+005	26	6512.11							

The quality of the model developed was evaluated based on the correlation coefficient value, R^2. The R^2 value for equation 4.10 was 0.989. This indicated that 98.9% of the total variation in the biodiesel yield was attributed to the experimental variables studied. The closer the R^2 value to unity, the better the model will be as it will give predicted values which are closer to the actual values for the response. From the ANOVA and regression analysis on table 4.6 and table 4.8, respectively it can be seen that the linear terms of A, B and C, the quadratic term A^2 and B^2 were significant (because Prob > F less than 0.05), but the interactions BC and CD were insignificant.

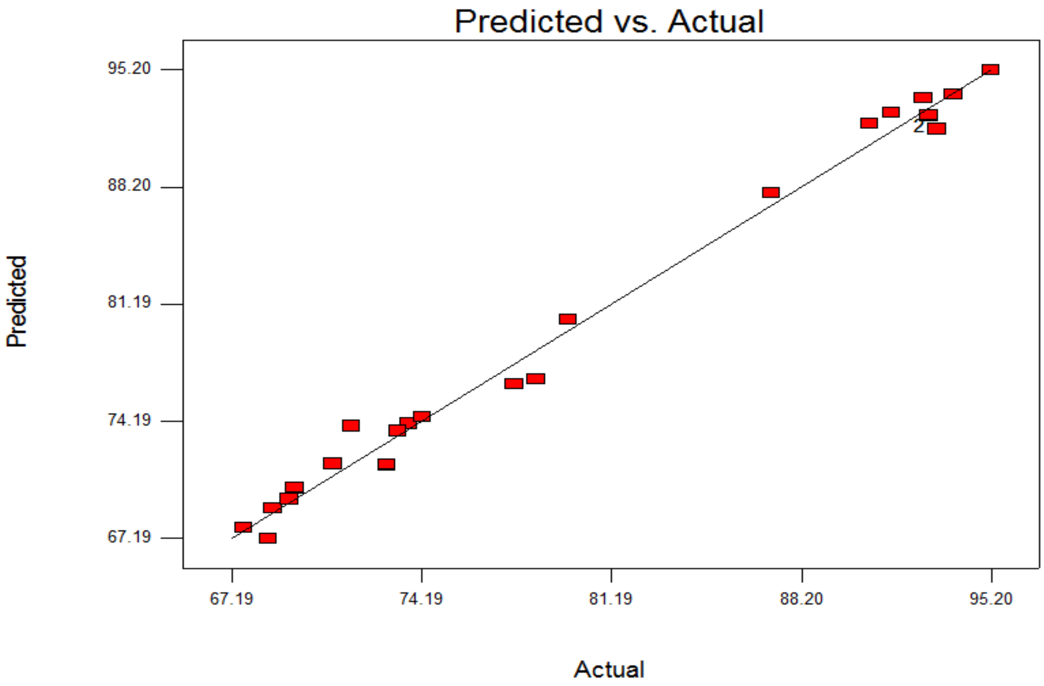


Figure 4.2 Yield Plot for the actual vs. predicted of FAME yield

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

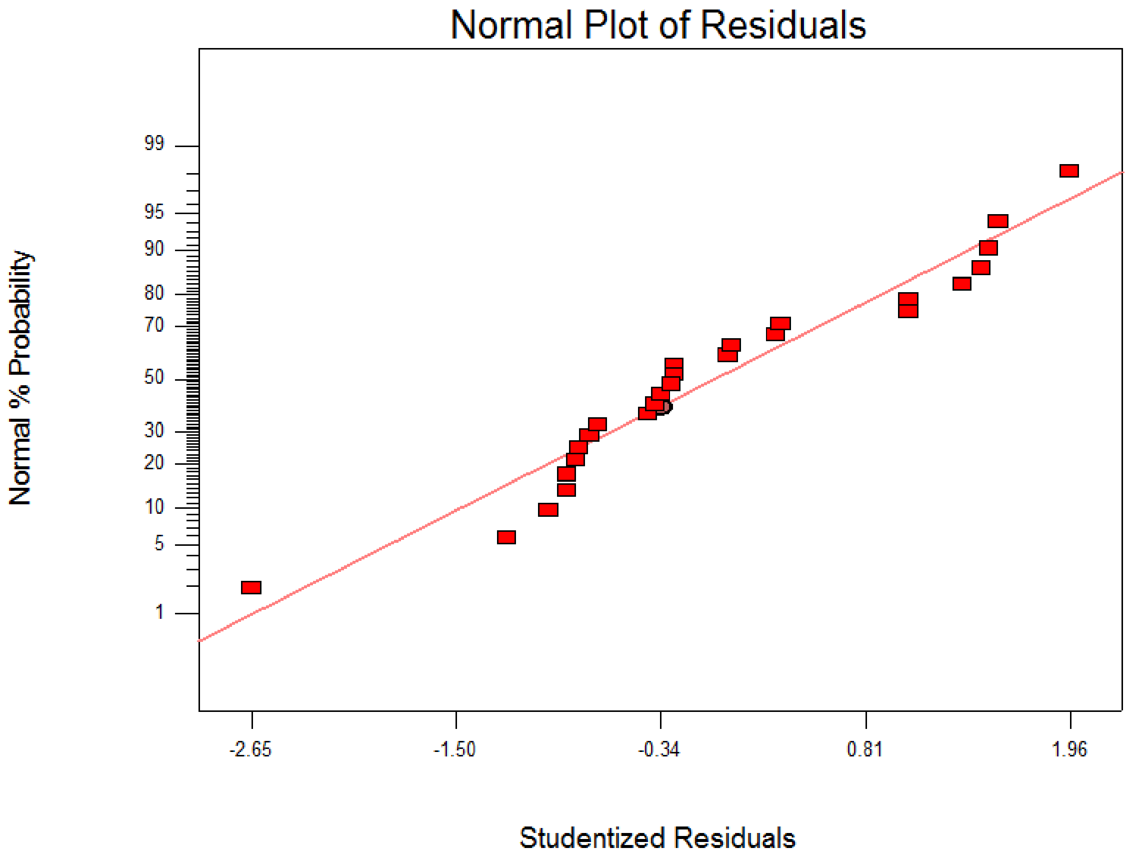


Figure 4.3 Normal plots of residuals

From the plot as shown above, the normal probability plot indicates the residuals following a normal distribution, in the case of this experiment the points in the plots shows fit to a straight line in the figure, this shows that the quadratic polynomial model satisfies the assumptions analysis of variance (ANOVA) i.e. the error distribution is approximately normal.

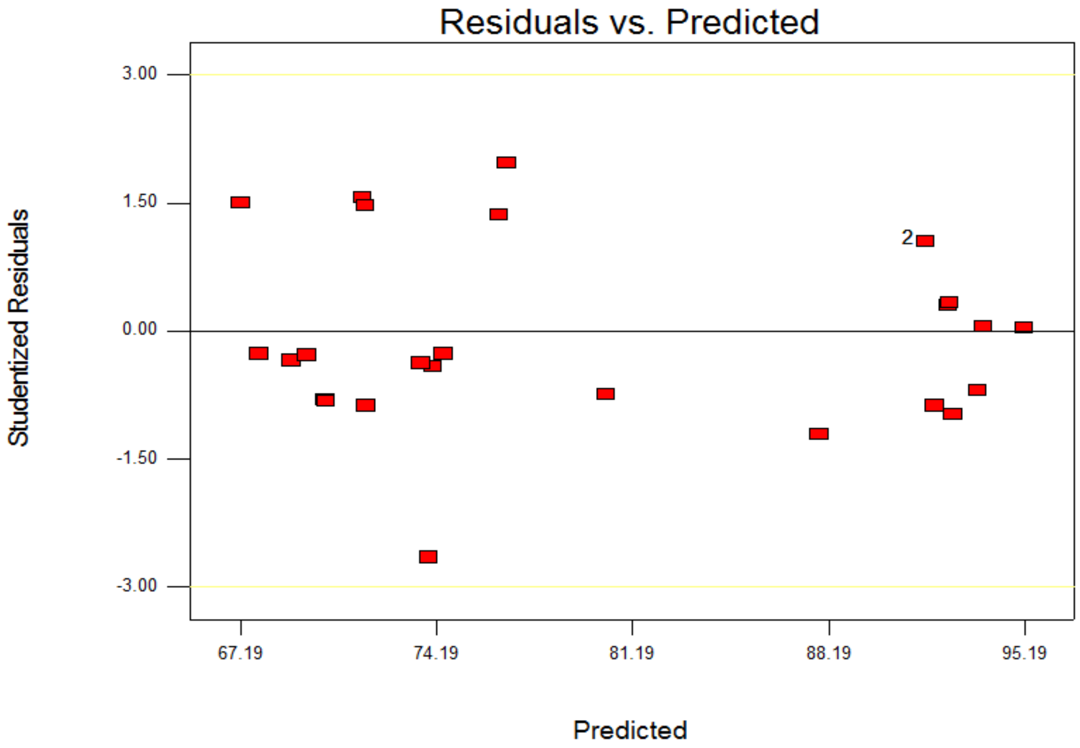


Figure 4.4 Residual vs. predicted values

From the model, the residuals should be structure less; in particular, they should be unrelated to any other variable including the predicted response. A plot of the residuals versus the rising predicted response values tests the assumption of constant variance. The plot shows random scatter which justifying no need for an alteration to minimize personal error.

4.3. Main Factor affecting on the Yield of Biodiesel Production

4.3.1. The effect of molar ratio oil to methanol

The effect of molar ratio of oil to alcohol is one of the main significant factors affecting the yield of biodiesel. An excess of alcohol is used in biodiesel production to ensure that the oils or fats will be completely converted to esters and a higher alcohol triglyceride ratio can result in a greater ester conversion in a shorter time. The yield of biodiesel is increased when the alcohol to triglyceride ratio was increased and reaches a maximum biodiesel yield.

Further increasing the alcohol amount beyond the optimal ratio will not increase the yield but will increase cost for alcohol recovery. The molar ratio of methanol to oil increased from 1: 3 to

8, the production yield also increased. From this ratio methanol to oil molar ratio was determined as 6:1, for maximum biodiesel yield (95.2%) of biodiesel than other molar ratio. Figure 4.5 was shown the effect of molar ratio on the biodiesel yields.

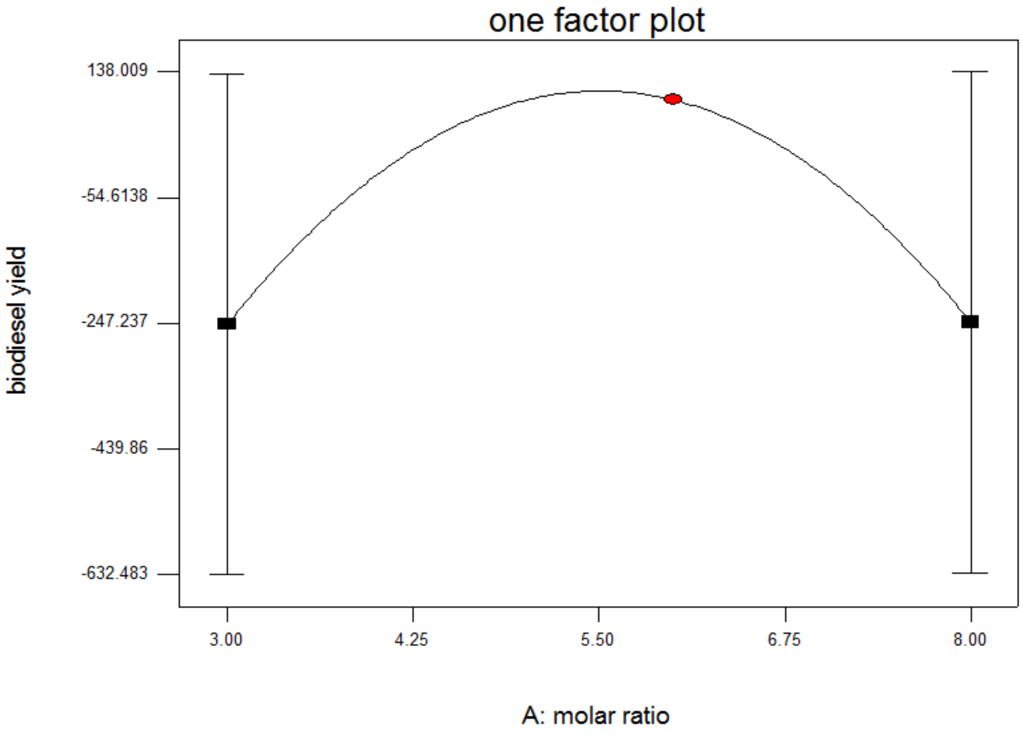


Figure 4.5 The individual effect of ratio methanol to oil

4.3.2. The effect of catalyst concentration

The effect of catalyst concentration affects the yield of the biodiesel production in a positive manner up to a certain concentration. As the catalyst concentration increases the conversion of the yield of biodiesel increase. This is because an insufficient amount of catalysts result in an incomplete conversion of the triglycerides into the fatty acid esters.

From the results, the maximum yield of biodiesel can be obtained at 1.21g of NaOH concentration and then decreases a little with a further increase in catalyst concentration. The reduction of the yield of the biodiesel is due to the addition of excessive alkali catalyst causing more triglycerides to react with the alkali catalyst and form more soap (Leung and Guo, 2006). It reached 95.2 % of the biodiesel yield. Figure 4.6 was shown the effect of catalyst concentration on the biodiesel yields.

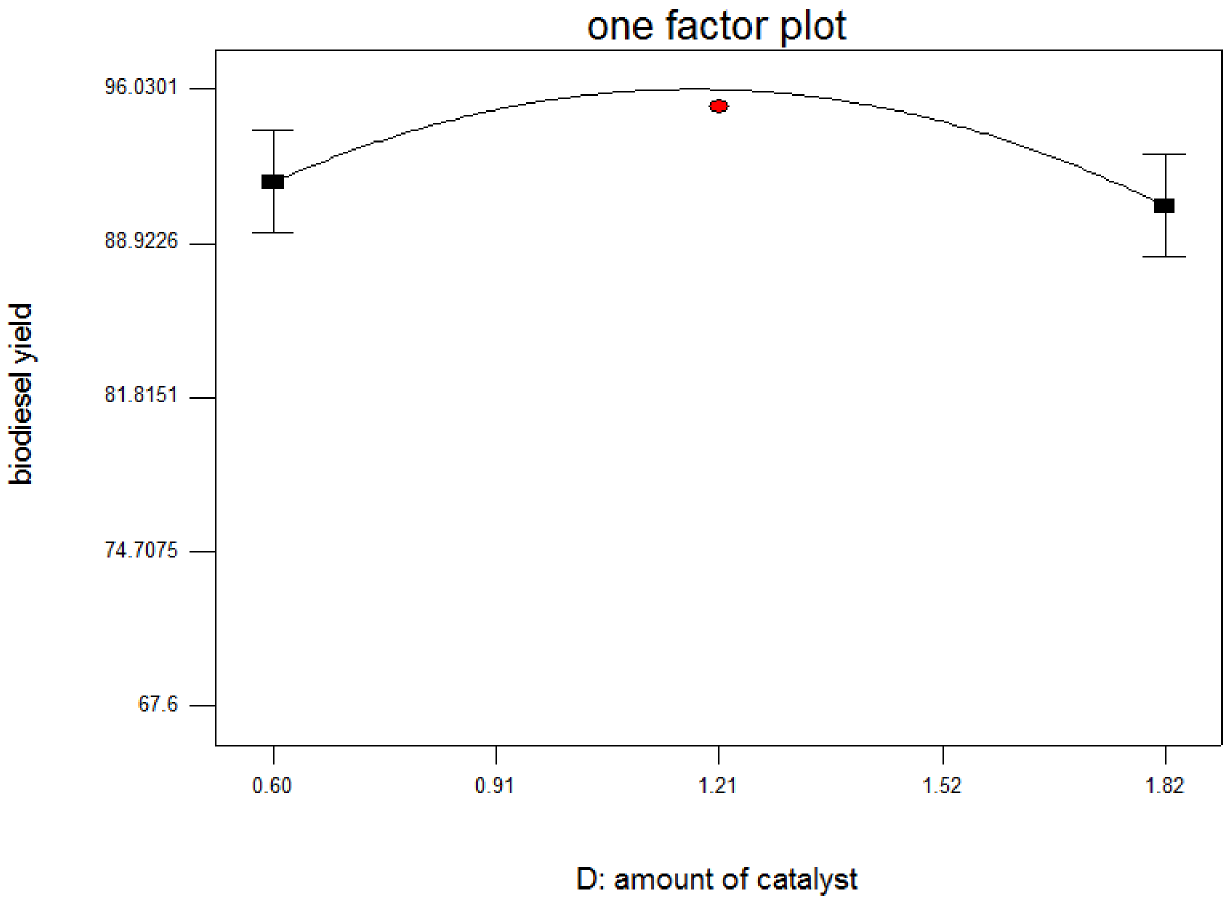


Fig.4.6.Effect of catalyst concentration on the biodiesel Production

4.3.3 Effect of Reaction time

The reaction time was an important factor, which influence the biodiesel yield. According to the result, the biodiesel yields are directly proportional to the reaction times. In other words, the biodiesel yields increase with increasing reaction times.

Experimental results presented in figure 4.7 show the biodiesel yield versus reaction time that the increase of the reaction time shifts the reaction equilibrium to the products, thus increasing biodiesel yield. Moreover, excess reaction time will lead to a reduction in the product yield and then remains relatively constant with a further increase in the reaction time due to the backward reaction of transesterification, resulting in a loss of esters as well as causing more fatty acids to form soaps (Alamu, 2007).

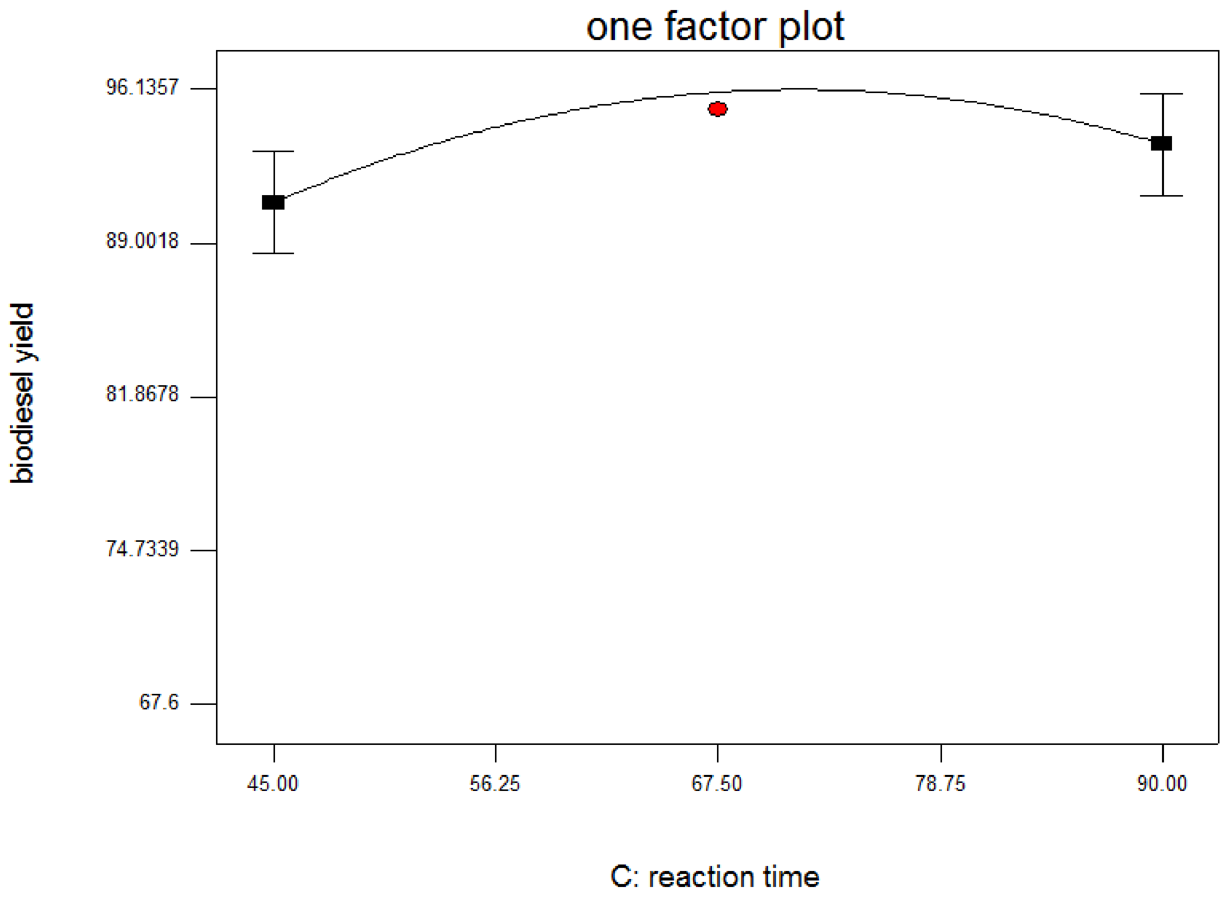


Figure 4.7 *Effect of the reaction time on the biodiesel yield*

4.3.4. Reaction temperature

The effect of temperature is significantly influences the transesterification reaction and yield of the biodiesel product. The boiling point of methanol is 64.7 ^{0}C and in order to avoid alcohol evaporation, reaction temperature must be less than boiling point. Increasing a reaction temperature above the boiling point would reduce the viscosity of the oil which leads to a sufficient result in an increased reaction rate and a shortened reaction time between the oil and the methanol. Results obtained in these experiments show that increasing of temperature clearly influences the biodiesel yield and the maximum yield of biodiesel was obtained at 60^{0}C. Further increasing of temperature did not lead to significant rising the biodiesel yield due to the evaporation of methanol, this indicating that the reaction is close to equilibrium and further increasing temperature decreases the product.

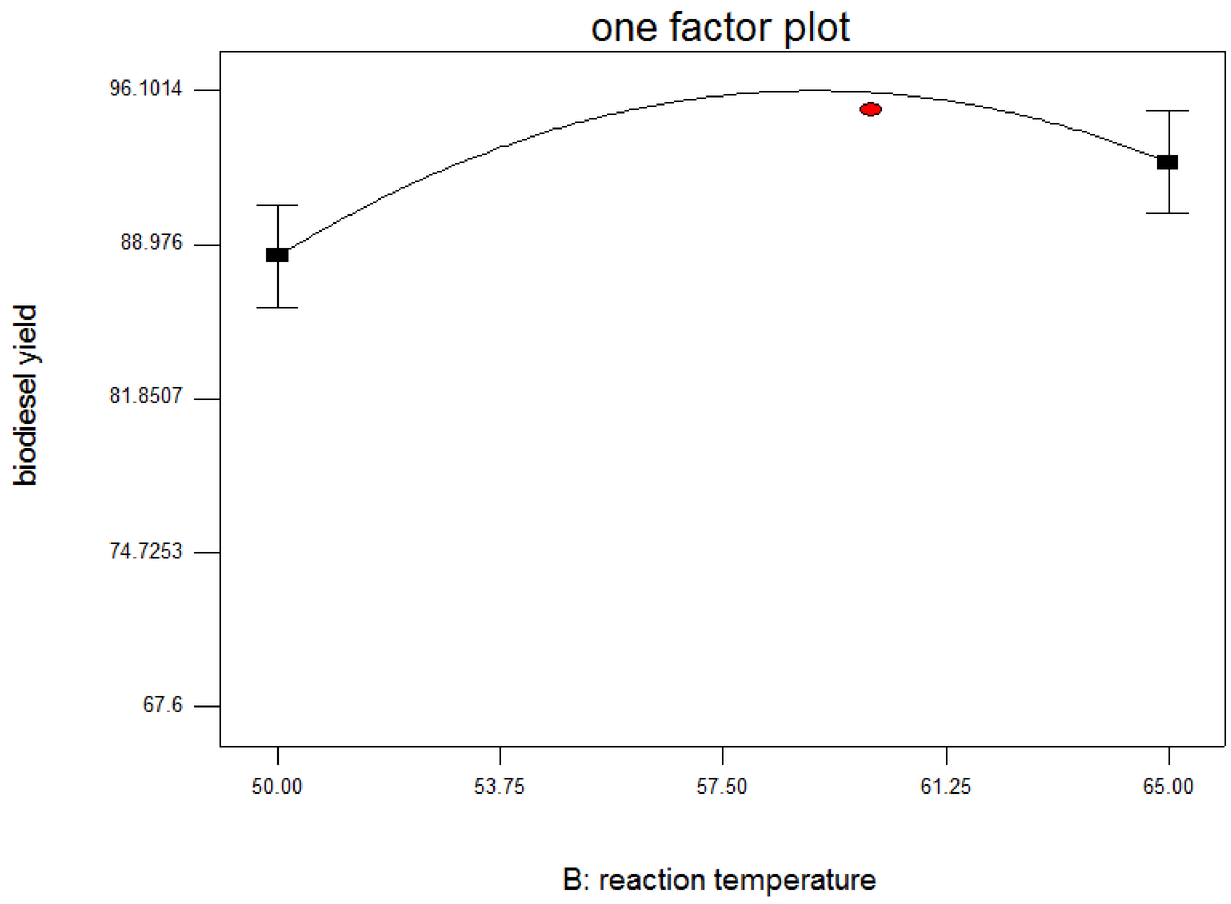
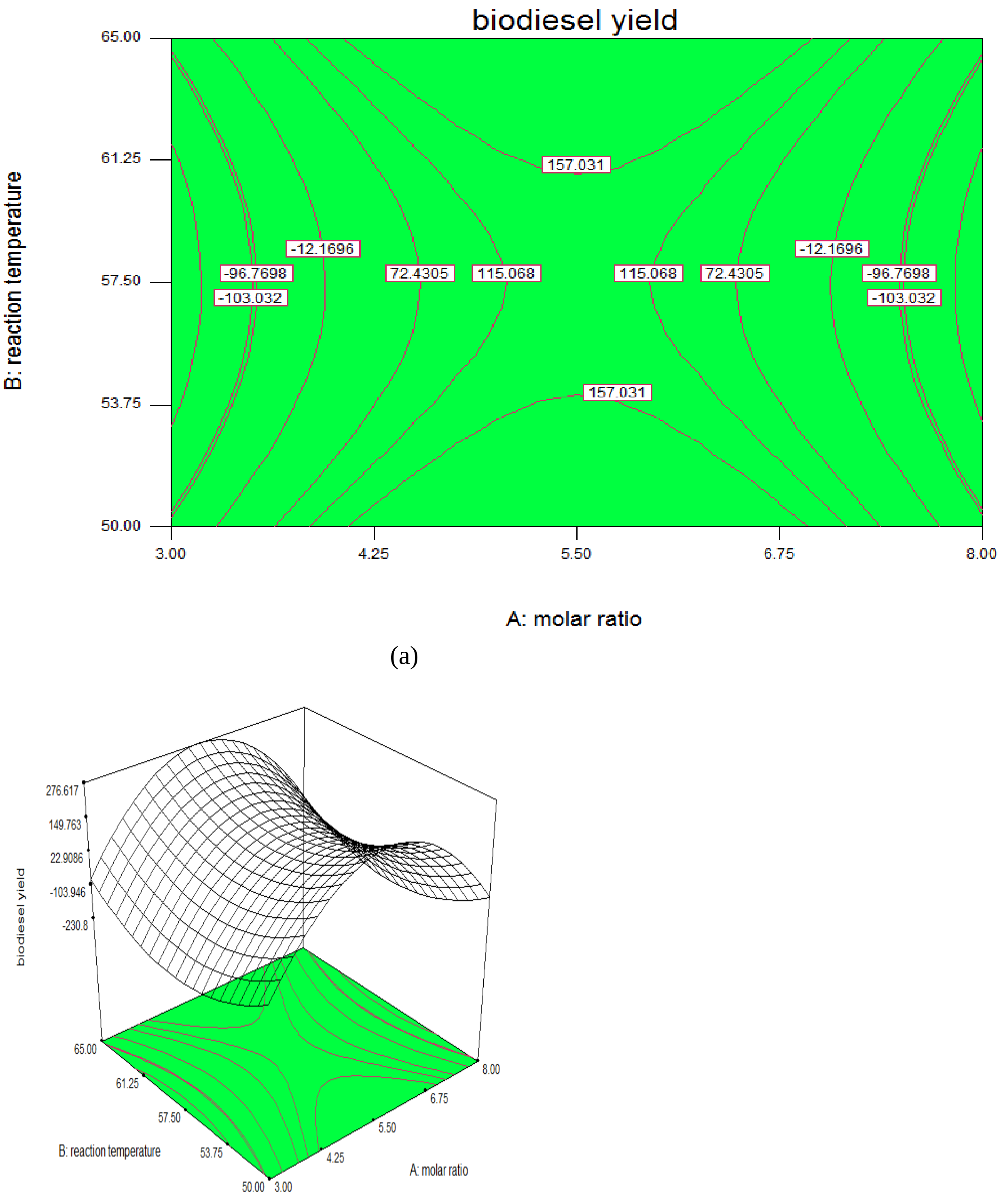


Figure 4.8.Effect of reaction temperature on biodiesel yield

Effect of interactive parameters on biodiesel yield

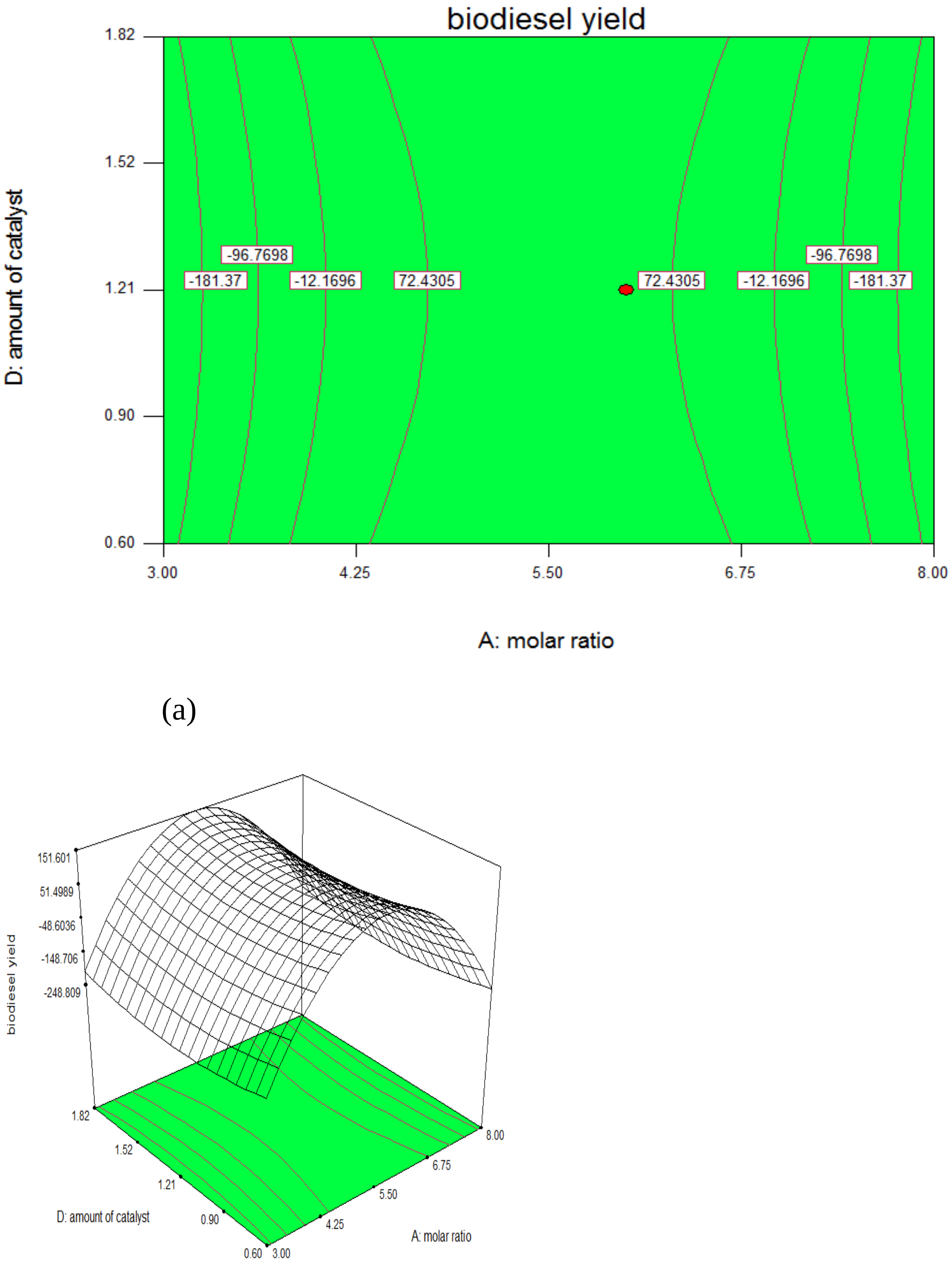
Contour plots and 3D surface (fig 4.9 a & b and fig 4.10 a & b below), show the relationships between dependent and independent variables of the developed model. Each contour curve presented the effect of two variables on the methyl ester yield, holding the third variable at constant level. The third variable is held at zero level. However, the interaction factor also must be considered as the individual effect plot does not give information regarding the significant interaction involved. Remarkable the interaction between the independent variables could be observed if the contour plots had an elliptical profile.



(a)

(b)

Figure 4.9 methanol to oil ratio vs. reaction temperature when concentration of catalyst is at 1.21 %



(a)

(b)

Figure 4.10 methanol to oil ratio vs. amount of catalyst when the reaction temperature is 60^0c

4.4. Analysis of Fourier transforms infrared (FT-IR)

Fourier transform infrared spectroscopy, FT-IR was to analysis the main function group presence in the produced biodiesel and it's the raw material avocado peel oil. The FT-IR techniques were used for qualitative analysis of the product. FT-IR analysis was performed using instrument, Perkin Elmer, model spectrum one for detection of transesterification efficiency of oil by determination of the active groups produced from these process. The FT-IR spectra will be recorded at ambient temperature in the wave number between 4000-400 cm^{-1}.

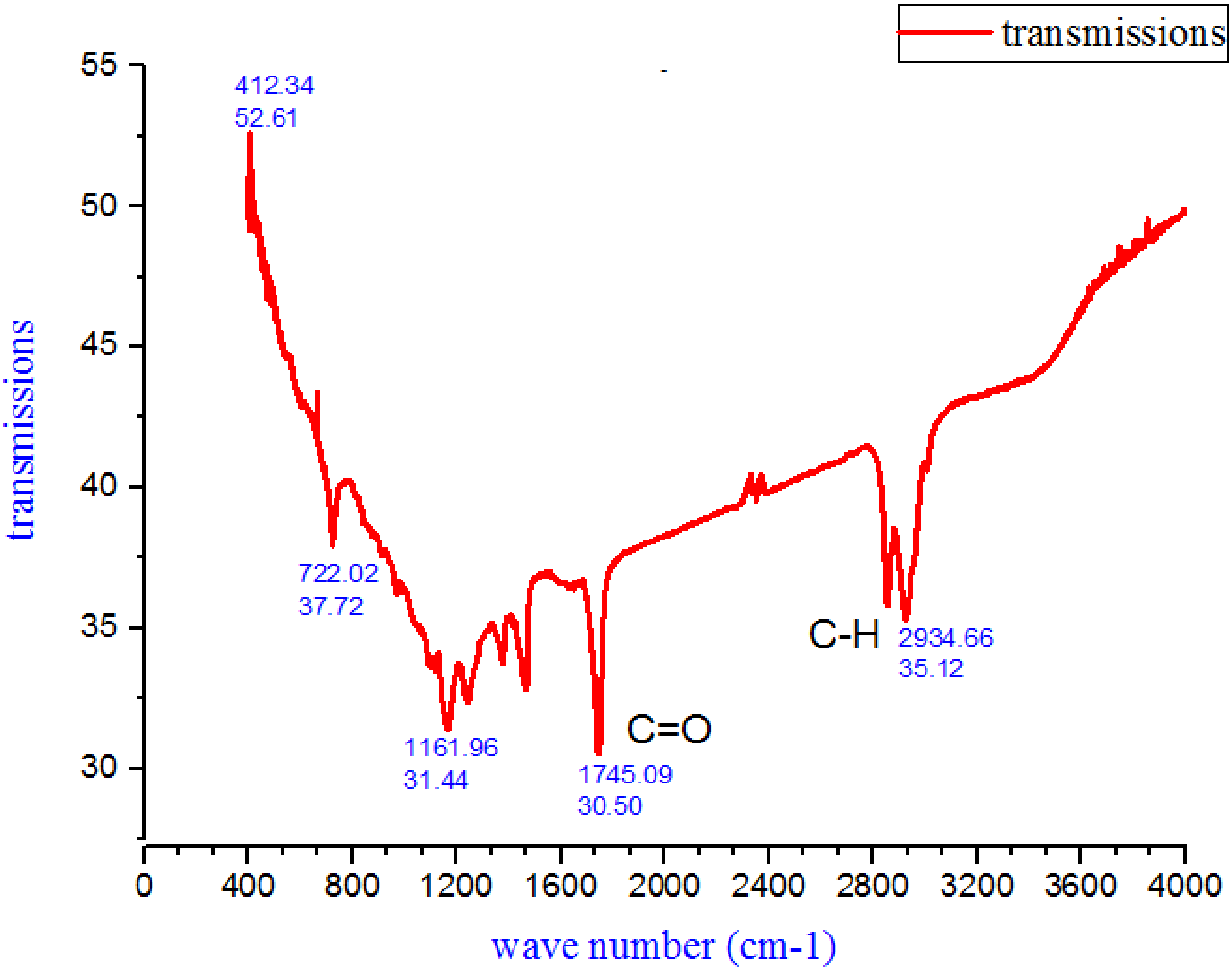


Figure 4.11 The FT-IR produced biodiesel process

An analysis of FT-IR spectrum showed in the above figure 4.11. The oil, biodiesel prepared from avocado peel oil was analyzed by FT- IR. The major change that takes place during the conversion from triglyceride oil to biodiesel was the gain of a CH_3 carbon in the methyl ester (biodiesel) product, which is found in the range of 1438- 1459 cm^{-1} which is not present in the spectra of the oil. Biodiesel results in the formation of carbon hydrogen bonds at 2855-3008 cm^{-1}, ester functionality at 1738-1759 cm^{-1}, the carbons at 1438-1459 cm^{-1}, and carbon oxygen bonds at 1171-1197 cm^{-1}. C= O carbonyl compound (aldehydes, acids, etc) are the strong C=O stretching absorption bands in the region of 1870-1540 cm^{-1}.If ester this band appears in the 1705 cm^{-1} and 1658 cm^{-1}. C-O-C (Ethers), these stretching vibrations produce a strong band in the 1200-900 cm^{-1} region. C-H, adsorption bands as an example 2931 cm^{-1} and 2954cm^{-1} correspond to the asymmetric and symmetric vibration modes of methyl group, ethylene groups respectively, H_2O the adsorption bands of water can be between 1800 -1200 cm^{-1}. Other identifying peaks found in the oil were at 2926 cm^{-1} and 2855 cm^{-1} that represents sp^3 hybridized carbon molecules that are found in the long carbon chain of the biodiesel (Hiwot, 2017).

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In this thesis biodiesel produced from avocado peel oil is obtained by transesterification process using sodium hydroxide as a catalyst. The process parameters affecting yield of FAME conversion has been studied and the statistical analysis and experimental design run was done by using design expert 6.8.0 software. The outputs of the experimental run conducted have been analyzed by using physicochemical parameter determination. The overall results showed that the avocado peel oil could be used to produce biodiesel as waste management and recycled process. The studied physicochemical properties of the produced biodiesel from APO, methyl ester could be used as an alternative energy resource in diesel engine. The conclusions from biodiesel feedstocks (APO) are as follows: -

- Biodiesel is an important alternative fuel and it possesses properties like renewability, non-toxicity biodegradability, and environmentally friendly benefits, since the model residuals would be structure less.
- The fuel property of biodiesel production is strongly affected by parameters such as effects of molar ratio of oil to alcohol; reaction temperature; reaction time and amount of catalyst concentration were observed. The density and the viscosity were indicators of the biodiesel quality against the process variables. Generally the ester yield, increased with increased molar ratio, catalyst concentration and reaction temperature until the optimum conversion. The best result was obtained at molar ratio of oil to methanol 6:1, reaction temperature of 60 ^{0}C, the reaction was complete at about 67.5 min and 1.21g catalyst concentration amount has played an important role in improving the biodiesel yield.
- Transesterification was the most commonly employed method for FAME production. The purpose of this method is to reduce the viscosity of oil using base catalyst in the presence of methanol. The ester yield obtained from the transesterification process ranged from 67.8 to 95.2%. The yield is strongly dependent on the product of the transterification step.

5.2. Recommendation

The present study in this thesis work, there are some further important studies that need to be investigated., In this work we recommended in order to find more optimum conditions for transesterification reaction, the main reaction parameters which affect to the biodiesel conversion has been studied and good results were achieved. However, further investigations effect studies have to be done to improve the reaction conditions, yield and increasing reaction time may give more good results, which could offer more opportunities for increasing income. In addition to this, in order to get a better yield in both quantity and quality of biodiesel:-

- There must be careful selection of catalyst and the reactor
- Appropriate characterization studies like density, viscosity, flashpoint measurement must be carried out on biodiesel.
- Moreover, in order to decrease the cost of chemicals, recycling is important. Therefore, the catalysts and also the excess alcohol should be reused. Sufficient laboratory equipment should be provided for the production of biodiesel.

However, the produced oil from avocado peel was not used until for food consumption or other purpose. So we recommend that all the extracted oil must be used for biodiesel production, which introduces more profit. Finally we recommended that the government should encourage the production of biodiesel from non-edible oil resources particularly from wastes using transesterification process because this process was less complex, require less investment cost and it needs less energy for production.

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Appendix

Table A1: Specification of EN 14214 comparing biodiesel to conventional diesel

Properties	**Diesel**	**Biodiesel**
density,15^0c	0.82 -0.86	0.86 -0.90
viscosity,40^0c	2.0 -4.5	3.5 -5.0
Flash point, ^{0}c	> 377	> 130
Sulfur, % mass	< 0.2	< 0.01
sulphated ash (% mass)	< 0.01	< 0.02
water (mg/Kg)	< 200	< 500
Carbon residues (% wt)	< 0.3	< 0.03
Cetane number	> 45	> 51
Acid Value(mg KOH/g)		< 0.8
Methanol(% mass)	-	< 0.2
MG content (% mass)	-	< 0.8
DG content (% mass)	-	< 0.2
TG content (% mass)	-	< 0.4
free glycerin (% mass)	-	< 0.02
Total glycerin	-	< 0.25
Iodine number	-	<120
Cloud Point		Report to the customer
Pour point		Report to customer
Phosphorus (mg/Kg)	-	< 10

Table B1: Physico-Chemical Properties of Biodiesel from Different oil raw material

Feed stock	Kinematic Viscosity (at 40^0C	Density (kg/m^3)	Saponification value	Iodine value	Acid value (mg KOH/g)	Cetane Number	Heating value (MJ/kg)
Soybean	4.08	885	201	138.7	0.15	52	40
Rapeseed	4.3-5.83	880-888			0.25-0.45	49-50	45
Sunflower	4.9	880	200	142.7	0.24	49	45.3
Palm	4.42	860-900	207	60.07	0.08	62	34
Peanut	4.42	883	200	67.45		54	40.1
Corn	3.39	880-890	202	120.3		58-59	45
Camelina	6.12-7	882-880		152-157	0.08-0.52		
Canola	3.53	880-900	182	103.8		56	45
Cotton	4.07	875	204	104.7	0.16	54	45
Pumpkin	4.41	884	202	115	0.48		38
jatropha	4.78	864	202	108.4	0.496	61-63	40-42
Pongamina pinnata	4.8	883			0.62	60-63	42
Palanga	3.99	869					41
Tallow		856	244.5	126	0.65	59	
Nile tilapia				88.1	1.4	51	
Poultry		867	251.23	130	0.25	61	
used cooking oil	4				0.15		

Table C1: Saponification value of APO

Run	N_{HCl}	V_{bHCl}	V_{aHCl}	$(Vb - Va)$	Mass of oil (g)	SV
1	0.562	47.2	29.4	17.8	2	200
2	0.562	47.2	27.9	19.3	2	216.9
3	0.562	47.2	30.9	16.3	2	183.212
Mean						200

Table C2: Infrared Correlations by Wavenumber

Functional Group	Frequency (cm^{-1})	Appearance
Free O-H	3590 – 3600	sharp
Alcohol O-H (H bonded)	3300 – 3500	medium to strong
Carboxylic acid O-H	2400 - 3600	variable, broad*
Amide N-H	3200 - 3400	medium, sharp, often two bands
sp C-H (C≡C-H)	3260 - 3390	strong
sp2 (C=C-H)	3000 - 3100	medium
Aromatic C-H	3000 - 3050	weak (see below)
sp3 C-H (C-C-H)	2850 - 2960	medium to strong
Aldehyde C-H	2700 - 2900	weak, two bands
Nitrile C≡N	2200 - 2270	medium
Alkyne C≡C	2100 - 2250	weak, may be absent if symmetric
Anhydride C=O	1800 - 1850 1740 – 1790	strong, two bands**
Acid chloride C=O	1790 – 1810	strong**
Ester C=O	1730 – 1750	strong**
Aldehyde and ketone C=O	1695 - 1740	strong**
Carboxylic acid C=O	1700 - 1730	strong, usually broad**
Amide C=O	1640 - 1690	strong**
Alkene C=C	1640 - 1680	often weak, may be absent
Conjugated C=C	1600 - 1650	intensity increased by conjugation
Aromatic C=C	1500 - 1600	medium, two or three bands
Nitro NO_2	1500 - 1570 1320 – 1360	strong, two bands
Amine C-N	1180 - 1360	strong
Chloride C-Cl	700 – 800	strong
Aromatic C-H	650 – 850	may distinguish substitution pattern
Monosubstituted benzene	690 – 710 730 – 770	strong, two bands
1, 2-disubstituted benzene	735 – 770	strong
1, 3-disubstituted benzene	690 - 710 750 - 810 880	strong, two bands sometimes observed
1,4-disubstituted benzene	810 - 833	Strong

*generally strong, but hydrogen bonded carboxylic acids may show a very weak O-H stretch

**lowered by 15-30 cm^{-1} by unsaturation (e.g. unsaturated aldehydes & ketones ca. 1670-1700cm^{-1})