ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

PROCESS ENGINEERING STREAM

OPTIMIZATION AND COMPARISON OF BIODIESEL (B_{100}) QUALITY EXTRACTED FROM NEEM (MARGOSA) AND *MORINGA STENOPETALA* SEED OIL

By

Tedros Hagos

Advisor: Dr. Solomon Kiros (Ass. Prof.)

October 2017

Ethiopia, Addis Ababa

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A Thesis Submitted to the Graduate Studies of Addis Ababa University in Partial Fulfillment of the Degree of Masters of Science in Chemical Engineering (process engineering)

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As members of the Examining Board of the Final M.Sc. Thesis Open Defense, we certify that we have read and evaluated the thesis prepared by Tedros Hagos, entitled " **OPTIMIZATION AND COMPARISON OF BIODIESEL (B_{100}) QUALITY EXTRACTED FROM NEEM (MARGOSA) AND *MORINGA STENOPETALA* SEED OIL** " and recommend that it be accepted as fulfilling the thesis requirement for the degree of Master of Science in Chemical Engineering (process Engineering)

By

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Declaration

I hereby declare that this thesis is my authentic work and that all sources of materials with references to specific authors used for this thesis have been duly acknowledged. This thesis has been submitted in partial fulfillment of the requirements for M.Sc. Degree at Addis Ababa University and is deposited at the University Library to be made available to borrowers under rules of the library. I solemnly declare that this thesis is not submitted to any other institution anywhere for the award of any academic degree, diploma, or certificate.

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Dr. Solomon Kiros _____ _____

(Advisor) Signature

Dedication

I would like to dedicate this thesis to my beloved family.

Abstract

This Study Focuses On Optimization and Comparison of Biodiesel (B_{100}) Quality Extracted from Neem (Margosa) and *Moringa Stenopetala* Seed Oils. The seeds were collected from different locations and drying until maintain constant weight. Oil was extracted by soxhlet extraction method using hexane as solvent for each plant species and the values were 43.3 and 48.8 %. Then, purification of the oils was performed by degumming, neutralization, washing and drying sequentially. Acid value, amount of free fatty acid, saponification value, density and kinematic viscosity of the purified oils were determined. The characterization test of the moringa stenopetala and neem seed oils confirmed that acceptable range of physico chemical properties for biodiesel production.

A two-step acid-base catalyzed method was successfully used in the synthesis of biodiesel from *moringa stenopetala* and neem seed oils. This is due to the high value free fatty acids which were 2.45% for *moringa stenopetala* seed oil and 8.6% for neem seed oil. The laboratory experiment was based on a full factorial design and two categorical factors with three levels were nominated which were catalyst weight (0.5, 1 &1.5%) and reaction temperature (55, 60 &65). The effect of these variables on biodiesel production was investigated using Design Expert 7.0.0 and optimum reaction conditions were 55^{o}C and 1wt. % for neem oil methyl ester with yield 86.6%. The optimum values for moringa stenopetala seed oil were 60^{o}C and 1wt. % with yield 91.65%.

The fuel properties of the biodiesel produced from *moringa stenopetala* were closer than the fuel property of neem oil methyl ester to number 2 diesels. Biodiesel produced from both plant species were found to comply with both the American ASTMD 6751 and the European standard EN 14214.Therefore, the major physicochemical properties of *Moringa stenopetala* seed and neem seed oil methyl ester make it an attractive alternative application to the existing feed stocks for biodiesel production in Ethiopia.

Key words: *Moringa stenopetala* seed oil, Neem (Margosa) seed oil, Acid - base transesterfication, Methyl ester, fuel properties.

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Table of Contents

List of Tables

List of Figures

List of Acronyms

ANOVA	Analysis of Variance
ASTM	American Society for Testing and Material
AV	Acid Value
CN	Cetane Number
CP	Cloud Point
DG	Diglycerides
DOE	Design of Experiments
EN	European committee for standardization
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FP	Flash Point
HHV	Higher Heating Value
IV	Iodine Value
MSOME	*Moringa stenopetala* seed oil methyl ester
NSOME	Neem seed oil methyl ester
SV	Saponification Value
SG	Specific Gravity
TG	Triglycerides

1. Introduction

1.1. Back-ground

Over past decades, the growth of the world population and industrialization has led to an increasing consumption of petro-fuels, resulting in a dramatic decline in petroleum reserves. The extensive use of fossil fuels also caused severe atmospheric pollution and growing concerns about global warming due to the emissions of greenhouse gases [1]. From the socioeconomic point of view, our dependence on these energy sources threatens energy security and affects economic growth especially in fuel importing countries like Ethiopia and the political environment in the greatest oil-exporting region is unstable as well. Ethiopia imports its entire petroleum fuel requirement by spending over 80% of the foreign earning annually. Even the demand for petroleum fuel is increasing rapidly due to a growing economy and expanding infrastructure. Hence, it is very critical to look for alternative energy sources in order to contribute for solving economic, environmental and social problems [2].

The alternative energy sources of fossil fuels include hydropower, wind, solar, geothermal, hydrogen, nuclear, and biomass. Most of them are just simply too expensive and high technology for people to sustain, as they are still exorbitant for developed countries. In reality, sub-Saharan Africa is still heavily dependent on wood fuel and other biomass resources, which together account for 85 per cent of the total energy consumption in Ethiopia. Among these alternative energy sources, biofuel derived from biomass are considered as the most promising alternative fuel sources because they are renewable, environmental friendly, applicable technology and economically viable [3]. Biofuels can be any liquid or gaseous fuels that can be produced from biomass, including biodiesel, ethanol and biogas. The most common biofuel used in transport sector is biodiesel. Ethiopia is said to have tremendous potential non edible plant species and marginal lands for ethanol and biodiesel production. Some estimates put the potential area of land suitable for production of biodiesel feedstock at about 25 million hectares [4]. However, it is not obvious how much production could come from first generation biofuels, such as cultivation of biofuel trees and cereal crops, and how much from second generation biofuels, both from agricultural residues and industrial byproducts such as molasses. The most popular biofuels such as ethanol from sugar cane, corn, wheat or cassava and biodiesel from sunflower, soybean, and canola are produced from food crops that require good quality land for plantation.

However, the use of edible biomass oil has been created concerns such as food versus fuel debate that might cause food insecurity especially in the developing countries like Ethiopia and environmental problems caused by utilizing much of the available arable land, chemical fertilizers and deforestation for search of arable land. These indicated that careful study against the effectiveness of biomass energy and recommended the potential of converting non-edible biomass oil into biodiesel must be well examined, which is the objective of the present study.

The Ethiopian government is currently in the process of revising its energy policy and has recently announced a strategy that encourages the expanded development and utilization of biofuels. One of the justifications for this policy is the possibility of saving scarce foreign currency that is used to import fossil fuels and shifting from high-cost fossil fuels to cost-effective biofuels [5]. In addition, Ethiopia has adopted a standard of a 5% blend of biofuels in transport fuel, which was recently increased to 10%. Ethiopia's Growth and Transformation Plan (GTP) also stipulates increasing production of bio-ethanol to 194.9 million liters and biodiesel to 1.6 million liters over five years [6]. To this effect, the government has invited investors from Ethiopia and foreign countries to invest on the production of biodiesel by allocating several thousands of hectares of lands both to produce the seeds and to plant the processing factory for biodiesel. However, due to lack of optimized technologies and research for each non edible crop, the country forced to export the seeds to foreign countries without any value addition.

Biodiesel is defined as the fatty acid alkyl esters of vegetable oils, animal fats or waste oils. It is a technically competitive and environmentally friendly alternative to conventional petro diesel fuel for use in compression–ignition (diesel) engines [7]. Biodiesel is biodegradable, renewable, non-toxic, possesses inherent lubricity, a relatively high flash point, and reduces most regulated exhaust emissions in comparison to petro diesel. The use of biodiesel reduces the dependence on imported fossil fuels, which continue to decrease in availability and affordability.

Vegetable oils for biodiesel production vary considerably with location according to climate and feedstock availability. Generally, the most abundant vegetable oil in a particular region is the most common feedstock. Thus, rapeseed and sunflower oils are predominantly used in Europe; palm oil predominates in tropical countries, and soybean oil and animal fats in the USA [7][8]. However, biodiesel production from conventional sources (soybean, rapeseed, palm, etc.) increasingly has placed strain on food production, price and availability [9]. Therefore, the

search for additional regional biodiesel non edible feed stocks is an important objective. Some recent examples, studies of biodiesel from less common or unconventional oils include tobacco, Neem, Moringa, Jatropha and rubber seed oils [10]. The use of non-edible oils as alternative feedstock is picking up as the demand for biodiesel is expected to increase sharply in the near future. Currently, only very few non edible sources of biodiesel are known compared to the edible oily crops and number of non-edible oily plant species identified, so that exploration of cheap and non-edible sources of biodiesel such as Neem and Moringa seeds, can help to increase the production and use of biodiesel in the developing countries particularly in Ethiopia since these plants have potential to grow on marginal and sloppy lands in which significantly reduce the impact of climate changes in the country.

Neem seed and *moringa stenopetala* seed have a potential oil content of 32 - 46 % [11] and 38-50% [12] that can be converted to biodiesel, respectively. The availability of this resource in Ethiopia is very promising used as biodiesel feedstock. However, the yield and properties of biodiesel products produced from Neem and Moringa feed stocks would be quite different from each other, so that choosing a right feedstock and optimum extraction methods through experimental verification was strongly needed.

This paper reports optimization and comparison of biodiesel (B_{100}) quality extracted from Neem seed oil and *moringa stenopetala* seed oil.

1.2. Statement of the problem

Reliable access to transport fuels concerns all countries. But for poor, oil importing countries such as Ethiopia it becomes an even more critical development and security issue. Ethiopia must exploit all possible alternatives to mitigate its dependence on petroleum imports. Diesel is the most important transport fuel in Ethiopia as practically all the commercial freight and public transport runs on it [13]. The issue of energy security resulting from the increase of petroleum price has stimulated Ethiopian government and researchers to look for alternative renewable energy sources that are technically feasible, economically competitive and environmentally acceptable. Substitution of fossil fuels by biodiesel production in Ethiopia will improve access and security of supply as well as crate job opportunities to supplier and youth to be employed in the process industries. Biodiesel is the most common biofuel used in transport sector; however,

compared to petroleum based diesel, the high cost of biodiesel is a major barrier to its commercialization. A convenient way to lower the costs of biodiesel is to use cheaper and non-edible feed stocks such as *Moringa stenopetala* seed and Neem seed oil. These two plant species are well known and have large availability in Ethiopia and better suited to a drier climate with marginal lands; yields of seeds are higher and the high contents of oil in the seeds: between 32 - 46 wt. % [11] oil for *morning stenopetala* seed oil and Neem seeds have the best oil fraction like (38-50) wt. % [12] compared to other parts of the tree.

Depending on the difference on the content of free fatty acid concentration and types of plant species, methods such as transesterification and esterification process were applied for oil extraction. It is difficult to trans esterify higher free fatty acid edible and non-edible crop oils using common alkaline or acid catalysts. This indicated that the potential of converting non-edible oil like Moringa and Neem seeds oil into biodiesel and find optimum conditions and properties of Moringa and Neem oil methyl ester must be well examined. This was because physical and chemical properties of biodiesel produced from Moringa and Neem feedstock must comply with the limits of international specifications for biodiesel fuels.

On our country context researchers were worked on *Moringa stenopetala* seed oil as a potential feed stock for biodiesel production and Neem seed oil extraction but they did not give emphasis on optimization and comparison of biodiesel (B_{100}) quality extracted from Neem seed oil and *moringa stenopetala* seed.

This thesis was focused to address the gaps on extraction, process variable optimization of quality biodiesel production and comparison of those products with fuel and ASTM standards.

1.3. Objectives

1.3.1. General objective

The general objective of this project work was Optimization and comparison of biodiesel (B_{100}) quality extracted from Neem (Margosa) and *Moringa stenopetala* seed oil.

1.3.2. Specific objectives

The specific objectives were

- ✓ To extract and characterize of *Moringa stenopetala* and Neem seed oils.
- ✓ To optimize the operating conditions such as catalyst concentration (wt. %) and reaction temperature for biodiesel production from *Moringa stenopetala* and Neem seed oil
- ✓ To characterize and compare biodiesel produced from *Moringa stenopetala* and Neem seed oil.

1.4. Significance of the study

This thesis has great significance in terms of assuring the production of an alternative form of energy from *Moringa stenopetala* seed oil and Neem seed oil in the determination of the potentials of the country in supplying balancing feedstock for biodiesel production. Biodiesel program from *Moringa stenopetala* seed oil and Neem seed oil can help close the trade gap by reducing imported petroleum and also by increasing exports. It also will be helpful to produce biodiesel from moringa stenopetala seed oil using methanol and alkali catalyst, which is locally available, can be abundantly cultivated and grown, nonrenewable and good for production of biodiesel. This helps to encourage rural communities to cultivate more moringa stenopetala and Neem tree to sustain their earnings. In addition, the study will be used as a reference material for *Moringa stenopetala* seed and Neem seed plant cultivation owners who are interested to produce biodiesel from moringa stenopetala seed oil using methanol with alkali catalyst at small scale.

1.5. Scope of the study

This thesis work covers extraction and characterization of moringa stenopetala and neem seed oils for biodiesel production and also optimizes the biodiesel production by taking catalyst weight and reaction temperature as factor and investigates the quality of the Fatty acid methyl ester from both plant species and compare with diesel and with ASTM norms.

2. Literature review

2.1. History of biodiesel

The diesel engine came into its existence in the year 1893 when the paper titled "The theory and construction of a rational heat engine" was published by a great German Inventor Dr. Rudolph Diesel. The use of vegetable oil was first started by Rudolph Diesel. He developed the first diesel engine working on peanut oil at the World's Exhibition in Paris, 1900 [14]. In the 1930s and 1940s vegetable oils were used as diesel fuels from time to time, usually only in emergency. The first International conference on plant and vegetable oils as fuels was held in Fargo, North Dakota in August 1982. The primary concern discussed were the cost of fuel, the effect of vegetable oil fuels on engine performance and durability and fuel preparation specification and additives. Oil production, oil seed processing and extraction also were considered in this meeting. Vegetable oils hold promise as alternative fuels for diesel engines. But their high viscosities, low volatilities and poor cold flow properties have led to the investigation of various derivatives. Fatty acid methyl esters, known as Biodiesel, derived from triglycerides by transesterification with methanol have received the most attention [15].

2.2. Biodiesel

In most general sense, biodiesel refers to any diesel fuel substitute derived from renewable biomass. More specially, biodiesel is defined as oxygenated, sulfur-free, biodegradable, non-toxic and eco-friendly alternative diesel oil. Chemically, it can be defined as a fuel composed of mono-alkyl esters of long chain fatty acids derived from renewable sources such as vegetable oil, animal fat, and used cooking oil designated as B100, and also it must meet the special requirement such as US Standard Specification for Biodiesel (ASTM D6751) and European standards (EN 14214). For those to be considered as viable transportation fuels, they must meet stringent quality standards. One popular process for producing biodiesel is transesterification process. Biodiesel is made from a variety of natural oils such as soybeans, rapeseeds, coconuts, and even recycled cooking oil. Rapeseed oil dominates the growing biodiesel industry in Europe. In the United States, biodiesel is made from soybean oil because more soybean oil is produced in the United States than all other sources of fats and oil combined [16].

2.3. Biodiesel production in the world

Global biodiesel production is expected to reach 39 Bln L by 2024 corresponding to a 27% increase from 2014 (Figure 2.1.). The European Union is expected to be by far the major producer of biodiesel (Figure 2.2.). Other significant players are Indonesia, the United States, Brazil, and Argentina. Policy rather than market forces will continue to influence production patterns in almost all countries. In the European Union, biodiesel production is projected to follow a similar path as ethanol production and to reach its maximum in 2020 with 13.6 Bln L when the RED (Renewable Energy Directive) target is met. By 2024, production is expected to decline to 13.1 Bln L due to lower demand for both biodiesel and diesel. The United States is expected to lose its position as the second largest biodiesel producer in the next ten years. In fact, the end of the biodiesel blenders' tax credit means that domestic biodiesel production will remain close to but not surpass the biodiesel mandate level of 4.8 Bln L [17].

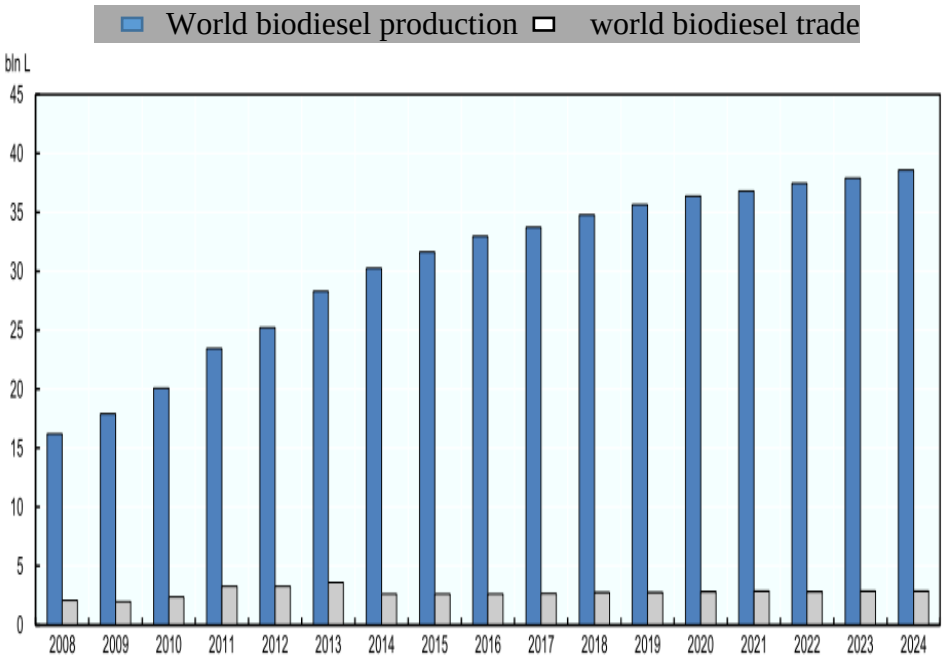


Figure 2. 1: Development of the world biodiesel market, Source [18].

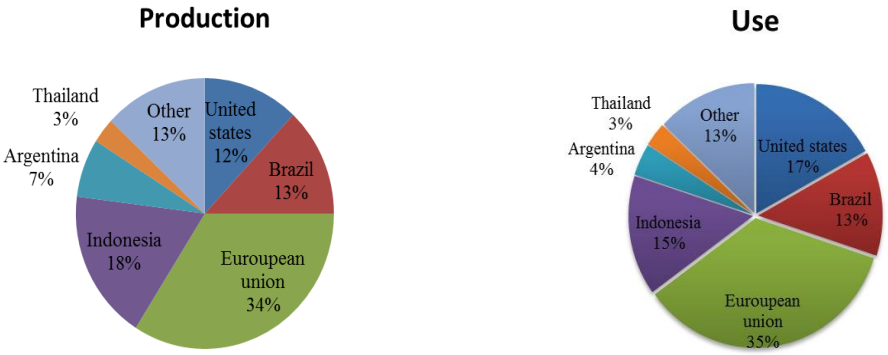


Figure 2. 2: Regional distributions of world biodiesel production and use in 2024, Source [18].

2.4. Biodiesel production in Ethiopia

Ethiopia is viewed as one of the most suitable nations in Africa for tapping renewable sources of energy because of its location. This is the case not only for its own economy, but also for export to economies in the region, such as Kenya, Djibouti and Sudan. The country has also been looking at enhancing its energy capacity, especially over the past two decades [19]. The governments recently issued biofuel strategy to encourage domestic biofuels production, with an objective of reducing the dependence on high-cost fossil oil, is also a manifestation of this endeavor [5]. Ethiopia is a country with a total land mass of 1.2 million km^2 and is said to have an estimated potential area of about 25 million hectares of land suitable for production of biodiesel feedstock [4]. Given rising world prices of fossil oil, the biofuels industry has developed a very significant national presence. Accordingly, there are biofuels investment activities in different regions of Ethiopia with a focus on bioethanol and biodiesel production. Besides, Ethiopia embarked on a 5% blend of bioethanol in transport fuel in 2008, which was doubled to 10% a few years later. Official reports also indicate that, by blending more than 38.2 million liters of bioethanol with gasoline, the country has been able to save 30.9 million US dollars on oil imports since 2008 [20]. Although the recently launched Climate Resilient Green Economy (CRGE) strategy of Ethiopia envisages 5% biodiesel blending in transport fuel by 2030, biodiesel blending in transport fuel has not yet started in Ethiopia [21].

Biofuels development in Ethiopia is unique in two important respects. Firstly, the biofuels sector is characterized by a diversity of biofuels feedstock crops (Jatropha, castor bean, sugarcane, and palm oil, including indigenous trees). Second generation biofuels, i.e., molasses, a byproduct, is

used for bioethanol production, whereas Jatropha, castor bean and palm are used for biodiesel production. There are also intercropping options with other crops in the case of castor beans. Secondly, the biofuels business model in Ethiopia includes a mix of plantations, out-growers' schemes, and community development models. For example, REST in Tigray and ORDA in the Amhara region are involved in biofuels under a community development model [22].

The biofuels investment survey was conducted in 2010 by the Environmental Economics Policy Forum for Ethiopia (EEPFE) at the Ethiopian Development Research Institute (EDRI). According to the biofuels investment survey, there are about 15 biofuels companies, including NGOs, involved in biofuels production in Ethiopia. The survey revealed that only one company exported biodiesel at least once, and two companies are at the product testing stage. The rest are still at a much younger stage. The recent biofuels investment survey, sugar cane accounted for a larger share of the total land allocated to biofuel crops (Figure 3). However, it is important to note that a small proportion of the total land allotted to biofuels production was utilized in 2007. For instance, while a fifth of the total land allocated for biofuels is utilized in castor bean, the figures for Jatropha and palm oil are very small, i.e., 1.5% and 0.8%, respectively, in 2009 (Figure 4). A little more than half of the total land allotted to sugarcane has been utilized over the same period [22].

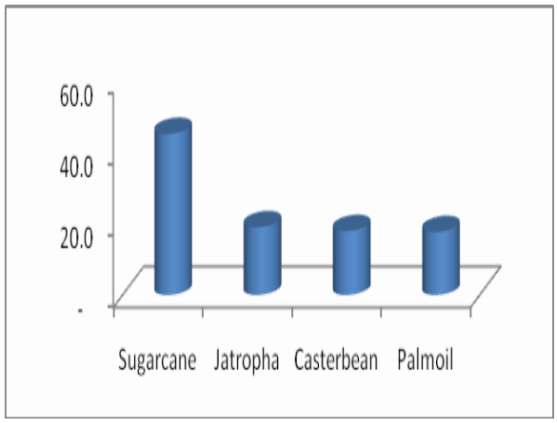


Figure 2. 3: Share in Total Biofuel Crop Land by Biofuel Crop Type (%), Source [23].

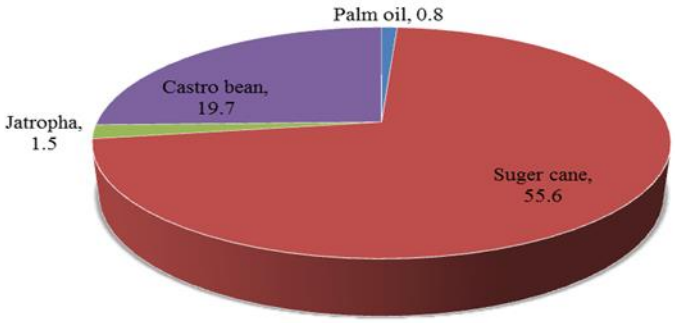


Figure 2. 4: Ratio of Utilized Land to Total Land Allocated to Each Biofuel Crop (%), Source [23].

2.5. Feed stocks for biodiesel production

The raw materials for biodiesel production are vegetable oils, waste cooking oils, animal fats and short chain alcohols. The oils most used for worldwide biodiesel production are rape-seed (mainly in the European Union countries), soybean (Argentina and the United States of America), palm (Asian and Central American countries) and sunflower, although other oils are also used, including peanut, linseed, safflower, used vegetable oils, and also animal fats. Since cost is the main concern in biodiesel production and trading (mainly due to oil prices), the use of non-edible vegetable oils has been studied for several years with good results. Besides its lower cost, another undeniable advantage of non-edible oils for biodiesel production lies in the fact that no foodstuffs are spent to produce fuel [24].

Non-edible oil sources are preferable for biodiesel production, particularly those requiring low agronomic demand for cultivation, a reasonable plant cycle, favorable geographic adaptability, high oil content and a low cost for cultivation and harvesting such as Moringa stenopetala plant and Neem (Margosa) plant.

Moringa stenopetala and Neem (Margosa) plant are the best raw material for producing biodiesel as they are non-edible, thus does not matter on food scarcity; it can be cultivated around poor soil, especially around dry valleys of Ethiopia that the land useful; biodiesel produced from it is less dense.

2.5.1. *Moringa stenopetala*- The Miracle Tree

2.5.1.1. Name and Plant description

Moringa is a tropical plant belonging to the family Moringaceae and grows throughout the tropics. The genus Moringa consists of 13 species of which only *Moringa oleifera* has been accorded research and development attention. It was highly valued in the ancient world. The Romans, Greeks and Egyptians extracted oil from the seeds and used it for perfume and skin lotion. In the 19th century, plantations of Moringa in the West India's exported the oil to Europe for perfumes and lubricants for machinery. *M. oleifera* is native to sub-Himalayan tracts of northern India and is commonly referred to as 'horseradish tree' or 'drumstick tree'. Moringa is a multipurpose tree of significant economic importance as it has vital nutritional, industrial and medicinal applications [25].

The rest species of Moringa, on the other hand, have not been studied in detail and their potential uses have not been fully understood. *Moringa stenopetala* was domesticated in East African lowlands and indigenous to northern Kenya and southern Ethiopia. Many different ecotypes and varieties of *M. stenopetala* are found in Ethiopia. *M. stenopetala* is often called "cabbage tree" and is an important indigenous vegetable in south western Ethiopia where it is cultivated as a food crop. Its leaves are consumed by Gofa, Konso, Burji and Gamo tribes as vegetable especially during the dry season [25]. M. stenopetala is native to Ethiopia and it is known by various vernacular names. It is called 'Haleko' in Gofa areas, 'Shelagda' in the Konso language and 'Shiferaw' in Amharic (26). *M. stenopetala* is particularly important as human food because the leaves, which have high nutritional value , appear towards the end of the dry season when few other sources of green vegetables are available. Haleko leaves contain high contents of essential amino acids and vitamins A and C [27].

The seeds of *M. stenopetala* contain edible oil that can be used for cooking and as salad dressings [28]. Besides, *M. stenopetala* seeds have traditionally been used to purify turbid water in many tropical countries like its Asian counterpart *Moringa oleifera*. It was reported that M. stenopetala seeds have better water purifying properties than *M. oleifera* seeds [29]. Crude extracts from the defatted seeds reported to exhibit antimicrobial effects [30] and thus could be used to preserve different food and non-food ingredients. *M. stenopetala* is a fast growing tree well adapted to semi-arid areas. It is quite drought tolerant and can grow at altitudes ranging

from 390 to 2,200 m above sea level, annual temperature ranging from 24-30°C and annual rainfall ranging from 250-1400 mm.

Given its high nutritional value, drought tolerance, fast growing habits and many of its potential uses, Haleko should have been given due attention by all concerned and considered as a priority crop to alleviate malnutrition and reduce poverty. However, Haleko is one of the forgotten tree crops in Ethiopia [29].

Figure 2. 5: *Moringa stenopetala* Tree

2.5.1.2. Physicochemical Properties of the *moringa stenopetala* Seeds

Moringa stenopetala seeds are triangular, have three wings, and are covered with a spongy, thick yellowish seed coat (Figure 2.6 a). The kernel has a whitish-grey color and oval shape, and its thickness decreases from the center towards either end along the length of the seed (Figure 2.6 b). It was reported that a single 4 to 13-year-old *M. stenopetala* tree can produce up to 4,500-10,000 seeds that weigh 2.3-5 kg from about 500-1,000 pods (Table 2.1). The same report indicated that 1 kg of *M. stenopetala* seed contains about 1,795-2,078 seeds [31].

(a) UnDehulled seed

(b) kernels

Figure 2. 6: *Moringa stenopetala* seeds

Table 2. 1: Physical properties of seeds of *Moringa stenopetala* plant

Variables	Range	Mean ±SD
Average number of seed/pod	9-10	-
Number of seed/tree	4500-10000	-
Weight of seed (g)/tree	2.3-5	-
Average weight (g)/100 seeds (kernel +hull)	48.12-55.71	73.6 ± 2.28
Average weight (g/seed)	0.5	0.6 ± 0.02
Average weight of kernel (g/100seeds)	-	59.6 ± 2.28
Kernel fraction (% of entire seed)	-	79.7 ± 0.95
Hull fraction (% of entire seed)	-	20.3 ± 0.95
Moisture of whole seed (%)	-	6.1 ± 0.24

The seed of M. stenopetala is an important source of oil that could be used for cooking or for different industrial applications. A recent report indicated that *M. Stenopetala* seed oil could be used as a potential feedstock for biodiesel production. Different studies indicate that *M. stenopetala* seeds yield 45% w/w of oil [32], 44.9 %w/w of oil [33] and 45.3% w/w of oil [13].

The gross composition of M. stenopetala seeds is indicated in Table 2.2.

Table 2. 2: Proximate composition (on dry matter basis) of seeds of *Moringa stenopetala*

Variables	**Source [32]**
	(g/100g)
Fat	41.4
Crude protein	42.6
Ash	4.6
Crude protein	5.1
Sugar	-

2.5.1.3. Fatty acid composition of *Moringa stenopetala* seed oil

The fatty acid composition of *moringa stenopetala* seed oil from different papers is listed below in Table 2.3.

Table 2. 3: Fatty acid composition of *Moringa stenopetala* seed oil

Fatty acid	Formula	Structure	Amount (%)	
			Source [13]	Source [33]
Palmitic	$C_{16}H_{32}O_2$	16:0	6.1	6.21
Stearic	$C_{18}H_{36}O_2$	18:0	7.5	4.32
Oleic	$C_{18}H_{34}O_2$	18:1	76.0	74.61
Arachidic	$C_{20}H_{40}O_2$	20:0	3.8	2.58
Arachideic	$C_{20}H_{38}O_2$	20:1	1.7	0.89
Behenic	$C_{22}H_{44}O_2$	22:0	4.4	6.01
others			0.5	5.38
Total			100	100

2.5.2. Neem (Margosa) tree

2.5.2.1. Name and plant description

Margosa (Neem) tree, which is also known as *Azadrichta indica*, is one of the best-known trees in India, which is known for its medicinal properties. The main reason behind the popularity of the Neem oil is that it is used to treat few of the most common problems that the people face. The Neem tree (*Azadrichta indica*) is among the fastest-growing trees, it attains a height of about 12-13 feet and easy to cultivate, can survive drought and poor soil and keeps its leaves all year round. Since Ethiopia is located around the tropical region, thus, the weather makes a suitable environment for the growth of Neem tree. Mostly, Margosa (Neem) tree is available in large amount in Amhara, Afar, Gambella, Somalia, Tigray region. Most Ethiopian people plant this tree without having a hardly known about its use. For example, merely, in Amhara region, the rural people use Neem leaves for village medicine, especially to cure malaria and diabetes disease. Neem tree will adapt to a mean annual rainfall of 450-1200 mm, mean temperatures of 25-35ºC and grow at altitudes of up to 800 meters above sea level.

From the literature, it is observed, world science approves the application of Neem trees for medicinal purpose for internal as well as external treatment problems. Unlike its medicinal purpose Neem (*Azadrichta indica*) is also used for production of cosmetics, soap, biodiesel, etc. from the Neem oil. Its waste also used for fertilizer. Neem oil has no any side effects and it is environmentally friendly [35].

a. Neem tree b. neem seed

Figure 2. 7: a. Neem (Margosa) tree and b, Neem seed

2.5.2.2. Fatty acid composition Neem (Margosa) seed oil

The fatty acid composition of Neem (Margosa) seed oil from different papers is listed below in

Table 2. 4: Fatty acid of Neem (Margosa) seed oil

Fatty acid		Composition %		
	Structure	Source [36]	Source [37]	Source [38]
Palmitic acid	16:0	26.00	18.1	15.55
Stearic acid	18:0	9.50	18.1	21.11
Oleic acid	18:1	51.00	44.5	56.98
Linoleic acid	18:2	13.00	18.3	3.69
Linolenic acid	18:3	0.06	0.2	0.28
Myristic acid		0.44	-	
Arachidic	20:0	-	0.8	0.18
Others				2.21
Total		100	100	100

2.6. Process description of oil extraction

2.6.1. Pre-treatment

Irrespective of the method used, certain pretreatments of raw seeds are essential, if highest possible recovery of quality oil at an economical rate is obtained. The following pretreatments are used to improve oil yields to be and their quality. These are:

Cleaning

Normally, the vegetable seeds are mixed with a variety of foreign materials called, sand, stones, stalks, weed seeds, foliage, etc., during harvesting, handling and transportation. In short, proper cleaning of oil seeds can increase in crushing capacity of oil expelling units, reduce in-plant maintenance and improve the quality of oil and cake.

De-hulling (decortications)

The hulls of oil seeds are fibrous and have low oil content. De-hulling of oilseeds extraction is advantageous as the hulls; reduce the total oil yields and the capacity of extraction equipment.

Size reduction

The process of particle size reduction improves ingredient performance during mixing and, in most cases; the nutritive value of an ingredient can be improved or more nearly realized. The extraction of oil from oilseeds, either by mechanical expression or by means of solvents, is facilitated by reduction of the seed in small particles by grinding or rolling. Hence the size reduction of oilseeds is important for efficient recovery of oils. Hammer mills are used for the preliminary reduction of size of large oilseeds while milling rolls are used for final reduction. There are many ways to reduce the particle size of feed ingredients. Two of the most common pieces of equipment used are the hammer mill and the roller mill. The choice of which to use depends upon the unique requirements of every individual situation.

Flaking

Flaking machines consist of a pair of horizontal counter-rotating smooth steel rolls. The main purpose of flaking is to increase the contact surface between the oilseed tissues and the solvent, and to reduce the distance that the solvent and the extract will have to travel in the process of extraction. It is also believed that flaking disrupts the oilseed cells to some degree and thus makes the oil droplets more available for solvent extraction.

2.6.2. Extraction Methods

Various extraction methods can be used in the extraction of oil and the method is normally dependent on what type of botanical material is been used. These methods include

1. **Mechanical,**

For oil extraction using mechanical pressing, vegetable seed is fed to mechanical presser which exerts high pressure for extracting oil. When pressure is exerted at the required amount, solid cake is removed in one region; oil and some impurities are collected in a different side. Finally, oil and impurities are separated using centrifuge or gravity settling.

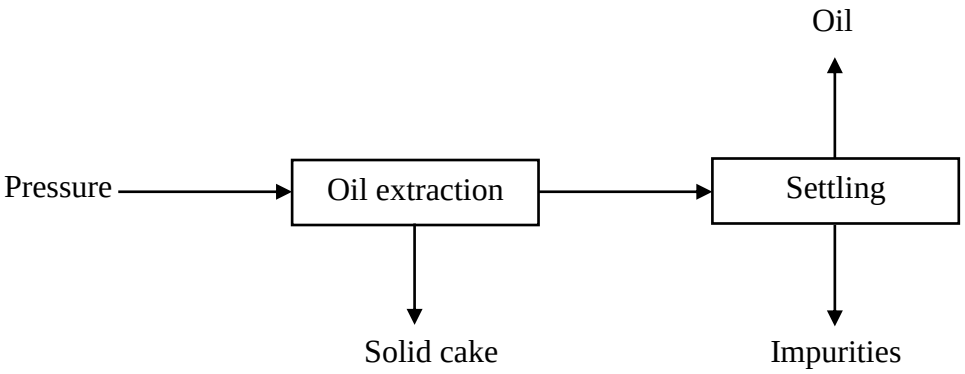


Figure 2. 8: Process flow of mechanical press oil extraction

2. **Solvent Extraction**.

Solvent extraction with n-hexane can produce about high yield by weight of oil per kilogram of the *moringa stanopetala* seed. To extract oil using solvent, *moringa stenopetala* seeds are crushed at the required size. The crushed seeds and hexane at ratio of 1:9 (w/v) respectively are fed to soxhlet apparatus to extract oil. The extraction temperature is near to the boiling point of hexane.

The solid cake and mixture of oil and hexane are separated using vacuum filter. Hexane and oil are separated using distillation at a temperature of slightly higher than the boiling temperature of hexane, which is recovered again for further extraction with fresh hexane.

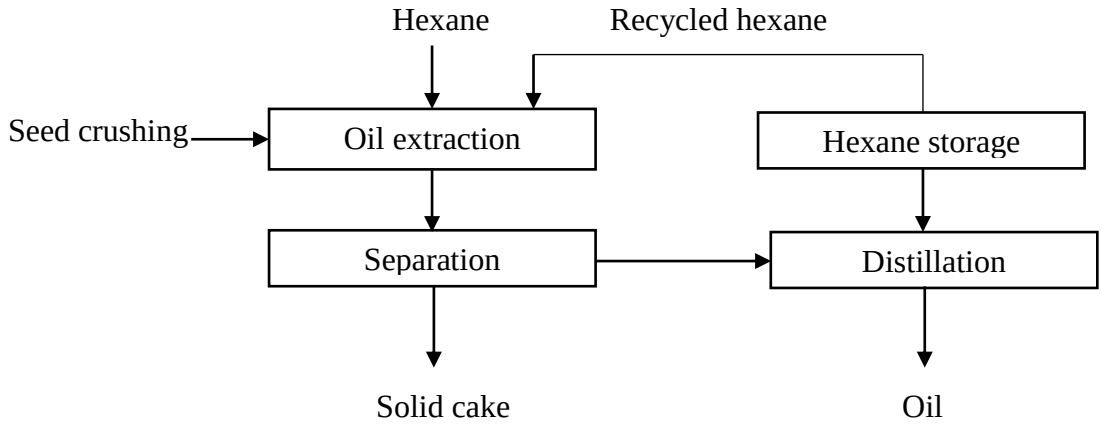


Figure 2. 9: Process flow of mechanical press oil extraction

2.7. Biodiesel Production Technologies

There are different technologies which are employed in the production of biodiesel. They have been discussed as follows [39]

2.7.1. Batch Process

The non-edible vegetable oil is charged to transesterification in a batch reactor in the presence of an excess amount of methanol, and catalyst. An excess of methanol is necessary chiefly to ensure full solubility of triglyceride and keep the viscosity of the reaction mixture low, but also for shifting the chemical equilibrium. The transesterification reaction may be considered finished when maximum conversion is achieved. However, the mixture composition should respect the quality of biodiesel specifications.

The excess methanol is recovered for the next batch. The remaining mixture is submitted to the separation of esters from glycerol. This can take place either by decantation or by centrifugation. Water may be added to improve the phase split.

The oil phase containing fatty esters is sent to finishing by neutralization with acid, followed by washing and drying. The methanol recovery takes place by flash distillation or film evaporation. The batch process allows high flexibility with respect to the composition of the feedstock. In turn, the economic indices are on the lower side because of lower equipment productivity and higher operation costs, such as manpower and automation.

2.7.2. Catalytic Continuous Processes

The Catalytic continuous process technology of biodiesel production is a conceptual scheme of a continuous process working at low pressure that is capable of processing a feedstock with a larger amount of free fatty acids, such as unrefined non-edible vegetable oils, tallow fat and used cooking oil. For this reason, in the first reactor the esterification of free acids with methanol is carried out. Then the transesterification reaction follows in the second reactor. A homogeneous catalyst is currently used, either as alkaline hydroxide or alkaline methoxide.

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

removal and recovery as FFA. Then, the methanol is recovered by evaporation and recycled. The crude ester follows the route of methanol separation. The material balance loop is closed by the recovery of excess methanol from water solution by distillation. Using a heterogeneous solid catalyst in the transesterification phase allows a substantial simplification of the process flow. Two reactors are employed with intermediate glycerol separation. Excess methanol is recovered by multistage flash. Phase separation of ester and glycerol are carried out by coalescence separation or centrifugation. It can be seen that the neutralization and washing steps are absent. Methanol can be recycled as vapor.

2.7.3. Supercritical Processes

Performing the esterification in supercritical conditions has been studied initially as a method to solve the problem of miscibility of oil and methanol that hinders the kinetics in normal condition. Since the critical coordinates of methanol are T_c=239 ^{o} C and P_c=80 bar, raising the temperature and pressures at sufficiently high values is necessary. Studies conducted in Japan demonstrated the feasibility of producing biodiesel by the esterification of rapeseed with methanol without a catalyst working around 350 ^{o} C and 200 bars at molar ration methanol to oil of 42:1 for reaction times below 4 min.

The advantage of avoiding a catalyst is obvious. However, the conditions of pressure and temperature are severe and need special equipment. Recent research showed the real yield can be reduced by thermal degradation of biodiesel, namely of unsaturated fatty esters. For this reason, lowering the reaction temperature and pressure is highly desirable.

The addition of co-solvent in combination with supercritical conditions seems to be an efficient means to reduce significantly the operating temperature. For example, soybean oil could be converted with methanol into biodiesel with 98% yield by using propane, at least in 0.05 molar ratio to methanol, at 280 ^{o} C and 12.8 MPa. Similar results have been reported with CO_2 in a molar ration of 0.1 with respect to methanol. In both cases the optimal ratio methanol/oil was 24 and residence time of 10 min. Due to the absence of the catalyst the process flow sheet implying the supercritical technology should be much simpler, but in exchange the manufacture of hardware is much more demanding.

Effective energy integration is also necessary. Despite these advantages the industrial implementation of super critical esterification has not reported.

2.7.4. Hydrolysis and esterification

A simpler manufacturing procedure would consist in first performing the hydrolysis of triglycerides and isolating the fatty acids followed by esterification. Significant advantages would be the possibility of extracting high value fatty acids from the lipid material, as well as obtaining high purity glycerol. The hydrolysis reaction can be carried out without a catalyst working in milder conditions compared to full esterification. A temperature close to 270^{0} C and pressures from 70 bar to 200 bar has been found applicable. Another advantage is that the overall yield can be increased by suppressing the back reaction of glycerol with the methyl ester. The reaction exhibits an autocatalytic effect due to the fatty acid produced, from which a small recycle can be provided.

2.7.5. Enzymatic process

The transesterification reaction can be catalyzed by enzymes, the most common being the lipase. The reaction takes place at normal pressure and temperatures 50 to 55^{0}C with low energy consumption. The yield of methanolysis depends on several factors such as temperature, pH, type of microorganism producing the enzyme, the use of co-solvents, etc. However, low yields in methyl esters and very long reaction times make the enzymatic processes not competitive enough at this time.

2.7.6. Vegetable oils

Vegetable oils are chemically complex esters of fatty acids. These are the fats naturally present in oil seeds, and known as triglycerides of fatty acids. The molecular weight of these triglycerides would be order of 800 kg/m or more Because of their high molecular weights these fats have high viscosity [40] causing to reduces fuel atomization and increases penetration, which is partially responsible for engine deposits, piston ring sticking, injector coking and the thickening of oil. Different methods have been developed to reduce the viscosity of vegetable oils such as dilution (blending), micro-emulsification, pyrolysis (thermal cracking), and transesterification [41].

2.7.7. Dilution (Blending)

Crude vegetable oils can be blended directly or diluted with diesel fuel to improve their viscosity. Dilution reduces the viscosity and engine performance problems such as injector

coking and the creation of carbon deposits. In 1980, Caterpillar Brazil used a 10% mixture of vegetable oil and diesel to maintain total power without any modification or adjustment to the engine. A diesel engine study with a blend of 20% vegetable oil and 80% diesel fuel has also been carried out. Twenty-five percent sunflower oil and 75% diesel were blended as a diesel fuel and the reduced viscosity was 4.88 cSt at 313 K, while the maximum specified American standard test method (ASTM) value is 4.0 cSt at 313 K.

This mixture was not suitable for long-term use in a direct-injection engine. The viscosity decreases with increasing percentage of diesel. Further, it was also reported that the viscosity of a 25: 75 high oleic sun flower oil: diesel fuel blend was 4.92 cSt at 40 ^{0}C and that it has passed the 200 h Engine Manufacturers Association (EMA) test. Another study was conducted by using the blending technique on frying oil.

2.7.8. Micro-emulsification

Micro-emulsification is another approach to reducing the viscosity of vegetable oils. A micro-emulsion is defined as a colloidal equilibrium dispersion of an optically isotropic fluid micro structure with dimensions generally in the 1–150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic amphiphiles. In other words; micro emulsions are clear, stable isotropic fluids with three components: an oil phase, an aqueous phase and a surfactant. The aqueous phase may contain salts or other ingredients, and the oil may consist of a complex mixture of different hydrocarbons and olefins. This ternary phase can improve spray characteristics by explosive vaporization of the low-boiling-point constituents in the micelles. All micro-emulsions with butanol, hexanol and octanol meet the maximum viscosity limitation for diesel engines. A micro-emulsion prepared by blending soybean oil, methanol, 2-octanol and a cetane improver in the ratio of 52.7: 13.3: 33.3: 1.0 has passed the 200 h EMA test.

2.7.9. Pyrolysis (Thermal Cracking)

Pyrolysis is a method of conversion of one substance into another through heating or heating with the aid of a catalyst in the absence of air or oxygen. It involves cleavage of chemical bonds to yield small molecules. The material used for pyrolysis can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The liquid fuel produced by this process has an almost identical chemical composition to conventional diesel fuel. Soybean oil has been thermally decomposed in air using the standard ASTM method for distillation. The viscosity of

the pyrolyzed soybean oil distillate is 10.2 cSt at 37.8 ^{0}C, which is higher than the ASTM specified range for No. 2 diesel fuel but acceptable as it is still well below the viscosity of soybean oil.

2.7.10. Transesterification: catalytic process

The process of transesterification emerged when Rochiede illustrated glycerol preparation through Ethanolysis of castor oil in the early 1846 period. Ever since that time many parts of the world started studying ethanolysis [42]. Transesterification process helps reduce the viscosity of the oil. The process proceeds well in the presence of homogenous catalysts such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sulphuric acid. The formation of fatty acid methyl ester (FAME) through transesterification of seed oils requires raw oil, 15% of methanol and %5 of sodium hydro oxide on mass basis. However, transesterification is an equilibrium reaction in which excess alcohol is required to drive the reaction very close to completion.

Transesterification transform the large branched molecule structure of the oils into smaller, straight chained molecules similar to the standard diesel hydrocarbons. Transesterification is the process of exchanging the organic group R" of an ester with the organic group R' of an alcohol. These reactions are often catalyzed by the addition of an acid or base. Transesterification is common and well-established chemical reaction in which alcohol reacts with triglycerides of fatty acids (non-edible oil) in the presence of catalyst. The transesterification reaction scheme is shown below [40].

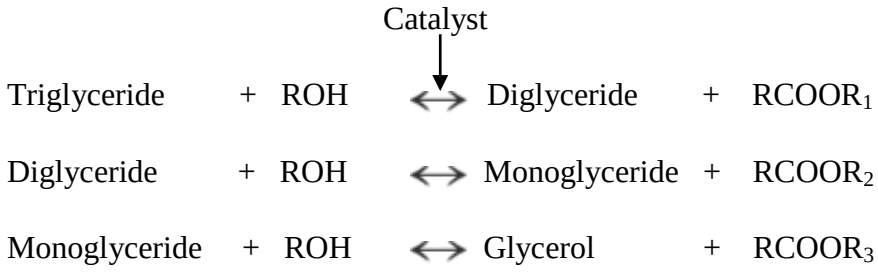


Figure 2. 10: The steps in transesterification.

Methanol and ethanol are used most frequently; especially methanol is preferred because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides and NaOH gets easily dissolved in it. Ethyl ester and methyl ester almost has same heat content [40].

The two methods preferred for the industrial production of biodiesel from non-edible oils are base catalyzed and acid catalyzed transesterification.

2.7.10.1. Base-Catalyzed Transesterification Process

This is the traditional technology commonly employed for the commercial production of biodiesel from the refined vegetable oils/fats that are low in free fatty acids (FFAs < 0.1 wt. %). It involves the transesterification of triglycerides present in oil/fat with a lower alcohol (mostly methanol) in the presence of a catalytic amount of a base (alcoholic solution of KOH/ NaOH or sodium methoxide) at the atmospheric pressure under the reflux condition for alcohol (60-70 °C). This reaction proceeds through the well-known mechanism as shown in Figure 2.11.and could produce the fatty acid methyl ester (FAME, called biodiesel) in an amount almost equal to that of the oil used. This reaction is fast and reversible. Therefore, one requires adding an excess amount of both methanol and the catalyst to drive the reaction to completion. Since this reaction is sensitive to the moisture, it essentially requires drying of all the reagents, particularly methanol, such that their moisture content is reduced to below 0.1% by weight [43]. To complete a transesterification reaction stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is necessary. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield. Further, prior to using oil in the transesterification process, its FFA content must be reduced to below 0.1 wt. % by neutralizing oil with an alkali, to prevent the formation of soap in the transesterification reaction. Base catalyzed transesterification is preferred over acid catalyzed transesterification reactions for the production of biodiesel at industrial level because it provides better conversion rates and efficiencies. The basic parameter reflecting the extent of the reaction could be the viscosity, since it is directly related with the fatty acid methyl ester (FAME) content of the product and is one of the specifications to comply with in biodiesel production [44].

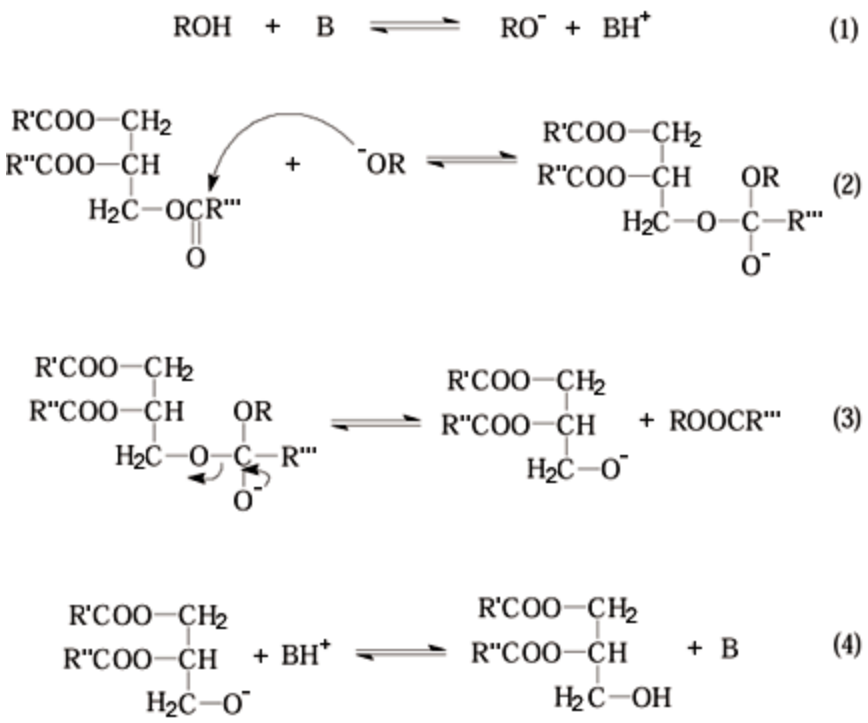


Figure 2. 11: Reaction mechanism for base-catalyzed transesterification during biodiesel production. Where B is a base and R1-4 are hydrocarbon groups

The base catalyzed production of biodiesel generally has the following process steps [45].

A. Mixing of alcohol and catalyst

This typical process is mainly done by mixing alkali hydroxide (commonly potassium hydroxide and sodium hydroxide) with common alcohols (methanol and ethanol) in the mixer with standard agitator to facilitate the mixing. Alkali hydroxide is dissolved in the alcohol to produce alkali oxide solution.

B. Chemical reaction

The alcohol and catalyst mixture is then charged into a closed reaction vessel and the oil is added. The reaction system is totally closed to the atmosphere to prevent the loss of alcohol, since it easily vaporizable. The reaction mixture is kept just near the boiling point of the alcohol to speed up the reaction. Excess alcohol is normally used to ensure total conversion of the oil to its esters as there is no problem of recovering of the alcohol for later use after recycling.

C. Separation

After the reaction is completed, there exists glycerol and biodiesel formation. Both have a significant amount of the excess alcohol that was used in the reaction which is in need of being recovered. The reacted mixture is sometimes neutralized at this step if the basic media that is caused by alkali hydroxide is occurred. The glycerol phase is much denser than biodiesel phase, making biodiesel to be floated. The two products can be separated by gravity using settling vessel. The glycerol is drawn off at the bottom of the settling vessel and biodiesel is drawn off at the top. In some cases, a centrifuge is used to separate the two materials faster by screening both phases.

D. Alcohol removal

After the glycerol and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation commonly. But currently extractive distillation can instead be used to fasten the process and to be more economical. On the other hand, the alcohol is removed and the mixture neutralized before the glycerol and esters have been separated to prevent the effect of basic media inside the reactor. After the alcohol is being recovered it is used as main raw material.

E. Biodiesel washing

After the Biodiesel is separated from the glycerol, it is sometimes purified by washing gently with warm water to remove residual catalyst, alcohol or soaps to make purer. The washed biodiesel needs drying in order to remove trace impurities. In some processes washing step is not necessary depending on the quality of biodiesel produced

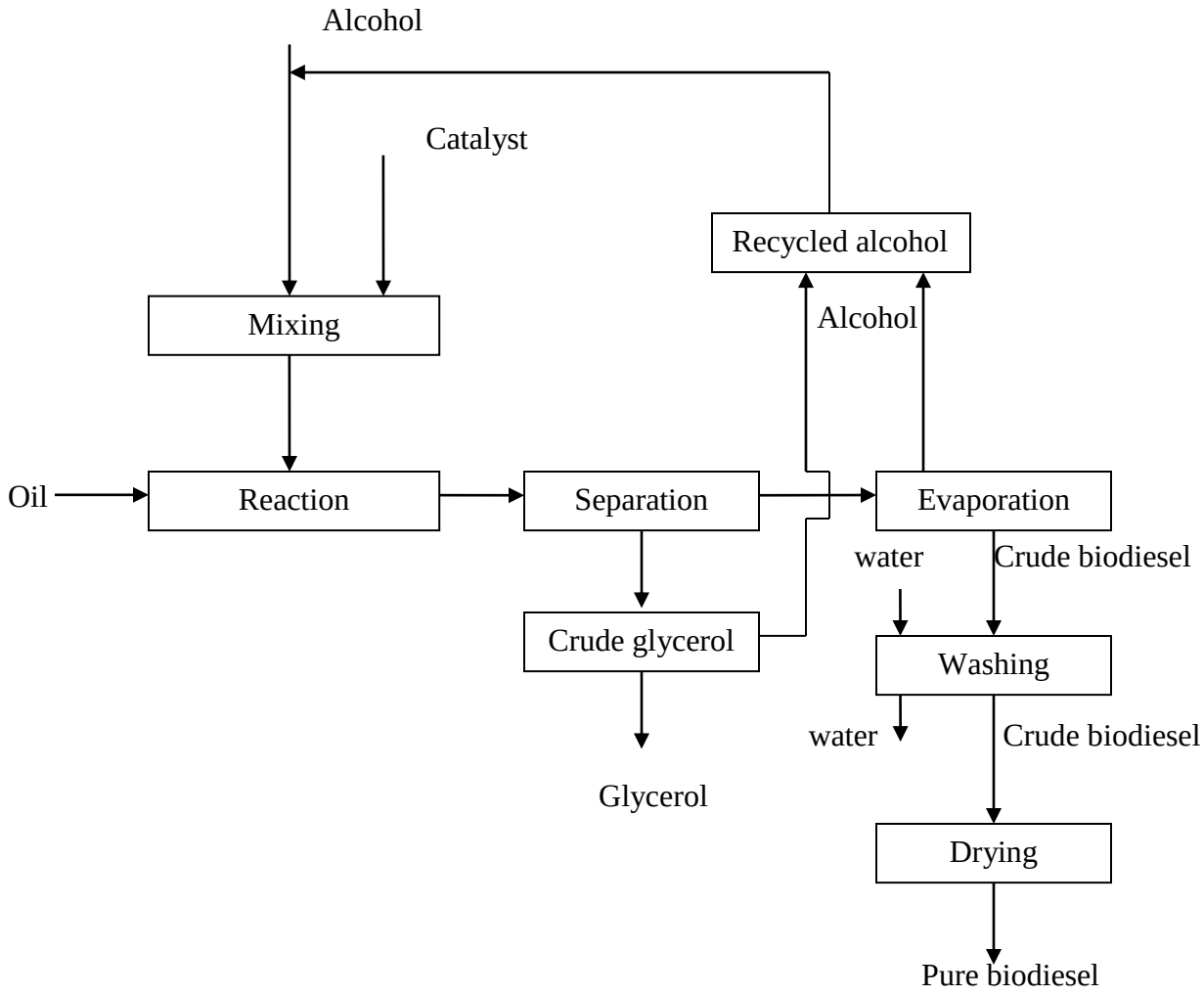


Figure 2. 12: Production of Biodiesel Process flow sheet

2.7.10.2. Acid-Catalyzed Transesterification process

This process is especially suitable for the feed stocks like unrefined or waste cooking oils that are high in FFAs. It uses an acid (commonly sulfuric acid) as the catalyst follows the well-known mechanism as shown below in (Fig. 2.12). This process does not require the pretreatment of oil with an alkali for reducing its FFA content. However, it has the following drawbacks. It is very slow and needs a very high methanol-to-oil molar ratio. The water produced by the reaction of FFA with the alcohol inhibits the transesterification of triglycerides in this process. The acid, if added in large amounts, would burn some oil, thus reducing the overall yield of biodiesel [43].

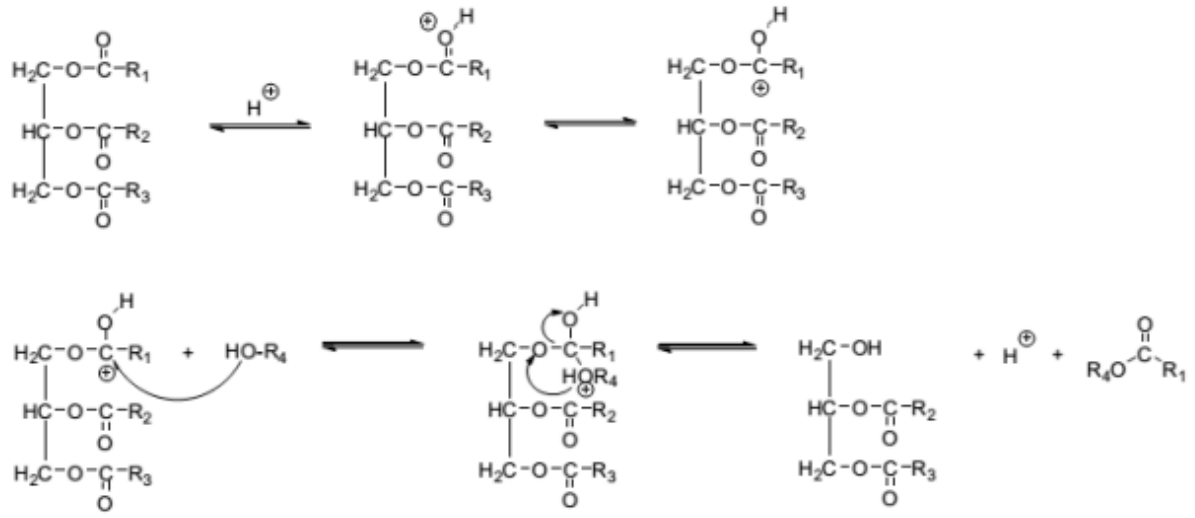


Figure 2.13**:** Reaction mechanism for acid-catalyzed transesterification during biodiesel production. Where R1-3 are hydrocarbon groups

2.7.10.3. Enzymatic Transesterification

Enzymatic transesterification using lipase looks attractive and encouraging for reasons of easy product separation, minimal wastewater treatment needs, easy glycerol recovery and the absence of side reactions. Practical use of lipase in pseudo homogenous reaction systems presents several technical difficulties such as contamination of the product with residual enzymatic activity and economic cost. In order to overcome this problem, the enzyme is usually used in immobilized form so that it can be reused several times to reduce the cost and also to improve the quality of the product. When free enzymes are used in a biodiesel process, the enzymatic activity can be partially recovered in the glycerol phase. However, the build-up of glycerol limits the possible number of reuses [46]. Compared to chemical approach, enzymatic approach for biodiesel production offers more advantages but cost of lipase is the major issue for the industrialization of lipase-mediated biodiesel production.

2.7.10.4. Microwave Assisted Transesterification

An alternative energy stimulant, ‘‘microwave irradiation’’, can be used for the production of the alternative energy source, bio-diesel. Microwave irradiation activates the smallest degree of variance of polar molecules and ions such as alcohol with the continuously changing electrical field. The changing electrical field, which interacts with the molecular dipoles and charged ion,

causes these molecules or ions to have a rapid rotation and heat, is generated due to molecular friction. The preparation of biodiesel using microwave offers a fast, easy route to this valuable biofuel with advantages of a short reaction time, a low oil/ methanol ratio, an ease of operation a drastic reduction in the quantity of by-products, and all with reduced energy consumption. Aside from the great advantages of microwave-assisted reactions, there are also a few drawbacks. Microwave synthesis is not easily scalable from laboratory small-scale synthesis to industrial multi kilogram production. The most significant limitation of the scale up of this technology is the penetration depth of microwave radiation into the absorbing materials, which is only a few centimeters, depending on their dielectric properties. The safety aspect is another reason for rejecting microwave reactors in industry [39].

2.7.10.5. Ultrasound Assisted Transesterification

Ultrasound has proven to be a very useful tool in enhancing the reaction rates in a variety of reacting systems. It has successfully increased the conversion, improved the yield, changed the reaction pathway, and/or initiated the reaction in biological, chemical, and electrochemical systems. Ultrasonic assisted transesterification method presents advantages such as shorter reaction time and less energy consumption than the conventional mechanical stirring method, efficient molar ratio of methanol to triglycerides, and simplicity [39].

2.7.10.6. Two-Step Acid - Base Catalyzed Transesterification

This process involves a two-step process for the production of biodiesel from oils having high FFA. Initially, the acid catalyzed esterification reaction takes place to convert the FFAs present in the oil to esters. After the reduction of FFA, transesterification reaction was carried out, in which the pre-treated oil reacts with methanol using conventional base catalysts. This method of biodiesel production alleviates the draw backs of the esterification process -requires longer time reaction to come to completion and transesterification- problem of soap formation process [39].

2.8. Variables Affecting Alkali Catalyzed Transesterification

Reaction Transesterification reaction process is influenced by a variety of working factors. These are molar ratio of alcohol to oil, presence of free fatty acids and moisture, amount and catalyst type, reaction time, reaction temperature, stirring rate.

2.8.1. The effects of moisture and free fatty acids

From the literature noted that the starting materials used for alkali-catalyzed transesterification of glycerides must meet certain specifications. The glyceride should have an acid value less than 1 and all materials should be substantially anhydrous. If the acid value was greater than 1, more NaOH was required to neutralize the free fatty acids. Water also caused soap formation, which consumed the catalyst and reduced catalyst efficiency. The resulting soaps caused an increase in viscosity, formation of gels and made the separation of glycerol difficult and therefore, water content should be less than 0.3% [47]. Bradshaw and Meuly [48] and Feuge and Grose [49] also stressed the importance of oils being dry and free (<0.5%) of free fatty acids. Freedman et al [50], stated that ester yields were significantly reduced if the reactants did not meet these requirements. Sodium hydroxide or sodium methoxide reacted with moisture and carbon dioxide in the air, which diminished their effectiveness. The effects of free fatty acids and water on transesterification of beef tallow with methanol were investigated. The results showed that the water content of beef tallow should be kept below 0.06% w/w and free fatty acid content of beef tallow should be kept below 0.5%, w/w in order to get the best conversion. Water content was a more critical variable in the transesterification process than were free fatty acids. The maximum content of free fatty acids confirmed the research results of Bradshaw and Meuly [48] and Feuge and Grose [49].

2.8.2. Molar Ratio of alcohol to oil

Another important variable is the molar ratio of alcohol to vegetable oil. As indicated earlier, the transesterification reaction requires 3 mol of alcohol per mole of triglyceride to give 3mol of fatty esters and 1 mol of glycerol. In order to shift the reaction to the right, it is necessary to either use excess alcohol or remove one of the products from the reaction mixture. The second option is usually preferred for the reaction to proceed to completion. The reaction rate is found to be highest when 100% excess methanol is used. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% (w/w) [51].

2.8.3. The effects of reaction temperature

The literature has revealed that the rate of reaction is strongly influenced by the reaction temperature. However, the reaction is strongly influenced by the reaction conducted close to the boiling point of methanol (60–70°C) at atmospheric pressure for a given time. Such mild

reaction conditions require the removal of free fatty acids from the oil by refining or pre-esterification. Therefore, degummed and deacidified oil is used as feedstock. Pretreatment is not required if the reaction is carried out under high pressure (9000 kPa) and high temperature (240°C), where simultaneous esterification and transesterification take place with maximum yield obtained at temperatures ranging from 60 to 80 ^{o}C at a molar ratio of 6:1 [51].

2.8.4. Effect of Reaction Time

The conversion rate increases with reaction time. Freedman et al. [50], trans esterified peanut, cottonseed, sunflower and soybean oils under the condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst and 60 ^{0} C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversions were almost the same for all four oils (93–98%). Investigation performed by [52] shows that at a reasonable alcohol to oil molar ratio and catalyst concentration a maximum yield is obtained after 40 minutes of reaction.

2.8.5. Effect of Catalyst Concentration

Partly due to faster esterification and partly because alkaline catalysts are less corrosive to industrial equipment than acidic catalysts, most commercial transesterification reactions are conducted with alkaline catalysts [53]. The alkaline catalyst concentrations in the range of 0.5–1% by weight yield 94–99% conversion of vegetable oils into esters [50]. Nakpong et al. [54], studied methanolysis of Jatropha oil with NaOH catalyst. The result indicated that catalyst concentration of 1.5% w/w of oil provided a higher methyl ester content than that of 1% w/w of oil for all reaction times, but they suggested that such a concentration should be avoided for two significant reasons: the cost of the additional NaOH, and the cost of removing the residual catalyst in the methyl ester layer. Moreover, the methyl ester layer obtained from using this catalyst concentration has to be washed with hot distilled water several times in the water washing step, so there is a possibility of losing some biodiesel product to emulsion formation. For these reasons, 1% w/w of oil was considered to be the optimum catalyst concentration [52].

Sodium methoxide was found to be more effective than sodium hydroxide presumably because a small amount of water is produced upon mixing NaOH and methanol [55]. Sodium alkoxides are among the most efficient catalysts used for this purpose, though NaOH, due to its low cost, has attracted its wide use in large scale transesterification [53].

2.9. Properties of Biodiesel Fuels

Since biodiesel is produced from vegetable oils of varying origin and quality, the pure biodiesel must meet before being used as a pure fuel or being blended with conventional diesel fuels. Various Parameters which define the quality of biodiesel are discussed below.

2.9.1. Density

Density is a key fuel property, which directly affects the engine performance characteristic. It affects the mass of fuel injected into the combustion chamber and thus, the air-fuel ratio. This is because fuel injection pumps meter fuel by volume not by mass and a denser fuel contains a greater mass in the same volume. Thus, the changes in the fuel density will influence engine output power due to a different mass of fuel injected. It is known that biodiesel density mainly depends on its esters content and the remained quantity of alcohol; hence this property is influenced primarily by the choice of vegetable oil [56].

The density of diesel fuels is another important property of the fuels that affects the fuel injection system, density is usually measured at 15 ^{o}C. Density of biodiesel is the weight of a unit volume of fluid while the specific gravity is the ratio of the density of a liquid to the density of water. The fuel injection equipment meters the fuel volumetrically and high densities translate into a high consumption of the fuel. it can be seen that biodiesel has densities between 0.860g/cm^3 and 0.897g/cm^3 at 15 ^{o}C which is higher than that of the petroleum diesel, however this high density can be said to make up for the low volumetric energy content of biodiesel [57].

2.9.2. Viscosity

The viscosity of a liquid is a measure of its resistance to flow due to internal friction; this is a very important property of a diesel fuel because it affects the engine fuel injection system predominantly at low temperatures. A highly viscous fuel will result in poor atomization hence a loss of power of the engine and production of smoke. Biodiesel is slightly viscous but their viscosities are still close to that of the petroleum diesel. This is an advantage of biodiesel over its source oils [57].

High values of kinematic viscosity give rise to poor fuel atomization, incomplete combustion, and carbon deposition on the injectors. Therefore, the biodiesel viscosity must be low. Biodiesel fuel blends generally have improved lubricity; however, their higher viscosity levels tend to form

larger droplets on injection which, can cause poor combustion and increased exhaust smoke. Moreover, this high viscosity generates operational problems like difficulty in engine starting, unreliable ignition and deterioration in thermal efficiency. Converting to biodiesel is one of the options to reduce the viscosity of vegetable oils [57]. The viscosity of fatty acid methyl esters can go to very high levels and hence it is important to control it within an acceptable level to avoid negative impacts on fuel injector system performance. Therefore, biodiesel viscosity must be nearly same to that of the diesel fuel [58].

2.9.3. Acid number and Free Fatty Acid value

Acid number is a measure of acids in the fuel. These acids emanate from two sources: acids utilized in the production of the biodiesel that are not completely removed in the production process; and degradation by oxidation [58]. This is the quantity of base required to titrate a sample to a specified end point. It is a measure of free fatty acid in biodiesel. Excessive free fatty acid in the fuel can be corrosive and may be a symptom of water in the fuel or poor production or subjected to oxidative degradation. Excessive free fatty acid in the fuel can inhibit the transesterification process and lead to soap formation [59].

For biodiesel blends the acid number will change as a result of the normal oxidation process over time. Biodiesel fuel blends that will not be utilized immediately should be monitored for changes in acid number as an indicator of fuel degradation. A high acid value will damage fuel pumps and fuel filters [58].

2.9.4. Sulfated Ash and Phosphorus content

This is the alkaline catalyst residue remaining after a fuel sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to a constant weight. It is a measure of the mineral ash residue when a fuel is burned. It is an important test for biodiesel because it is an indicator of the quantity of residue metals in the fuel that came from the catalyst used in the transesterification process. Especially for base catalyzed transesterification in which the sodium hydroxide and potassium hydroxide commonly used have low melting points and may cause engine damage in combustion chamber, injector deposits or fuel system fouling. The sulfated ashes for FAME are 0.010 % (mol/mol) and lower than the 0.05 ASTM maximum limit. Phosphorus in biodiesel originates from phospholipids (animal and vegetable material) and inorganic salts contained in the feedstock. Phosphorus as adverse effect on long term activity of

exhausts emission catalytic systems and therefore limited by specification. The value for the oil is less than the maximum of 10 mg/kg specified by EN standard [59].

2.9.5. Iodine number

Iodine number is a measure of total unsaturation within a mixture of fatty material. Its value only depends on the origin of the vegetable oil; the biodiesel obtained from the same oil should have similar iodine values [56]. It is related to the chemical structure of the fuel. Higher iodine value indicates higher unsaturation in fats and oils. Standard iodine value for biodiesel is 120 for Europe's EN 14214 specification. This requirement is limited by the standard limits of linolenic acid methyl ester composition for biodiesel. The limitation of unsaturated fatty acids is necessary due to the fact that heating higher unsaturated fatty acids results in polymerization of glycerides. This can lead to the formation of deposits or deterioration of the lubricating property. Fuels with this characteristic are also likely to produce thick sludges in the sump of the engine, when fuel seeps down the sides of the cylinder into the crank [58].

2.9.6. The Cetane number

The cetane number of a fuel is a measure of the ignition quality of the fuel, the higher the cetane number the better the ignition quality, which is conceptually similar to the octane number used for gasoline. Generally, a compound that has a high-octane number tends to have a low cetane number and vice versa. The cetane number measures how easily ignition occurs and the smoothness of combustion. Higher is the cetane number better it is in its ignition properties. Cetane number affects a number of engine performance parameters like combustion, stability, drivability, white smoke, noise an emission of CO and hydrocarbons [58]. On the basis of ignition quality, biodiesel can be said to be better than the petroleum diesel because they have cetane numbers higher than that of the petroleum diesel, this high cetane number is due to higher oxygen contents. This means that they will burn smoothly and with less noise in a diesel engine than petroleum diesel [57].

2.9.7. Lubricity and Cold flow

Biodiesel's have higher lubricity than the petroleum diesel which means that an engine run on biodiesel will be less prone to wear and will last longer. However, the major property of biodiesel, which hampers its use as a neat fuel (B100), is the cold flow property otherwise known

as the low temperature flow property. Biodiesel's have been reported to have relatively high cloud and pour point. The cloud point is the temperature at which is the fuel starts to form crystals, with further decrease in temperature these crystals increase in size and quantity until the fuel gels and does not move again. The cloud point is of more importance because it indicates the onset of filterability problems of the fuel in the fuel filter equipment [57].

2.9.8. Cloud point and Pour point

The two most important criteria are the cloud and pour points. The cloud point is the temperature at which is the fuel starts to form crystals, with further decrease in temperature these crystals increase in size and quantity until the fuel gels and does not move again. The pour point is the lowest temperature at which the oil specimen will flow. Both parameters are often used to specify cold temperature usability of fuel oils. The cloud and pour points are related to the cold start of the motor. Biodiesel's have been reported to have relatively high cloud and pour point. Both points must be sufficiently low, because if the biodiesel is frozen, the motor will not start [58].

The cloud point for Diesel is $4^{o}C$ which is very low and the fuel performs satisfactorily even in cold climatic conditions. The higher cloud point can affect the engine performance and emission adversely under cold climatic conditions. The pour point for Diesel is - 4 ^{o}C. In general, higher pour point often limits their use as fuels for Diesel engines in cold climatic conditions. When the ambient temperature is below the pour point of the oil, wax precipitates in the vegetable oils and they lose their flow characteristics, wax can block the filters and fuel supply line. Under these conditions fuel cannot be pumped through the injector [60].

2.9.9. Flash point

Flash point of a fuel indicates the minimum temperature at which the fuel will ignite (flash) on application of an ignition source under specified conditions. Flash point varies inversely with the fuel's volatility. Flash point minimum temperatures are required for proper safety and handling of fuels. It is noted that the biodiesel component must meet a flash point criteria, prior to blending, for the purpose of assuring that the biodiesel component does not contain methanol. The flash point of biodiesel is higher than the petro diesel, which is safe for transport purpose. High values of flash point decrease the risk of fire [58].

Biodiesel's have higher flash and fire points than the petroleum diesel meaning that they are less flammable hence they are safer to handle. However, biodiesel has worse oxidation stability than petroleum diesel and will deteriorate under prolonged storage due to oxidation in the presence of air [57].

3. Materials and Methods

In this Chapter, the materials and methods used for oil extraction, biodiesel production and characterization of the oil and biodiesel were described. Laboratory work was undertaken in Addis Ababa Institute of Technology School of Chemical and Bio Engineering Laboratory.

3.1. Oil extraction and characterization

3.1.1. Materials

The *Moringa stenopetala* kernel process was purchased from Malalia Moringa products PLC. Addis Ababa and Neem (Margosa) was collected from Hawzen, Tigray. All the chemicals were analytical grade and obtained from Chemical Engineering Laboratory and Neway PLC. Addis Ababa.

Equipments

- ✓ Oven (GALLENKAMP DAS 42000): - to dry the sample.
- ✓ Cross beater mill: - to crush the dried sample
- ✓ Balances (ADAM, PW 124): - to weigh samples.
- ✓ Measuring cylinder: - to measure volume
- ✓ Beaker: - to hold samples
- ✓ Water bath (model no. HWs-26):- to heat the samples
- ✓ Clamps, Thimble, Burette
- ✓ Soxhlet unit:- extraction going on
- ✓ Condenser
- ✓ 250,500,1000 ml round bottom flask
- ✓ 25 ml Pycnometer: - to measure specific gravity
- ✓ Vibro-viscometer (SV 10): - to measure viscosity
- ✓ Furnace (NR 72158):- to measure ash content

Chemicals

Table 3. 1: Chemicals used for oil extraction and characterization

Methods	**Chemicals**
Oil extraction	Hexane (98% India)
Acid value test	Potassium hydroxide, ethanol alcohol, phenolphthalein and distilled water.
Saponification value test	Potassium hydroxide, hydrochloric acid, ethanol alcohol, phenolphthalein and distilled water
Oil degumming and neutralization	Phosphoric acid and sodium hydroxide, salt

3.1.2. Methods

3.1.2.1. Raw Material Preparation

The Neem (Margosa) seeds and moringa stanopetala seeds undergo various processing in the course of its preparation for extraction. The unit operations involved was

- Clearing: The seeds of Neem and Moringa had some foreign materials and dirt which was separated by hand picking.
- Drying: The cleaned seeds of both plants were sun dried in the open, until the casing splits and sheds the seeds. The seeds were further dried in the oven at 60°C for 8 hrs. to a constant weight in order to reduce its moisture content.
- Winnowing: The separation of the shell from the nibs (cotyledon) of both plants was carried out using tray to blow away the cover in order to achieve very high yield.
- Grinding: Cross beater mill were used to crush the seeds of both plants to obtain a size of 1-2 mm sieve size, in order to weaken or rupture the cell walls to release fat for extraction and to increase surface area for better extraction.

3.1.2.2. Determination of Moisture Content of the seeds

300g of the cleaned samples from each plant was weighed and dried in an oven at 105 °C for 12 hrs. and the weight was taken after every 2hrs. The procedure was repeated until a constant weight was obtained. After each 2 hour, the samples were removed from the oven and placed in

the desiccator for 30 minutes to cool. It was then removed and re-weighed. The percentage moisture in the seed was calculated from the formula [61]:

$$\% \text{ Moisture Content} = \frac{w_1 - w_2}{w_1} \times 100 \qquad 3.1$$

Where: W_1 = Original weight of the sample before drying; W_2 = Weight of the sample after drying

3.1.2.3. Soxhlet Extraction of Moringa and Neem seed oil

Soxhlet Extraction using solvent has several advantages. It gives higher yield and less turbid oil than mechanical extraction, and relative low operating cost compared with supercritical fluid extraction [35]. 270 ml of normal hexane was poured into round bottom flask. 30g of the sample from each plant species was placed in the thimble and was inserted in the center of the extractor. The Soxhlet was heated to 70 ^{o}C. This was allowed to continue for five hours. The experiment for each plant species was repeated by placing the same amount of sample into the thimble again and again (Fig. 3.1). The weight of oil extracted was determined for each run. At the end of the extraction, the resulting mixture (miscella) containing the oil was heated to recover hexane from the oil.

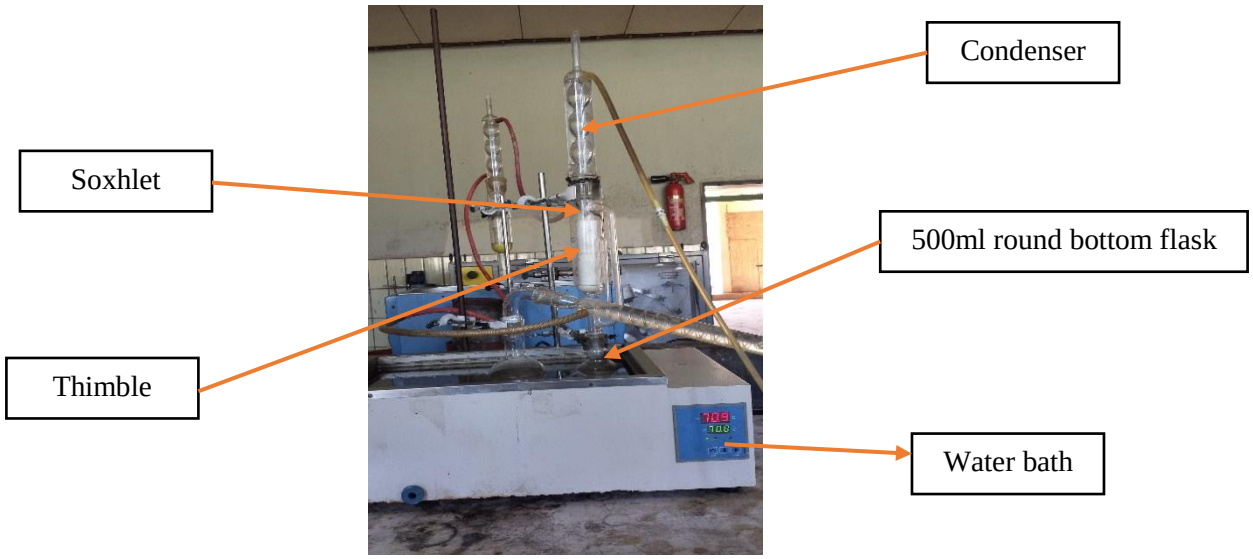


Figure 3. 1: Laboratory setup of soxhlet extraction unit

3.1.2.4. Extraction Yield

The cake was weighed and dried in the oven at 100 ^{o}C until the constant weight (W_2) is attained and the percentage of oil extracted was determined as:

$$\% \text{ yield} = \frac{W_1 - W_2}{W_1} \times 100\% \qquad 3.2$$

Where: W_1 =Sample weight initially placed in the thimble and W_2 = sample weight after dried in the oven.

3.1.2.5. Extracted oil refining

For refining the oil settling, degumming and neutralization methods were applied [61].

1. Settling: It was crude oil separating from impurities by using a centrifuge at a speed of 800 rpm for 20 minutes.

2. Degumming: It was used to remove phosphorus compounds of crude oil using a phosphoric acid and a hot water. Distilled water 3% (v/v) of oil at 70 ^{o} C and 1.5% phosphoric acid (v/v) of oil were mixed with the oil which was heated at 70 ^{o}C. The mixtures were stirred at speed of 200 rpm for 1 hour at a temperature of 70 ^{o}C.

3.1.2.6. Determination of specific gravity

Density is a key fuel property, which directly affects the engine performance characteristic. It affects the mass of fuel injected into the combustion chamber and thus, the air-fuel ratio. In order to determine density of the oil, Density bottle (pycnometer) was used. A clean and dry bottle with stopper of 25ml capacity was weighed (W_0) and then filled with the oil, stopper inserted and reweighed to give (W_1). The oil was substituted with water after washing and drying the bottle and weighed to give (W_2). The expression for specific gravity (Sp.gr) was [61]:

$$\text{Sp.gr} = \frac{W_1 - W_0}{W_2 - W_0} = \frac{\text{Mass of the substance}}{\text{Mass of an equal volume of water}} \qquad 3.3$$

3.1.2.7. Determination of Viscosity

Viscosity is a measure of internal friction. It is an essential property which affects atomization of fuel and mixing of air and fuel in the combustion chamber. A digitalized Vibro-viscometer was employed to determine the viscosity of Neem and Moringa seed oil. The sample from each plant was kept in the bath for 30 minutes to reach the required temperature. The reading was recorded

for a fixed volume of liquid. Since the reading of the Vibro-viscometer was dynamic viscosity the value had to be corrected to find the kinematic viscosity using the following equation [62]:

$$\upsilon = \frac{\mu}{\rho} \quad \text{.....3.4}$$

Where: **μ** = dynamic viscosity of the oil, $^{mm^2}/_{s}$

ρ = density of the oil**,** $^{kg}/_{m^3}$

υ = kinematic viscosity, mPa.sec

3.1.2.8. Determination of Acid value

Acid value is a measure of free fatty acid in biodiesel. Excessive free fatty acid in the fuel can be corrosive and may be a symptom of water in the fuel, poor production or subjected to oxidative degradation. Excessive free fatty acid in the fuel can inhibit the transesterification process and lead to soap formation. For determining acid value, firstly, a titration solution of 0.1N of KOH in distilled water was prepared. Subsequently, from each plant species, 5g of oil was added to the 250ml conical flask and heated at 70 ^{o}C for 3 minutes. Then, 25ml of absolute ethanol (99.5%w/w) and 2-3 drops of phenolphthalein were added into the titration beaker with sample oil. Then oil sample was mixed with 25 ml of absolute ethanol and 2-3 drops of phenolphthalein. Finally, titration solution, 0.1N of KOH was being added 1 drop at a time until the first color change was observed. Once the color change was observed, the titration volume (ml) was recorded and titration was stopped. The titration volume recorded (ml) was used to calculate the acid value [62].

$$\text{Acid value (AV)} = \frac{N \times 0.05611 \times 1000}{W} \quad 3.5$$

Where: N = number of ml (0.1N), W = weight sample in gram

$$\% \text{ free fatty acid} = AV \times 0.503 \quad 3.6$$

3.1.2.9. Determination of Saponification Value

Saponification value indicates the average molecular weight of triglycerides in the oil. The quality of oil decreases as saponification value increases. Indicator method was use as specified by ISO 3657 (1988). From each two plant species, 2g of the sample was weighed into a conical flask; 25ml of 0.1N ethanoic potassium hydroxide of was then added. The content which was constantly stirred was allowed to boil gently for 60min.A reflux condenser was placed on the flask containing the mixture. Few drops of phenolphthalein indicator were added to the warm solution and then titrated with 0.5M HCl to the end point until the pink color of the indicator just disappeared. The same procedure was used for other samples and blank. The expression for saponification value (S.V.) is given by [63]:

$$S.V = \frac{56.1 \times N(V_0 - V_1)}{M} \quad 3.7$$

Where,

$\mathbf{V_0}$ = the volume of the solution used for blank test; $\mathbf{V_1}$ = the volume of the solution used for determination; **N** = Actual normality of the HCl used; **M** = Mass of the sample

3.1.2.10. Ash content of oil

Ash content measures the amount of ash left after a sample is burned. The presence of ash may indicate undesirable impurities or contaminants. As such, it provides one measure of the suitability of a product for a given application. Ash content of oil was determined using a furnace. A 20 g of oil was added in a burning cup. Then, the sample was placed in a furnace. A furnace was located at a temperature of 500 ^{o}C for 1 hour and after burning the residue sample was weighted and ash content was calculated [63].

$$\text{Ash content\% (w/w)} = \frac{\text{Final mass of oil after burning}}{\text{Initial mass of sample}} \times 100\% \quad \text{.....3.8}$$

3.2. Optimize the operating conditions for biodiesel production

The biodiesel produced in this work was prepared using a purified Neem and Moringa Stenopetala seed oil, consecutively, Methanol alcohol (approximately 98 %) and analytical grade sodium hydroxide were used. Among Different reaction parameters, catalyst weight (wt. %) and reaction temperature, were considering while producing the biodiesel. The reaction period, rotation speed, type of catalyst and reaction time was set at optimum point where the maximum conversion could be achieved based on literature data for each plant species

Atmospheric pressure is used for all the runs. The parameters considered were discussed in the following section.

3.2.1. Materials used for biodiesel production

Equipments

- Purified moringa Stanopetala seed oil and Neem seed oil
- Measuring cylinder
- Stirrer
- Water bath
- Overhead stirrer (Type 18 µr)
- 500 ml round bottom flask
- Condenser
- Y tube vessel
- Furnace

Chemicals

- ✓ Methanol
- ✓ Sodium hydroxide
- ✓ Potassium hydroxide

3.2.2. Methods used for biodiesel production

3.2.2.1. Calculation For biodiesel production from *Moringa Stenopetala* seed oil

- ❖ Amount of purified *Moringa stenopetala* seed oil was 30ml in each experiment
- ❖ Oil molecular weight for *moringa stenopetala* seed oil =285gm/mol from Appendix 1
- ❖ Oil weight = oil volume*oil density
  = 30ml*0.92gm/ml = 27.6 gm.
- ❖ Oil mol = oil weight/oil molecular weight = 27.6/285 = 0.097mol

Thus, theoretically for 3:1 alcohol to oil molar ratio was calculated based on assuming 100%conversion of oil to FAME. Here amount of alcohol required was calculated based on/or by using mole-mole Stoichiometric relationship.

Catalyst

1Trayglyceride +3 Alcohols ⇌ 1Glceride + 3FAME……3.9

3alcohol=1Tg

6 mol of alcohol = 1 mol of TG

X = 0.097 oil mol

- Alcohol required = 6*oil mol/1 mol of TG = 0.58mol
- Alcohol weight = Alcohol required*molecular weight of alcohol

  = 0.58*32= 18.62gm
- Alcohol volume = alcohol weight/alcohol density

  = 18.62/0.79= <u>23.5ml</u>

Note: Methanol (CH_3OH) density =0.79gm/cm^3

Methanol (CH_3OH) molecular weight = 32gm/mol

3.2.2.2. Calculation For biodiesel production from Neem seed oil

- Amount of volume of Neem seed oil was 30ml in each experiment
- **Oil weight** = oil volume*oil density

  = 30ml*0.88gm/ml = 26.4 gm.
- Oil molecular weight = 244gm/mol from Appendix 1
- Oil mol=oil weight/oil molecular weight=27.6/244 = <u>0.11mol</u>

Thus, theoretically for 3:1 alcohol to oil molar ratio was calculated based on assuming 100%conversion of oil to FAME. Here amount of alcohol required was calculated based on/or by using mole-mole Stoichiometric relationship.

Catalyst

1Trayglyceride +3 Alcohols ⇌ 1Glceride + 3FAME

3alcohol=1Tg

6 mol of alcohol = 1 mol of TG

X = 0.11 oil mol

- Alcohol required= 6*oil mol/1 mol of TG = 0.66mol
- Alcohol weight = Alcohol required*molecular weight of alcohol

  = 0.66*32 = 21.12 gm.
- Alcohol volume = alcohol weight/alcohol density

  = 21.12/0.79 = <u>26.7ml</u>

Note: Methanol (CH3OH) density =0.79gm/cm^3

Methanol (CH3OH) molecular weight = 32gm/mol

3.2.2.3. Experimental Design for biodiesel production from MSO and NSO

Data analysis for this study was carried out by DESIGN EXPERT 7.0.0 (Full factorial design expert) trial software to evaluate the effects of the process variables. A three-level 2-factor with three replications was applied for carrying out the optimization studies to maximize the yield of FAME in the transesterification process respectively. Reaction temperature (55^{o}C, 60^{o}C and 65^{o}C), catalyst concentration (0.5%, 1% and 1.5 %) % weight of the oil were the two variables selected for optimization. The reaction time, mixing intensity, type of catalyst and oil to methanol ratio were fixed at 1 hours, 600 rpm, NaOH (sodium hydroxide) and 6:1 respectively for all experimental runs according to the previous work reported by Aransiola et.al. [37]. A total of 27experiments were conducted separately for each raw material (*Moringa Stanopetala* and Neem seed oil) for biodiesel production and the data was statistically analyzed by the Design Expert 7.0.0 software and to get suitable model for the percentage of fatty acid methyl ester as a function of the independent variables.

Table 3. 2: Experimental design matrix

Variables	**Unit**	**Levels**		
		-1	0	1
Catalyst concentration	% (w/w)	0.5	1	1.5
Reaction temperature	^{o}C	55	60	65

3.2.2.4. Two step acid-base Transesterification reaction of seed oil

Crude neem and moringa stenopetala seed oils were FFA > 2% when transesterified using NaOH catalyst. Therefore, a two - step process acid catalyzed esterification followed by alkali catalyzed transesterification was employed according to the method of Berchmans and Hirata [74].

Acid pretreatment (acid catalyzed esterification)

The crude oil of each plant species were weighed, heated at 60°C for about 10 min and mixed with 55.8 ml of methanol (60%w/w of oil). To the mixture was added 1.2%w/w of concentrated

H_2SO_4. The resulting mixture was then stirred on magnetic hot plate for 1 h at 50°C, after which it was allowed to settle for 2 h. The pre-treated oils were separated from the methanol - water phase at the top.

Neutralization: 0.05 N of NaOH solutions was added to the esterified oil and heated to 70 ^{o}C with constant stirring at 800 rpm using a 500ml flask vessel for 20 minutes in order to neutralize and remove impurities. Sodium chloride (about 6% of the weight of the oil) was added to the heated oil to facilitate the settling of the soap formed during the neutralization process. Hot water (about 90 ^{o}C) was added to the neutralized oil slowly again and again.

Base catalyzed transesterification

The transesterification of pretreated seed oil was carried out with 6:1 molar ratio of methanol to oil for period of 1h at 55, 60and 65℃ respectively. A 0.5,1 and 1.5% by weight of the seed oil was used as the catalyst. [65]. A fresh solution of methanol and sodium hydroxide was prepared to maximize catalyst usage. The batch was set up by charging and preheating the oil in the reactor, and an established amount of the catalyst-methanol solution was then added and the reaction was timed (Fig. 3.2). At the end of the reaction the mixture was allowed to cool to room temperature without agitation and settle to two phase separation under gravity after 24 h. The upper phase of the mixture was (FAME) i.e. the biodiesel while the lower phase consists of glycerol, excess methanol, the catalyst, soap formed during the reaction, some entrained FAME and traces of glycerides. The two phases where separated by decantation. The FAME was purified by gently washing with distilled water until a desired purity was achieved. The final products were used to determine fuel related properties and biodiesel yield.

$$\text{Biodiesel yield} = \frac{\text{mass of biodiesel}}{\text{mass of raw seed oil}} \times 100\ \% \qquad 3.10$$

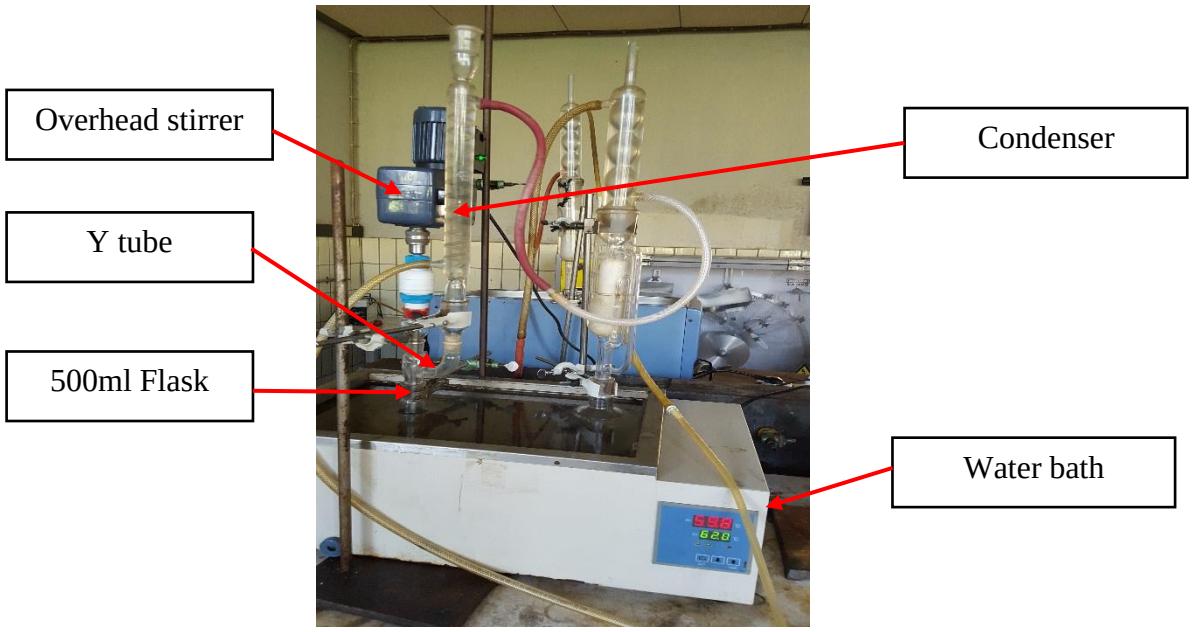


Figure 3. 2: Experimental set-up of transesterification reaction

3.3. Characterization and Comparison of MSOME and NOME

3.3.1. Characterization of biodiesel produced

The characterization of MSOME and NOME involves determination of specific gravity, viscosity, acid value, saponification value; ash content was done in school of Chemical and Bio Engineering Laboratory whereas iodine value and cetane number were done by mathematical relations.

3.3.1.1. Specific gravity

The procedure described in section 3.1.2.6 was used to determine the specific gravity of biodiesel.

3.3.1.2. Kinematic viscosity

The procedure described in section 3.1.2.7 was used to determine the kinematic viscosity of biodiesel.

3.3.1.3. Acid Value, ASTM D 664 and free fatty acid value

The procedure described in section 3.1.2.9 was used to determine the acid value and FFA value of biodiesel.

3.3.1.4. Flash point, ASTM D 93

The flash point of the biodiesel was determined using open cup method for each plant species. The cup was filled with the biodiesel (about 75 ml) and the cup was heated by a Bunsen burner. A hand thermometer was inserted into the cup to read the temperature. A small open flame was maintained from an external supply of candle. Periodically, the flame was passed over the surface of the oil. When the flash temperature was reached the surface of the oil catch the flame. Therefore the temperature at which the surface of the oil catches the flame was noted and reported as flash point temperature.

3.3.1.5. Ash content

The procedure described in section 3.1.2.11 was used to determine the Ash content of biodiesel.

3.3.1.6. Higher heating value (HHV)

The heating value of the MSOME and NOME was calculated using the model developed by Demirbas [6]:

$$HHV = 49.43 - (0.015IV) - (0.041SV) \quad 3.11$$

The equations between viscosity and higher heating values are

$$HHV = 0.4625\,\nu + 39.450 \quad 3.12$$

Rearranging equation 3.9 to calculate IV

$$IV = \frac{49.3 - HHV + 0.041SV}{0.015} \quad 3.13$$

Where: IV is the iodine value; SV is the saponification value and ν is viscosity

3.3.1.7. Cetane Number ASTM D613

CN was determined using correlation reported by Patel [66]:

$$CN = CI - 1.5 \quad 3.14$$

Where: CI is the Cetane Index determined by the correlation of Krisnangkura [67]:

$$CI = 46.3 + \frac{54.58}{SV} - 0.225IV \quad 3.15$$

4. Result and Discussion

4.1. Extraction and characterization of Moringa and Neem seed oil

4.1.1. Moisture content determination

The moisture content of the Moringa stenopetala and Neem seed kernel was triplicated and the results were summarized in Table 4.1 and Table 4.2 respectively based on equation 3.1.

Table 4. 1: Moisture content of *Moringa stenopetala* and Neem kernel

N0.	**Extract**	**Moisture content (%w/w)**
1	Moringa stenopetala kernel	5.57
2	Neem kernel	6.7

Moisture content of moringa stenopetala and neem seed were 5.7% and 6.7 % respectively. These results were in agreement with the result reported, 5% of moringa seed by Andinet Ejigu [13] and 6.71% of neem seed by Wondesen W. [37] .Water caused soap formation, which consumed the catalyst and reduced catalyst efficiency. The resulting soaps caused an increase in viscosity, formation of gels and made the separation of glycerol difficult and therefore, water content should be less than 0.3% [48, 49].

4.1.2. Extraction yield of *Moringa stenopetala* and Neem seed

The yield of MSSO (*Moringa stenopetala* seed oil) was found to be 43.3% whereas the yield of NSO (Neem seed oil) was found 48.8%. These results fall within the range of the percentage oil content (30-60%) reported by Azam et al. [68], and Sneha et.al.[69] and in agreement with result reported,44.9 % (MSSO) by Andinet Ejigu [13]. The results indicate that all the sample seed contains appreciable quantity of oil enough to be extracted for commercial scale production of biodiesel.

4.1.3. Characterization of *Moringa Stenopetala* and Neem seed oils

The physicochemical properties of the Moringa seed oil and Neem seed oil were characterized and the obtained values for the free fatty acid level of the oils were presented in Table4.3.

Table 4.2: Physicochemical properties of Moringa and Neem seed oil

Properties	**Moringa seed oil**	**Neem seed oil**	**Unit**
Specific gravity	0.89	0.92	
Kinematic Viscosity @40 ^{o}C	10.5	35.83	mm^2/s (cst)
Acid value	4.9	17.2	mgKOH/g
Free fatty acid	2.45	8.6	Mg/g
Saponification value	185	198	mgKOH/g
Ash content	6.8	10.20	%

The acid value is a measure of the amount of carboxylic acid groups present per gram of the oil and the higher value significantly affect efficiency of transesterification and consequently result in low yield [70]. The present result shows that the neem seed oil contain high acid value than that of moringa seed; as such both the oils cannot be directly transesterified (Table 4.3). Transesterification can only be achieved when the acid value is 2% or 1% FFA. There is therefore the need to carry out acid esterification of the oil as to reduce high acid value to 2% or less prior to alkaline transesterification, and this could probably lead to optimal biodiesel yield. The quality of oils expressed in terms of the physicochemical properties such as specific gravity, viscosity, pH value, ash content and saponification value (Table 4.3) were in agreement with previous work reported by Zaku.et.al [71] and Aransiola et al. [44]. This signifies that these oils are of good quality for use as feedstock for biodiesel production.

4.2. Biodiesel production

The transesterification was carried out at reflux of methanol, using a 500 ml capacity glass reactor which is equipped with a stirrer, condenser and water bath according to experimental procedure discussed in section 3.2.2. The statistical analysis was discussed below for both Moringa stenopetala and Neem oil methyl esters.

4.2.1. Experimental design

The experimental design selected for this study was Full Factorial Design (FFD) and the response measured is the yield of fatty acid methyl esters (FAME). The two transesterification process categorical variables studied were reaction temperature and weight percentage of catalyst.

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

The actual yield of biodiesel produced at different process parameters was calculated using equation 3.11 and is given in Appendix c. Accordingly, the maximum yield of Moringa seed oil methyl ester and Neem seed oil methyl ester was 93 % at experiment number three and 90% at experiment number eleven respectively. Maximum biodiesel yield was gained at 1 % (w/w) catalyst weight with $60^{O}C$ for MSOME whereas 0.5% (w/w) catalyst weight with 55 ^{O}C temperatures for NSOME. The result for neem seed oil methyl ester was appreciable in agreement with works reported by Deepak T. et.al [76] and the result for moringa oil methyl ester was in agreement with work reported by Andinet ejigu [13].

4.2.2. Statistical Analysis of Moringa seed oil methyl ester

Table 4.3: Analysis of variance for Moringa oil methyl ester

Response 1	**MSOME**					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	4583.28	8	572.91	35.22	< 0.0001	significant
A-Catalyst Weight	1177.31	2	588.65	36.18	< 0.0001	
B-Temperature	2981.61	2	1490.8	91.64	< 0.0001	
AB	424.36	4	106.09	6.52	0.002	
Pure Error	292.84	18	16.27			
Cor Total	4876.12	26				

F-value is a test for comparing model variance with residual (error) variance. If the variances are close to the same, the ratio will be close to one and it is less likely that any of the factors have a significant effect on the response. It is calculated by Model Mean Square divided by Residual Mean Square. From table 4.4 The Model F-value of 35.22 implies the model was 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, AB were significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Table 4.4: Model adequacy measures of MSOME

Std. Dev.	4.03	R-Squared	0.9399
Mean	69.92	Adj R-Squared	0.9133
C.V. %	5.77	Pred R-Squared	0.8649
Press	658.89	Adeq Precision	18.373

According to data generated in table 4.5 The "Pred R-Squared" of 0.8649 is in reasonable agreement with the "Adj R-Squared" of 0.9133."Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable.The ratio of 18.373 indicates an adequate signal.This model can be used to navigate the design space.

The model quality can be evaluated from its coefficients of correlation (R^2). The value of R-squared for the developed correlation is 0.9399. It implies that 93.99% of the total variation in the yield of MSOME is attributed to the experimental variables studied. The graph of the predicted values (obtained using the developed correlation) versus actual response values is shown in Figure 4.1.

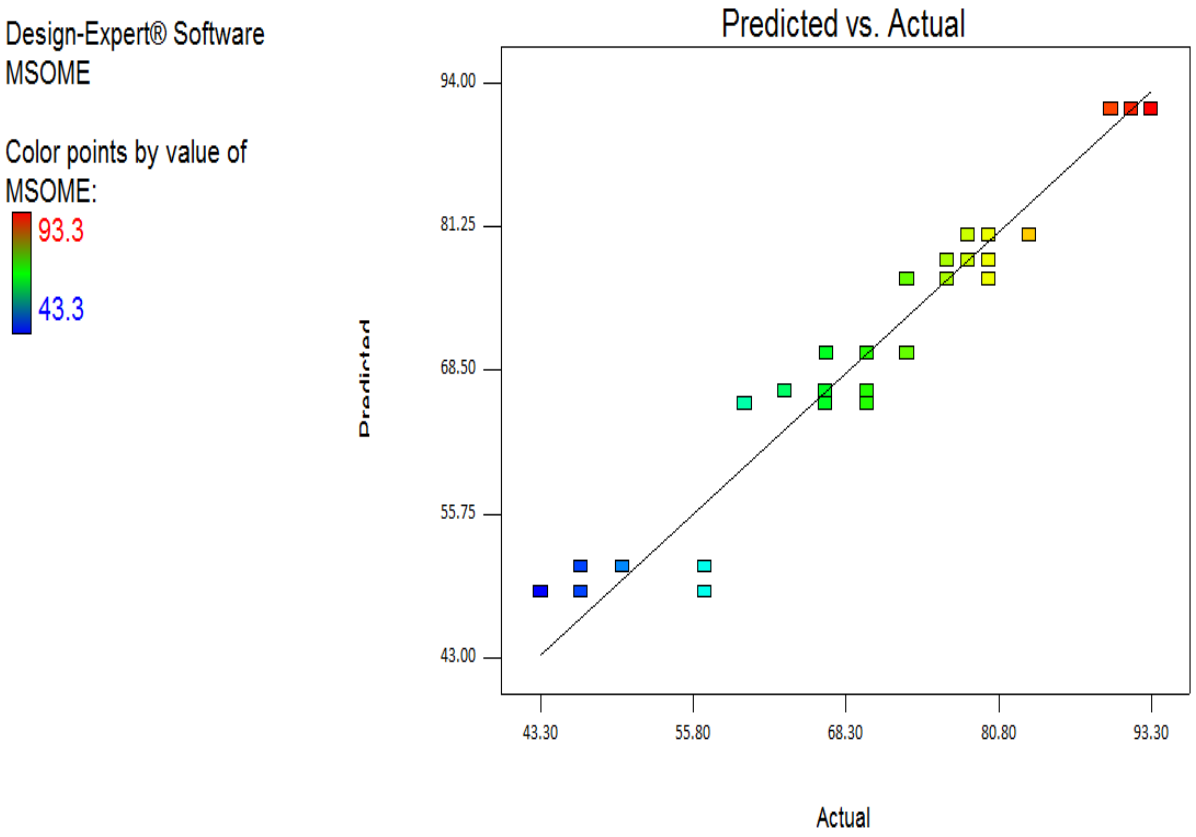


Figure 4. 1: The graph of the predicted values versus actual response value of MSOME

A graph of the predicted response values versus the actual response values helps us to detect a value, or group of values, that are not easily predicted by the model. The data points should be split evenly by the 45 degree line. If they are not, it is necessary to try a transformation to improve the fit. But in the case of this experimental result it is not necessary to try transformation since it is adequately checked by 45 degree line(y = x graph)

Table 4.5: Regression coefficients and the corresponding 95% CI High and Low

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High
Intercept	69.92	1	0.78	68.29	71.55
A[1]	-5.13	1	1.1	-7.43	-2.82
A[2]	9.32	1	1.1	7.02	11.63
B[1]	5.81	1	1.1	3.5	8.11
B[2]	8.95	1	1.1	6.64	11.25
A[1]B[1]	6.04	1	1.55	2.78	9.3
A[2]B[1]	-4.51	1	1.55	-7.77	-1.25
A[1]B[2]	-7.1	1	1.55	-10.36	-3.84
A[2]B[2]	3.47	1	1.55	0.21	6.73

Final Equation in Terms of Coded Factors:

Yield of MSOME (%) = +69.92 - 5.13* A[1] + 9.32 * A[2] + 5.81 * B[1] + 8.95 * B[2] + 6.04 * A[1]B[1] - 4.51* A[2]B[1] - 7.10 * A[1]B[2] + 3.47 * A[2]B[2]

Where A = Catalyst Weight (%w/w)

B = Reaction temperature (^{O}C)

4.2.3. Statistical Analysis of Neem seed oil methyl ester

Table 4.6: Analysis of variance for Neem seed oil methyl ester

Response 2	NSOME					
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	5190.45	8	648.81	17.12	< 0.0001	significant
A-Catalyst Weight	891.83	2	445.92	11.76	0.0005	
B-Temperature	3471.19	2	1735.59	45.79	< 0.0001	
AB	827.43	4	206.86	5.46	0.0047	
Pure Error	682.31	18	37.91			
Cor Total	5872.77	26				

The model F-value of 17.12 implies the model is significant.there is only a 0.01% chance that "Model F-Value" this large could occur due to noise.values of "Prob > F" less than 0.050 indicate model terms are significance.

In this case A, B, AB are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Table 4.7: Model adequacy measures of NSOME

Std. Dev.	6.16	R-squared	0.8838
Mean	62.94	Adj R-squared	0.8322
C.V.%	9.78	Pred R-squared	0.7386
Press	1525.2	Adeq precision	11.872

The "Predicted R-Squared" of 0.7386 is in reasonable agreement with the "Adj R-Squared" of 0.8322."Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 11.872 from table 4.8 indicates an adequate signal. This model can be used to navigate the design space.

The model quality can be evaluated from its coefficients of correlation (R^2). The value of R-squared for the developed correlation is 0.8838. It implies that 88.38% of the total variation in the yield of NSOME is attributed to the experimental variables studied. The graph of the predicted values (obtained using the developed correlation) versus actual response values is shown in Figure 4.2.

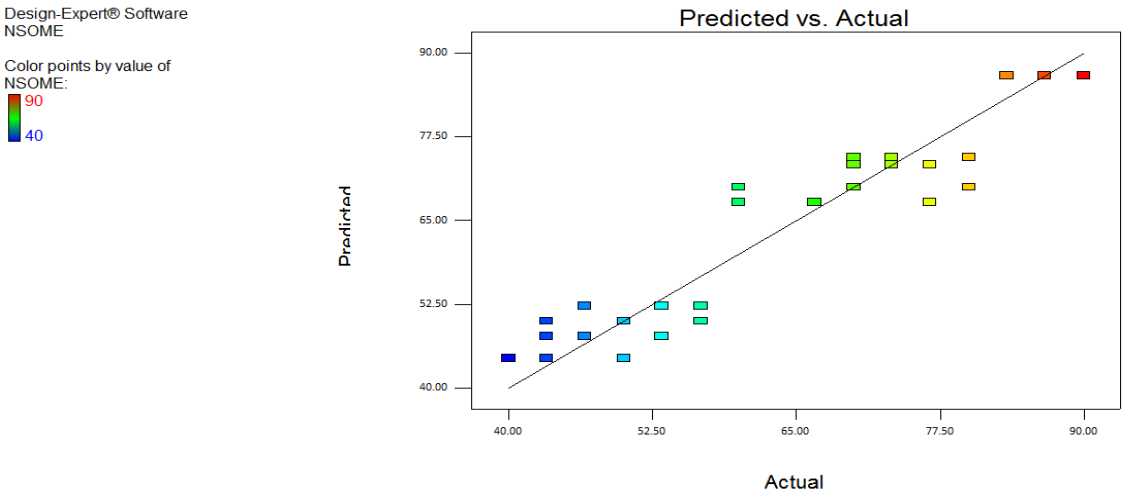


Figure 4. 2: The graph of the predicted values versus actual response value of NSOME

The results in Figure 4.2 demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit and splits evenly by the 45 degree line. This result indicates that it was successful in capturing the correlation between the two transesterification process variables to the yield of NSOME.

Table 4. 8: Regression coefficients and the corresponding 95% CI High and Low

Term	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High
Intercept	62.94	1	1.18	60.45	65.43
A[1]	-7.79	1	1.68	-11.31	-4.26
A[2]	5.91	1	1.68	2.39	9.44
B[1]	13.7	1	1.68	10.18	17.22
B[2]	0.36	1	1.68	-3.16	3.88
A[1]B[1]	4.44	1	2.37	-0.54	9.42
A[2]B[1]	4.07	1	2.37	-0.9	9.05
A[1]B[2]	-7.78	1	2.37	-12.76	-2.8
A[2]B[2]	-1.48	1	2.37	-6.46	3.5

Final Equation in Terms of Coded Factors:

Yild of NSOME = +62.94 - 7.79 * A[1] + 5.91 * A[2] +13.70 * B[1] +0.36 * B[2] +4.44 * A[1]B[1] + 4.07 * A[2]B[1] -7.78 * A[1]B[2] - 1.48 * A[2]B[2]

4.2.4. Effect of Process Parameters for MSOME and NSOME

The statistical analysis of DOE software indicated that the FAME yield of alkali catalyzed transesterfication reaction was significantly affected by the individual process variables and by their interaction for both MSOME and NSOME. The individual process variables that significantly affected biodiesel yield was catalyst weight (A), reaction temperature (B), and the interaction effect between catalysts with temperature (AB). This detailed parameter effect analysis result shows that DOE software is a best tool in examining the experimental findings. The individual and interaction effects of the variables were well discussed below:

4.2.4.1. Effect of temperature on MSOME and NSOME yield

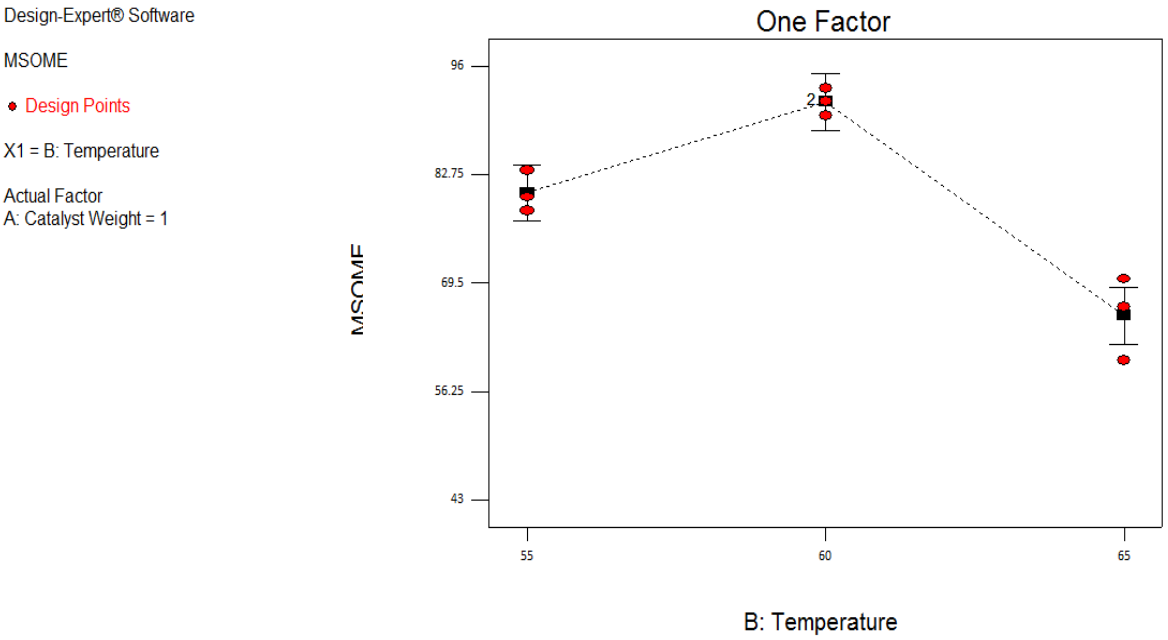


Figure 4. 3: The effect of temperature on MSOME yield

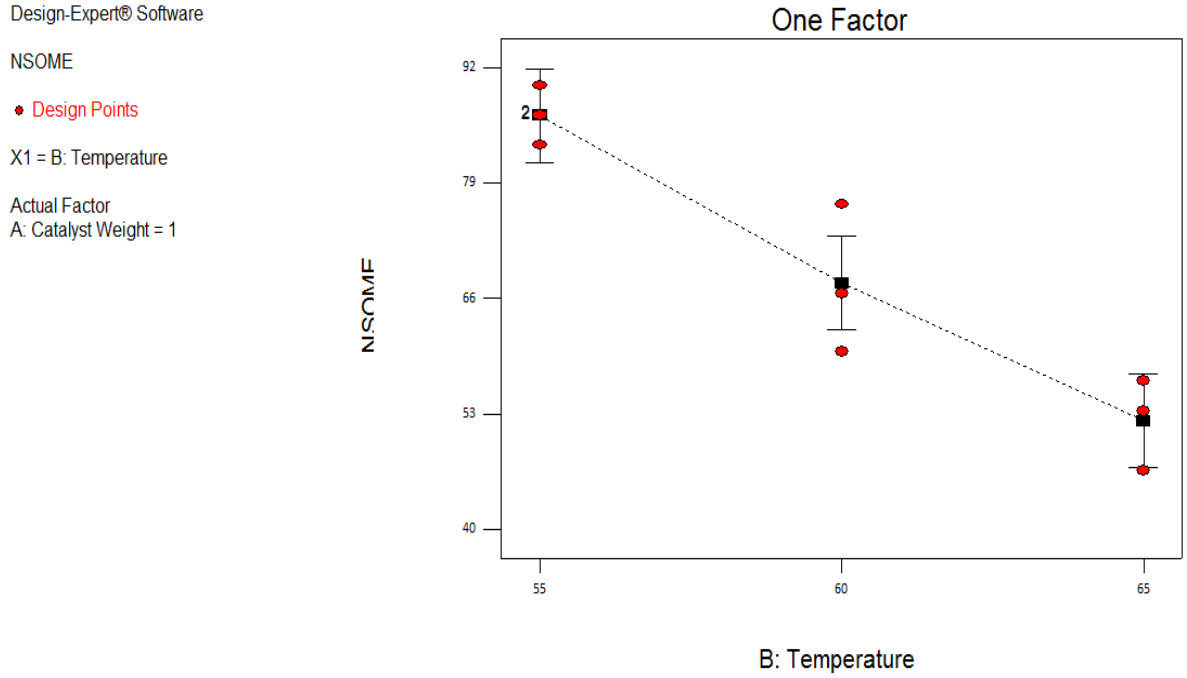


Figure 4. 4: The effect of temperature on NSOME yield

The reaction temperature has important role in base catalyzed transesterification .At room temperature no significant yield is notified for even 2hr reaction. The yield is increased with increase in reaction temperature. The effect of temperature variation on conversion efficiency is shown in Fig.4.3 and Fig.4.4 for MSOME and NSOME respectively. By varying temperature in three different levels such as 55, 60 and 65 ^{o}C among these 60 °C gave maximum methyl ester yield for biodiesel production from *Moringa stenopetala* seed oil and 55 ^{o}C gave maximum yield for biodiesel production from Neem seed oil.

Generally the transesterification reaction was diffusion controlled reaction. At lower temperature the viscosity of the fleshing oil is higher. So it's difficult for the methanol and the catalyst easily to come to the reaction site and react. But at optimum temperature the viscosity will be very low and the reactants will be easily contacted to give a better yield with the help of better mixing and reaction time rate.

4.2.4.2. Effect of catalyst weight ratio on MSOME and NSOME yield

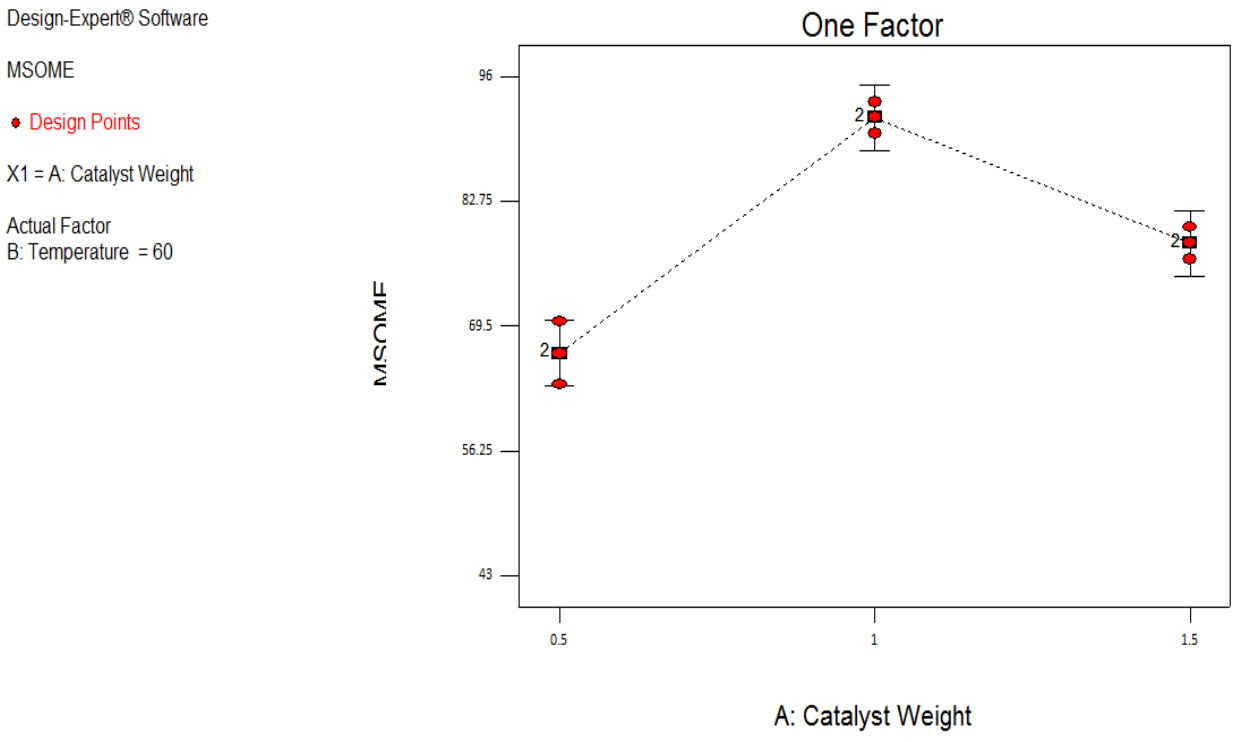


Figure 4. 5: The effect of catalyst weight ratio on MSOME yield

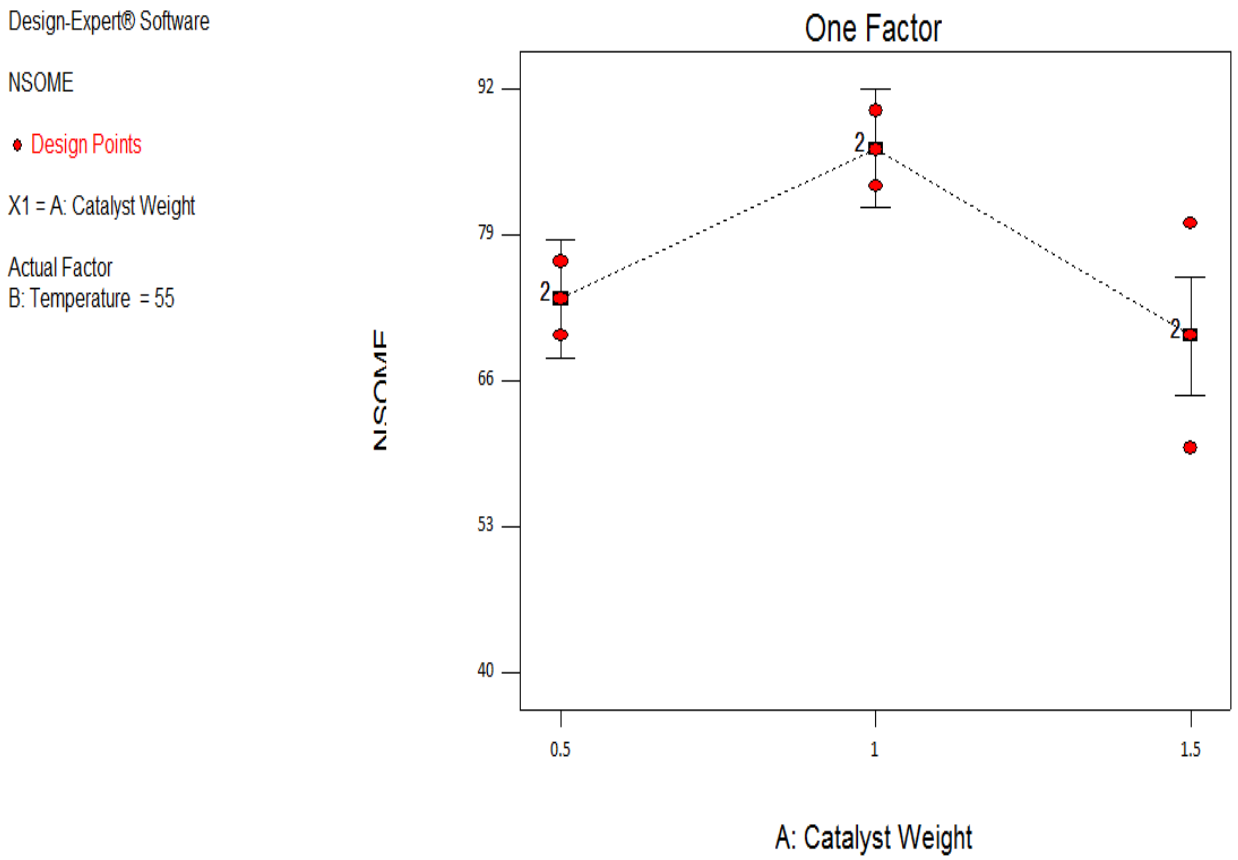
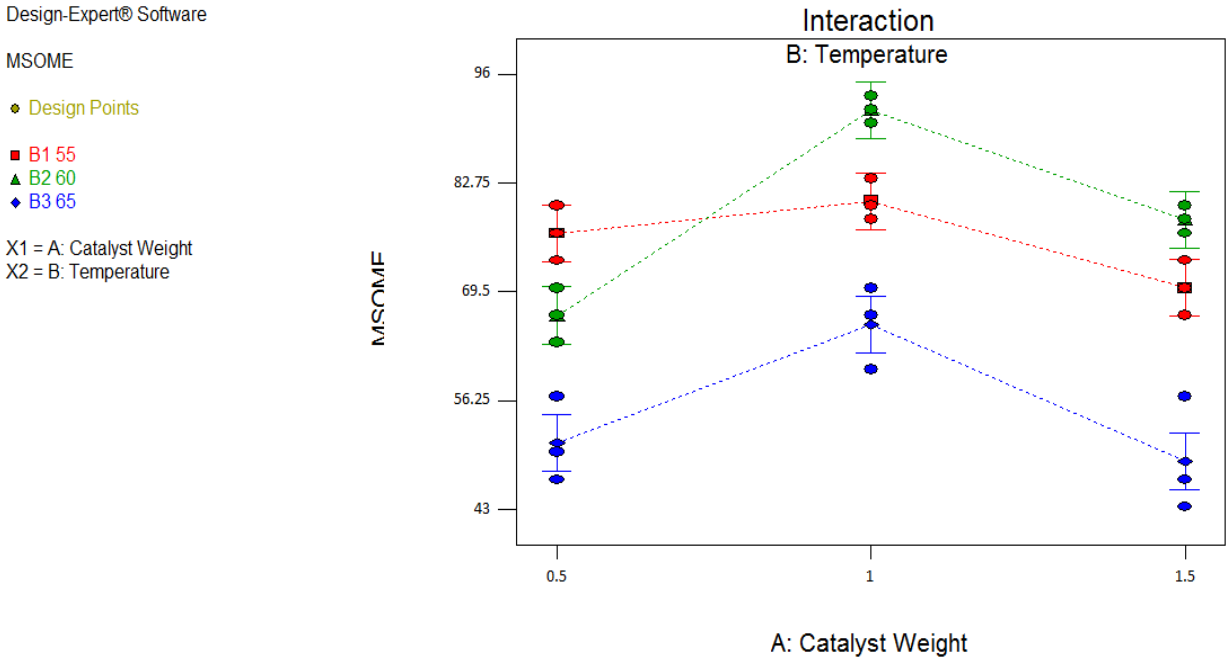


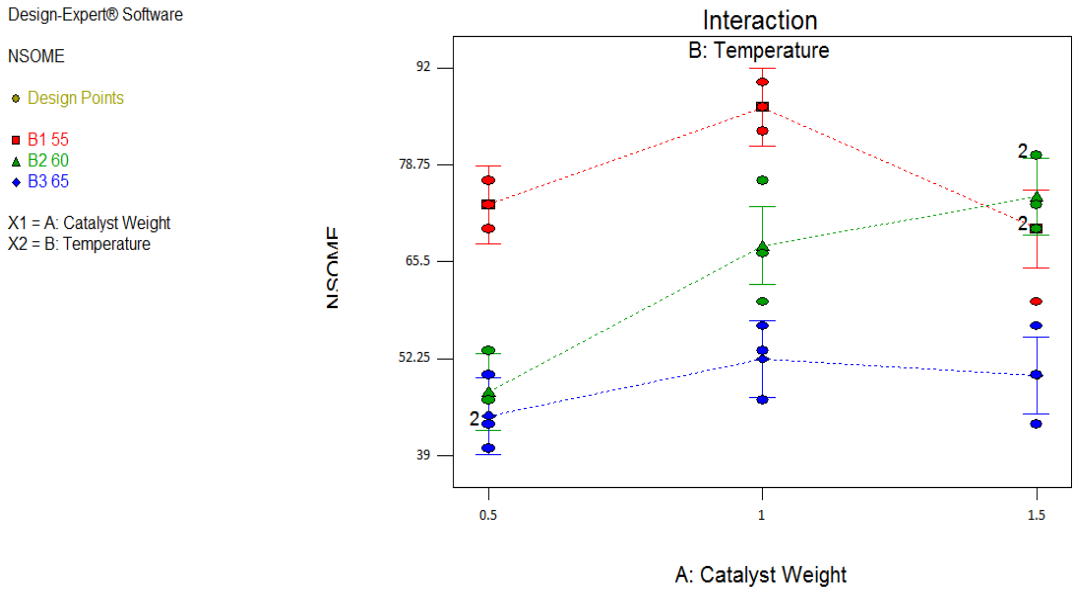
Figure 4. 6: The effect of catalyst weight ratio on NSOME yield

Catalysts, by their nature, facilitate the chemical reaction towards completion. But since the catalysts do not consumed by the chemical reaction their amount has to be optimized for the cost they incurred and for the reactor space they will occupy. In this regard fig. 4.5 and fig. 4.6 shows that the biodiesel yield very much enhanced as the catalyst ratio increases from 0.5% to 1% for both MSOME and NSOME. This is because that at optimum catalyst concentration, the reactants will have a better chance to the catalyst active site where they can easily reacted and converted to fatty acid methyl ester.

4.2.4.3. Effect of Interaction of Process Variables on MSOME and NSOME Yield



a.MSOME



b.NSOME

Figure 4. 7: The interaction effect of catalyst weight and temperature a. MSOME yield

b. NSOME yield

The categorical process variables were found to have significant interaction effects. Figure 4.7 (a) and (b), shows the interaction between catalyst weight and reaction temperature, of MSOME and NSOME respectively, on the yield of biodiesel yield. Generally, an increase in reaction temperature is found to increase the yield of biodiesel up to some optimal value for MSOME and vice versa for NSOME.

4.2.5. Optimization of transesterification of process variables

The objective here was to obtain maximum yield in the given interval of the investigated independent variables. The individual and interaction effects of process parameters have shown that these parameters had a positive effect at their optimum values on the FAME yield. Using design expert software the maximum yield of Moringa seed oil methyl ester was obtained at combination of the second level of the first factor (1% w/w) and the second level of the second factor 60 ^{o}C which was 91.65% and desirability equal to 0.967. Also the maximum yield of Neem seed oil methyl ester was achieved at the combination of the second level of the first factor (1%w/w) and the first level of the second factor (55 ^{O}C) which was 86.6% and the desirability equal to 0.985 . An experiment were conducted at these suggested values for moringa stenopetala and neem seed oil methyl ester to verify the optimum values and a good approximation of the predicted optimum value was obtained, which is 93 and 90 % FAME yield respectively.

Table 4.10 and Table 4.11 showed that combinations of optimized categorical factor levels that give maximum yield result for both *Moringa stenopetala* and Neem seed oil methyl ester respectively.

Table 4.9: Numerical optimization solution for MSOME

Name	**Goal**	**Lower Limit**	**Upper Limit**	**Lower Weight**	**Upper Weight**	**Importance**
Catalyst Weight	is in range	0.5	1.5	1	1	3
Temperature	is in range	55	65	1	1	3
MSOME	maximize	43.3	93.3	1	1	3

Solutions for 9 combinations of categorical factor levels

Number	Catalyst Weight	Temperature	MSOME	Desirability		
1	1	60	91.6533	0.967	Selected	
2	1	55	80.5333	0.745		
3	1.5	60	78.3	0.7		
4	0.5	55	76.6333	0.667		
5	1.5	55	70	0.534		
6	0.5	60	66.6333	0.467		
7	1	65	65.5333	0.445		
8	0.5	65	51.1	0.156		
9	1.5	65	48.8667	0.111		

Table 4.10: Numerical optimization solution for NSOME

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Catalyst Weight	is in range	0.5	1.5	1	1	3
Temperature	is in range	55	65	1	1	3
NSOME	maximize	40	90	1	1	3
Solutions for 9 combinations of categorical factor levels						
Number	Catalyst Weight	Temperature	NSOME	Desirability		
1	1	55	86.6333	0.933	Selected	
2	1.5	60	74.4333	0.689		
3	0.5	55	73.3	0.666		
4	1.5	55	70	0.6		
5	1	60	67.7333	0.555		
6	1	65	52.2	0.244		
7	1.5	65	50	0.2		
8	0.5	60	47.7333	0.155		
9	0.5	65	44.4333	0.089		

4.2.6. Characterization and Comparison of MSOME and NOME

The physical and chemical properties of the high yield Moringa oil methyl esters (MOME) and Neem oil methyl esters (NOME) which was obtained by Acid base catalyzed transesterification process was characterized by the methods indicated in previous chapter under section 3.3.was Summarized under Table 4.12. These fuel properties were in agreement with works reported by Andinet ejigu[13],Aransiola et al[44] and Zaku.et.al [71].Comparison between those two biodiesel produced, ASTM D6751, EN 14214 standards and diesel are also discussed.

Table 4.11: Fuel properties of MSOME, NSOME, diesel fuel and biodiesel standards

Property	**MSOME**	**NSOME**	**Diesel fuel** [72]	**Biodiesel standards**		**Unit**
				ASTM D-6751 [72]	EN14214 [72]	
Density	0.86	0.89	0.85	--	0.86-0.9	kg/m^3
Kinematic Viscosity @40 ^oC	3.3	5.7	2.60	--	1.9-6.0	mm^2/s (cst)
Acid value	0.128	0.13	--	≤ 0.8	≤ 0.5	mgKOH/g
Free fatty acid	0.064	0.065	--	--	--	Mg/g
Flash point	182	153	78	Min. 120	Min. 130	^oC
Higher heating value (HHV)	40.97	42	44.4	40-42	--	MJ/kg
Ash content	0.013	0.12	--	< 0.02	--	Wt %
Iodine value	71	82	10	--	≤ 120	gI/100gm
Cetane number	56	41	49	≥ 47	> 51	

4.2.6.1. Specific Gravity (Density)

The density of MSOME and NSOME were $860kg/m^3$ and $890kg/m^3$ respectively. The ASTM D6751 for biodiesel indicates that the density of the biodiesel should be in the range of 860kg/m-$900kg/m^3$. Therefore the density of both biodiesel produced were in agreement with ASTM standard. The density MSOME is higher than diesel fuel but it is lower than density of NSOME. According to Clark (1988) [73], low relative density is indicator of good ignition.

4.2.6.2. Kinematic Viscosity

The viscosity is a very crucial property of biodiesel that affects the atomization of a fuel upon injection into the combustion chamber and thereby, ultimately, the formation of engine deposits; the higher the viscosity, the greater the tendency of the fuel to cause such problems.

Viscosity of a fluid is indirectly proportional to the temperature. That means, as the temperature increases the viscosity decreases and vice versa. In agreement with this chemical engineering concept, the experimental result shows that the viscosity of the biodiesel which is

trans esterified at higher temperature are low and that the viscosity of biodiesel that reacted at lower temperature is higher [39].

The EN 14214 standard states that the kinematic viscosity of biodiesel has to be in the range 1.9 – 6 mm^2/s at 40^oC. The kinematic viscosity of the biodiesel obtained from Moringa seed oil methyl ester and Neem seed oil methyl ester was 3.3 and $5.7mm^2/s$, which is acceptable in ASTM standard but these values are lower than viscosity of diesel fuel which is $2.60mm^2/s$.

4.2.6.3. Acid Value (AV) and FFA Composition

The recommended Acid value of biodiesel is ≤ 0.8 and ≤ 0.5 mg KOH/g for ASTM D 6751 and EN 14214 specifications respectively. The acid value determination is an important test to assess the quality of a particular biodiesel. It can indicate the degree of hydrolysis of the fatty acid methyl ester, particularly important aspect when considering storage and transportation as large quantities of free fatty acids can cause corrosion in tanks.

The acid value of the biodiesel produced from Moringa seed oil and Neem seed oil was found to be 0.128mgKOH/g and 0.13mgKOH/g respectively. The results were within the ASTM standard specification, which indicates that this will not pose problem on the long-term performance of the engine [13].

4.2.6.4. Flash point

The flash point temperature is the measure of the fuel to form a flammable mixture with air and it was determined after the sample was preheated to remove residual methanol. For biodiesel, a flash point of below 130°C is considered to be out of specification according to ASTM D6751 standard.

The measured flash point of the produced Moringa stenopetala and Neem seed oil methyl esters were 182 and 153 ^oC, respectively. This high flash point is probably not only due to very low methanol content but more likely due to the presence of methyl esters with C16 and C18 carbon chain lengths which predominate in this biodiesel. The flash points of both esters are far greater than that of the conventional fuel diesel. The flash point of diesel fuel was 78 ^oC.

4.2.6.5. Higher Heating Value, HHV

The heating value is the amount of heat energy released during combustion of biodiesel. The heating value depends on the composition of the biodiesel. Since all the oils have very nearly the

same carbon, hydrogen and oxygen contents the gross and net heating values of each fuel per unit mass will be close to each other. The ASTM standard value of the HHV is between 40-42MJ/kg [39].

The HHV of the produced biodiesel from Moringa seed oil and Neem seed oil was 40.97 MJ/kg and 42 MJ/kg which is in agreement with ASTM standard.

4.2.6.6. Ash content

This is the alkaline catalyst residue remaining after a fuel sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to a constant weight. It is a measure of the mineral ash residue when a fuel is burned. It is an important test for biodiesel because it is an indicator of the quantity of residue metals in the fuel that came from the catalyst used in the transesterification process. Especially for base catalyzed transesterification in which the sodium hydroxide and potassium hydroxide commonly used have low melting points and may cause engine damage in combustion chamber, injector deposits or fuel system fouling. The sulfated ash for FAME is 0.010 % (mol/mol) and lower than the 0.05 ASTM maximum limit [40] **.**

The ash content of Moringa seed oil methyl ester and Neem seed oil methyl ester was 0.013 and 0.12 easily meets the requirements of the ASTM D6751 biodiesel standards, which prescribe a maximum of 0.01%.

4.2.6.7. Iodine value

Iodine number is a measure of total unsaturation within a mixture of fatty material. Its value only depends on the origin of the vegetable oil; the biodiesel obtained from the same oil should have similar iodine values [56]. It is related to the chemical structure of the fuel. Higher iodine value indicates a higher quantity of double bonds in the sample and greater potential to polymerize in engine and hence lesser stability. The Process of transesterification reduces the iodine value to a small extent. Standard iodine value for biodiesel is 120 for Europe's EN 14214 specification.

The iodine value of produced biodiesel was obtained by the empirical equation that correlates HHV and the SV. According to ASTM standard FAMEs used as diesel fuel must have an iodine value of less than 120 gI/100g of sample. The FAME obtained in this study had an average

iodine value of 71 g I_2/100 g for MSOME and 82 g I_2/100 g for NOME. The iodine values were in a very good agreement with ASTM standard.

4.2.6.8. Cetane number

The cetane number of a fuel is a measure of the ignition quality of the fuel, the higher the cetane number the better the ignition quality, which is conceptually similar to the octane number used for gasoline. Generally, a compound that has a high octane number tends to have a low cetane number and vice versa. The cetane number measures how easily ignition occurs and the smoothness of combustion. Higher is the cetane number better it is in its ignition properties. Cetane number affects a number of engine performance parameters like combustion, stability, drivability, white smoke, noise and emissions of CO and hydrocarbons [40].

Fuels with low CN will result in difficult starting, noise and exhaust smoke. In general, diesel engines will operate on fuels with cetane number > 47 (ASTM D613). Cetane number was calculated using empirical formulas [66] which are given in materials and methods part 3.3.1.7, using the results for Saponification number (SN) and Iodine value (IV) of the oil. The calculated average result of the CN was found to be 56 for MSOME and 41 for NSOME which is a very a good agreement with the indicated ASTM standard. The cetane number MSOME is higher than that of NSOME and diesel fuel with the value of 49 as indicated in table 4.12.

4.3. Comparison of MSOME, NSOME and diesel

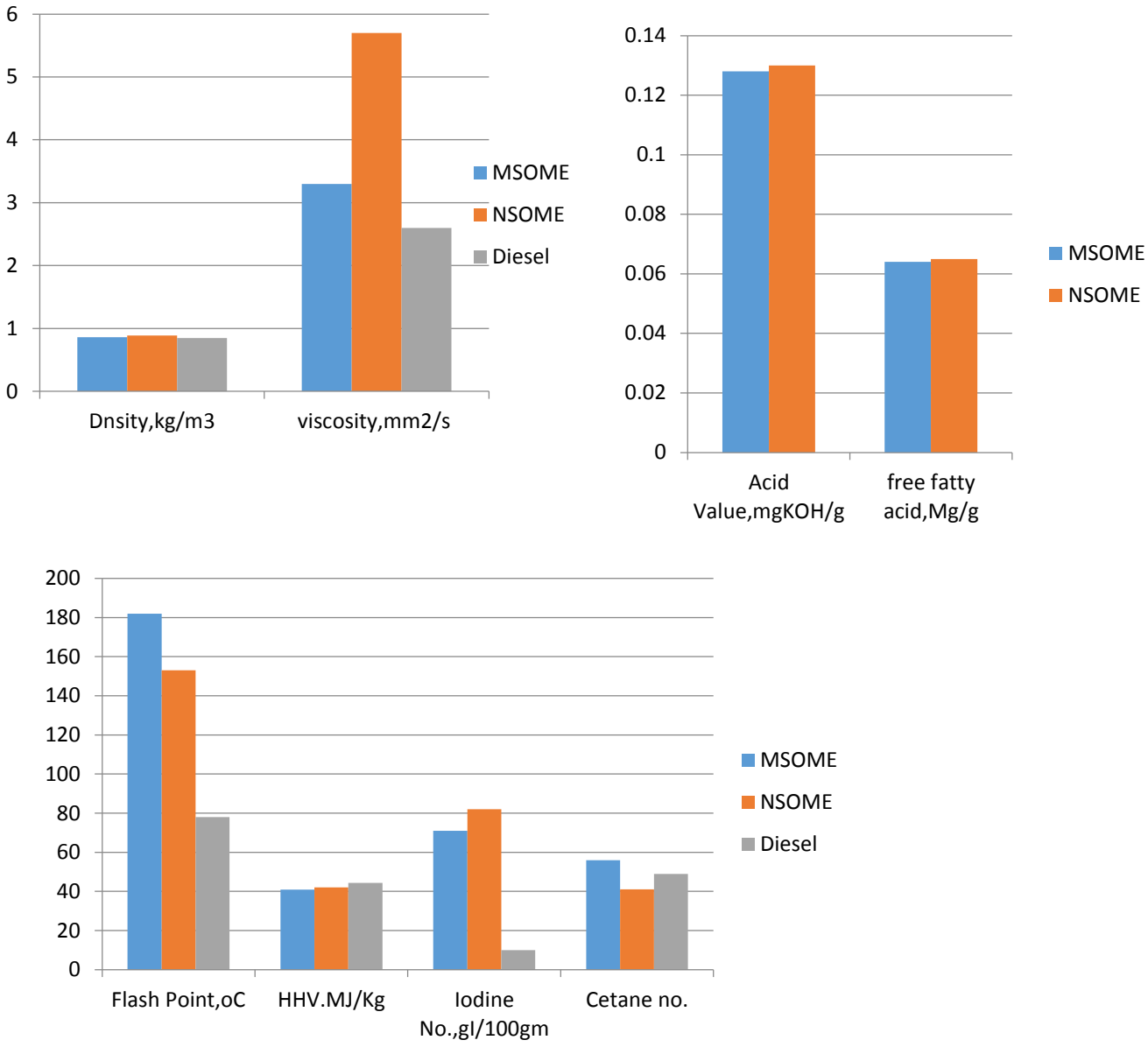


Figure 4. 8: Comparison of fuel properties between MSOME, NSOME and Diesel

Comparison of fuel properties such as density, viscosity, Acid value, free fatty acid value, flash point, high heating value, iodine and cetane number of quality produced biodiesel (B_{100}) from *Moringa stenopetala*, Neem seed oil and # 2 diesels was shown in the above figure. Based on this the density of biodiesel produced from *moringa stenopetala* oil was less than the density of neem seed oil and it was close to the density of number 2 diesel. This indicates that the lower the relative density was good ignition property.

The kinematic viscosity measured for #2diesel and biodiesel produced from *Moringa stenopetala* and Neem seed oil were 2.60, 3.3 and 5.7mm^2/s. The results are still within the limit of the ASTM specification i.e. (1.9–6.0 mm^2/s). According to the result the MSOME is fewer tendencies to poorer atomization of the fuel spray and less accurate operation of the fuel injectors than NSOME.

The acid value for the moringa stenopetala and neem seed oil methyl ester were 0.128 and 0.13 mKOH/gm. respectively. The acid number of the biodiesel produced is within ASTM standard for biodiesel sets the maximum acid value of 0.8mg KOH/g of oil, which indicates that this will not pose problem on the long-term performance of the engine.

The flash points of the biodiesels were determined according to the standard procedure for flash point measurement of biodiesel, i.e. ASTM D93. The flash point of moringa stenopetala seed oil was higher than neem seed oil methyl ester and #2 diesels. Biodiesel and diesel have a common boiling point, but biodiesel has a higher flash point because biodiesel has a high number of FAMEs, which are generally not volatile. Thus, biodiesel is safer to handle at higher temperatures than diesel according to national renewable energy laboratory [75]. Accordingly moringa seed oil methyl ester safer to handle at higher temperature than neem and diesel.

The iodine numbers of *moringa stenopetala* and neem seed oil methyl esters were much higher than #2 diesels which were 10.This means biodiesels had significantly high degree of unsaturation than diesel. A higher Iodine number indicates a higher quantity of double bonds in the sample, greater potential to polymerize and hence lesser stability [13]. *M. stenopetala* and neem seed oils were easily meets the requirements of the EN 14214 biodiesel standards, which prescribe a maximum iodine value of 120g I_2/100g of oil.

Cetane number is a measure of the self-ignition quality of the fuel. Higher Cetane numbers Indicate shorter times between the injection of the fuel and its ignition. Moringa stenopetala methyl ester was higher cetane number than Neem oil methyl ester and #2 diesels.

Generally from the above discussion moringa Stenopetala and neem seed oil methyl esters had properties close to # 2 diesels therefore this signifies that these oils were good quality for use as feedstock for biodiesel production.

5. Conclusion and recommendation

5.1. Conclusion

The aim of this study was to optimize the operating condition (catalyst weight, wt. % and Temperature, ^{o}C) and to compare the fuel properties of quality produced biodiesel (B_{100}) from moringa stenopetala and neem seed oil with number 2 diesel, ASTM standards to use as alternative source for biodiesel production.

This research was started from extraction and characterization of *moringa stenopetala* and neem seed oil .The extraction of both plant species were done by solvent extraction (soxhlet) using hexane as a solvent. *Moringa stenopetala* and neem seed were found to be rich in oil with an average yield of 43.3 and 48.8 %.The acid values of moringa and neem seed oils were 4.9 and 17.2mgKOH/gm. The acid catalyzed esterification reaction showed that it is a suitable pretreatment method to reduce the acid value of feed stocks with high content of free fatty acids. It was found that the moringa stenopetala seed oil acid value (AV) was 4.9 mg KOH/g with 2.45% free fatty acid content (FFA) and the neem seed oil acid value 17.2mgKOH/gm with 8.6% FFA. The acid catalyzes esterification was brought this acid value to 1.72 mg KOH/g with 0.86% free fatty acid content for *moringa stenopetala* and 5.4mgKOH/gm with 2.7% FFA content. The neutralization on this step was further reduced the acid value which is ideal for alkali catalyzed transesterfication.

In the second, alkali catalyzed esterification was carried out and the effects of catalyst weight and reaction temperature was investigated using Design expert software for both plant species. The statistical analysis showed that the two process variables, catalyst weight, reaction temperature and interaction of both variables had significant effects on the yield of transesterfication reaction. The maximum yield of Moringa seed oil methyl ester was obtained at combination of 1% catalyst weight and the 60 ^{o}C reaction temperatures which was 91.65% and desirability equal to 0.967. Also the maximum yield of Neem seed oil methyl ester was achieved 1%w/w catalyst weight and 55 ^{O}C reaction temperatures which were 86.6% and the desirability equal to 0.985. An experiment were conducted at these suggested values for moringa stenopetala and neem seed oil methyl ester to verify the optimum values and a good approximation of the predicted optimum value was obtained, which is 93 and 90 % FAME yield respectively. .

The fuel properties tested are within the ASTM and EN norms and were found to be very close to those of petroleum diesel. The results showed that the two step acid base transesterification improved the important fuel properties tested. Biodiesel produced from moringa stenopetala seed oil had improved cetane number, and flash point as compared with neem oil methyl ester and petro diesel. But low iodine values compared with neem oil methyl ester. This high iodine value of biodiesel shows that there is a greater probability of polymerization and solidification if it is used directly for car engines without blending.

Generally, the FAME of moringa seed oil had relative closer fuel properties than neem seed oil. The fuel properties of the biodiesel obtained from both plant species were in a good agreement with the standard.

5.2. Recommendations

- Full characterization of both plant species should be should be conducted to identify medicinal value.
- Full characterization of *Moringa stenopetala* seed and neem seed oil using GC, HPLC analysis should be conducted to identify the free fatty acid content.
- Full characterization of *moringa stenopetala* should be conducted to identify oil for human consumption and pharmaceutical purpose.
- Full characterization of neem seed oil should be conducted to identify the properties of the oil for production of pesticides, medicines.
- This research work was conducted using homogeneous catalyst and methanol. Since ethanol is available in Ethiopia in near future, I recommend future work on investigation of biodiesel production from both plant species seed oil using heterogeneous catalyst and ethanol.
- Optimization of process variables such as oil to methanol ratio, catalyst type, reaction time and different oil transesterfication process should be done for better conclusion.
- Further research and development on additional fuel property using HPLC or GC analysis, blending conditions, engine performance and emission tests and techno-economic analysis are necessary.

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Appendices

Appendix A

Experimental procedure of oil extraction

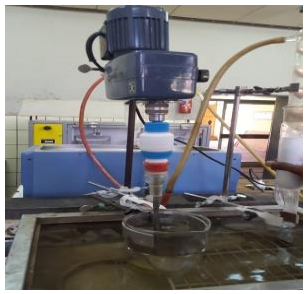




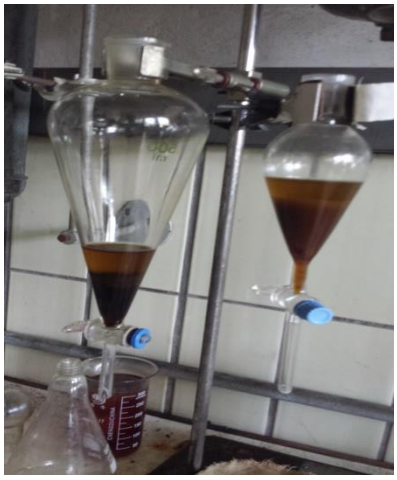




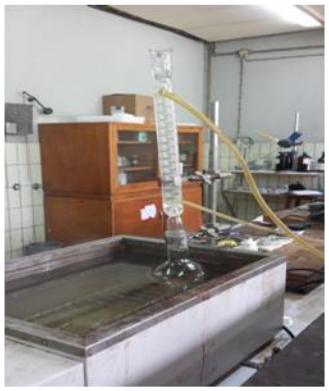
Oil refining


Experimental procedure of Biodiesel production



Oil and bio diesel characterization



Appendix B:

Fatty acid profile of Moringa seed oil [13]

Fatty acid	Systemic name	Formula	Structure	Amount (wt. %)
Palmitic acid	Hexadecanoic	$C_{16}H_{32}O_2$	16:0	6.1
Oleic acid	Cis-9-octadecenoic	$C_{18}H_{34}O_2$	18:1	76.0
Stearic	Octadecenoic	$C_{18}H_{36}O_2$	18:0	7.5
Arachidic	Eicosanoic	$C_{20}H_{40}O_2$	20:0	3.8
Arachideic	Eicosenoic	$C_{20}H_{38}O_2$	20:1	1.7
Behenic	Docosanoic	$C_{22}H_{44}O_2$	22:0	4.4
others	-	-	-	0.5
TOTAL	-	-	-	100%

Fatty acid profile of Moringa seed oil [12]

Fatty acid	Composition %
Linoleic acid	13.00
Oleic acid	51.00
Palmitic acid	26.00
Stearic acid	9.50
Linolenic acid	0.06
Myristic acid	0.44
Total	100

Appendix C

Results from experimental design software (ANOVA)

Table c-1:- Experimentally obtained values MSOME and NSOME

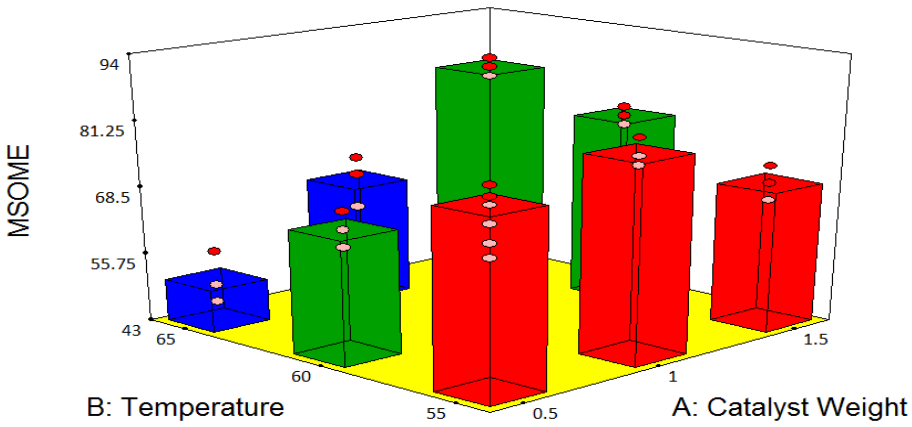
Std	Run	Block	A-Catalyst Weight (%w)	B-Temperature ^{o}C	MSOME %	NSOME bb%
1	1	Block 1	0.5	55	80	76.6
2	14	Block 1	0.5	55	73.3	70
3	10	Block 1	0.5	55	76.6	73.3
4	23	Block 1	1	55	80	90
5	12	Block 1	1	55	78.3	83.3
6	27	Block 1	1	55	83.3	86.6
7	22	Block 1	1.5	55	66.7	80
8	16	Block 1	1.5	55	70	70
9	2	Block 1	1.5	55	73.3	60
10	17	Block 1	0.5	60	66.6	53.3
11	20	Block 1	0.5	60	70	46.6
12	15	Block 1	0.5	60	63.3	43.3
13	7	Block 1	1	60	93.3	76.6
14	13	Block 1	1	60	90	66.6
15	3	Block 1	1	60	91.66	60
16	6	Block 1	1.5	60	76.6	80
17	26	Block 1	1.5	60	80	73.3
18	25	Block 1	1.5	60	78.3	70
19	4	Block 1	0.5	65	50	40
20	8	Block 1	0.5	65	56.7	50
21	11	Block 1	0.5	65	46.6	43.3
22	19	Block 1	1	65	60	53.3
23	18	Block 1	1	65	66.6	46.6
24	21	Block 1	1	65	70	56.7
25	9	Block 1	1.5	65	46.6	56.7
26	5	Block 1	1.5	65	56.7	50
27	24	Block 1	1.5	65	43.3	43.3

ANOVA results for MSOME

Design-Expert® Software

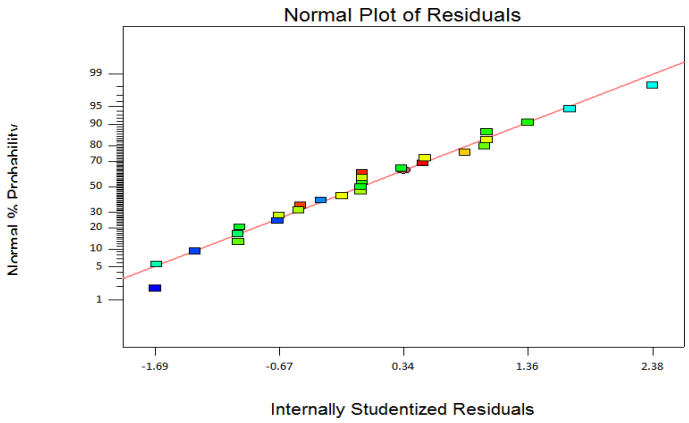
MSOME

X1 = A: Catalyst Weight
X2 = B: Temperature



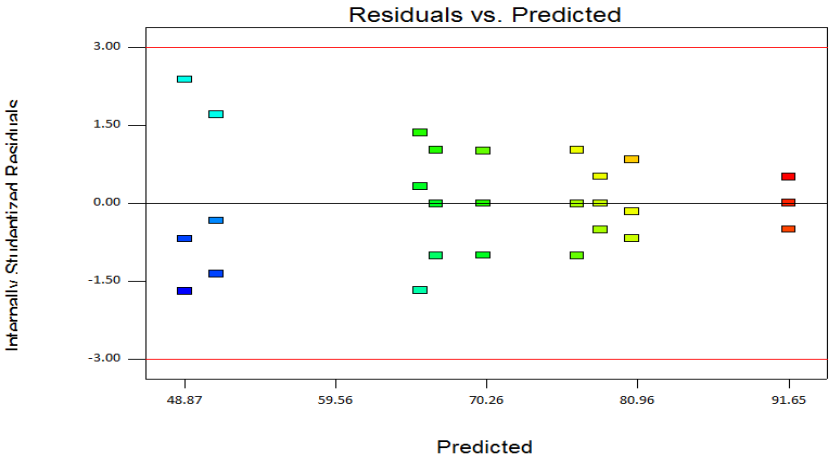
Design-Expert® Software
MSOME

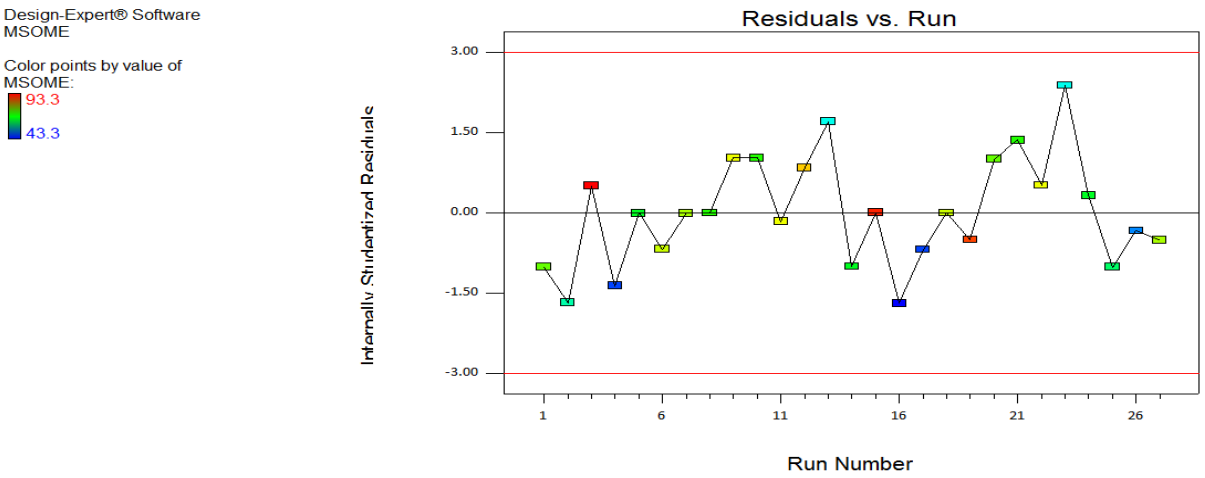
Color points by value of
MSOME:
93.3
43.3

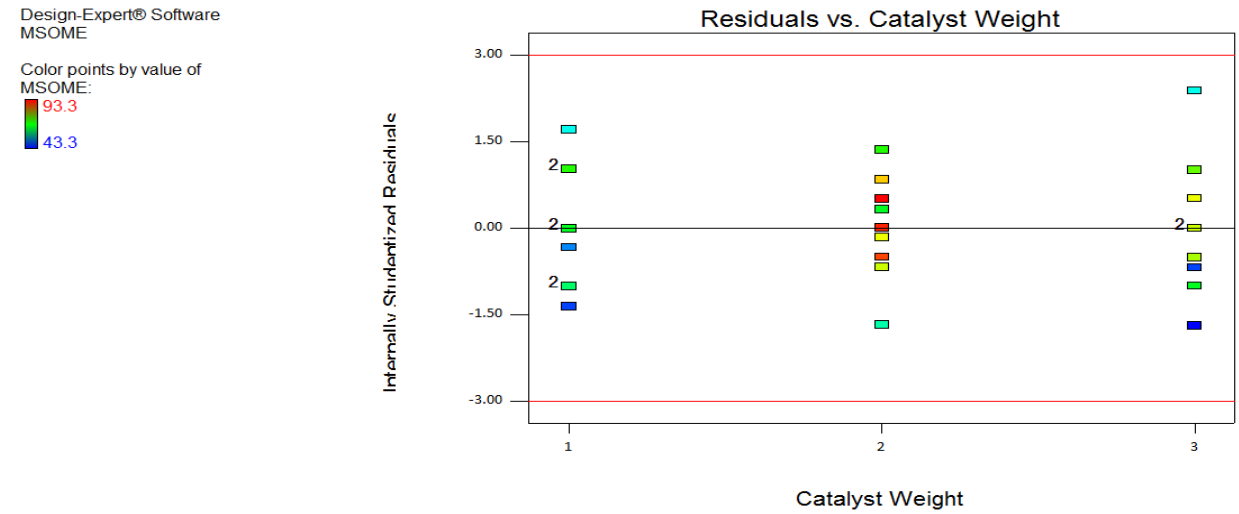


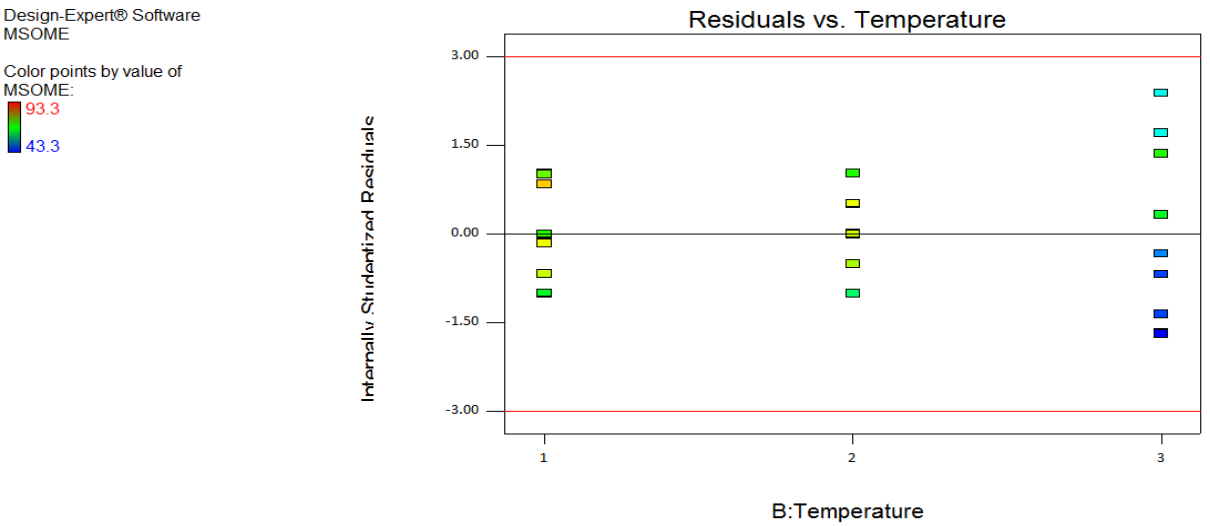
Design-Expert® Software
MSOME

Color points by value of
MSOME:
93.3
43.3




Design-Expert® Software
MSOME
Color points by value of
MSOME:
93.3
43.3
Residuals vs. Run
Internally Studentized Residuals
3.00
1.50
0.00
-1.50
-3.00
1
6
11
16
21
26
Run Number


Design-Expert® Software
MSOME
Color points by value of
MSOME:
93.3
43.3
Residuals vs. Catalyst Weight
Internally Studentized Residuals
3.00
1.50
0.00
-1.50
-3.00
2
2
2
2
1
2
3
Catalyst Weight

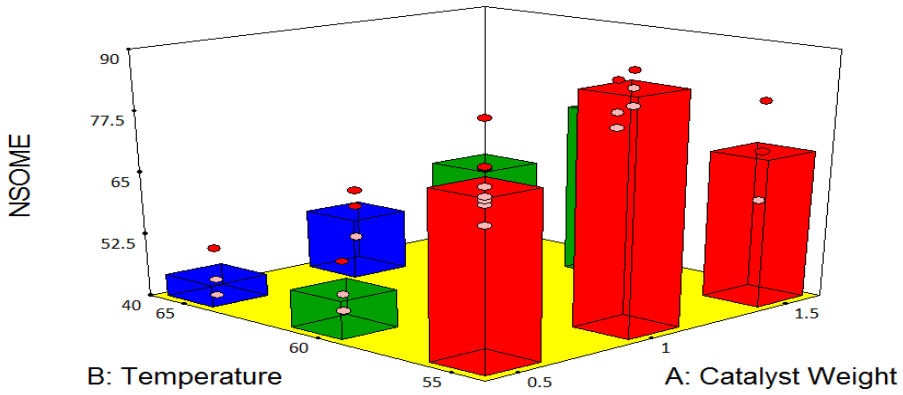

Design-Expert® Software
MSOME
Color points by value of
MSOME:
93.3
43.3
Residuals vs. Temperature
Internally Studentized Residuals
3.00
1.50
0.00
-1.50
-3.00
1
2
3
B:Temperature

ANOVA results for NSOME

Design-Expert® Software

NSOME

X1 = A: Catalyst Weight
X2 = B: Temperature



Design-Expert® Software
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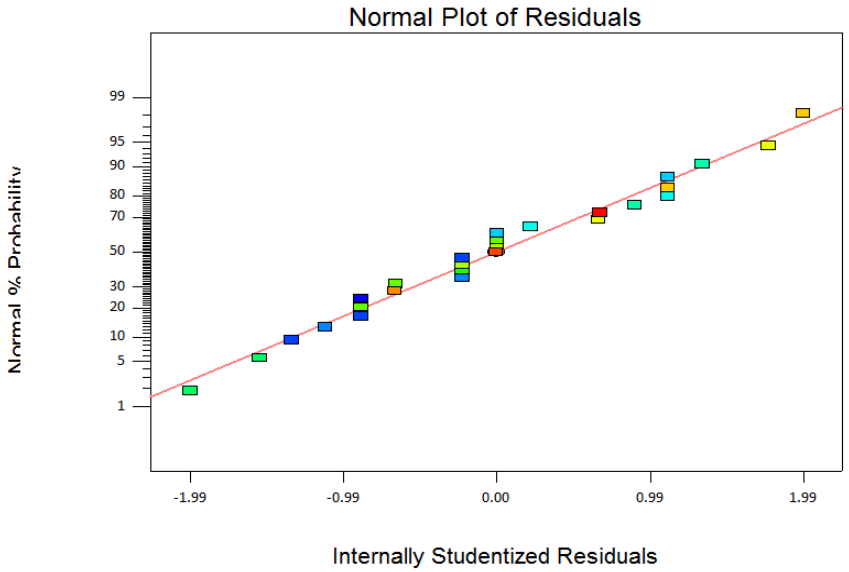

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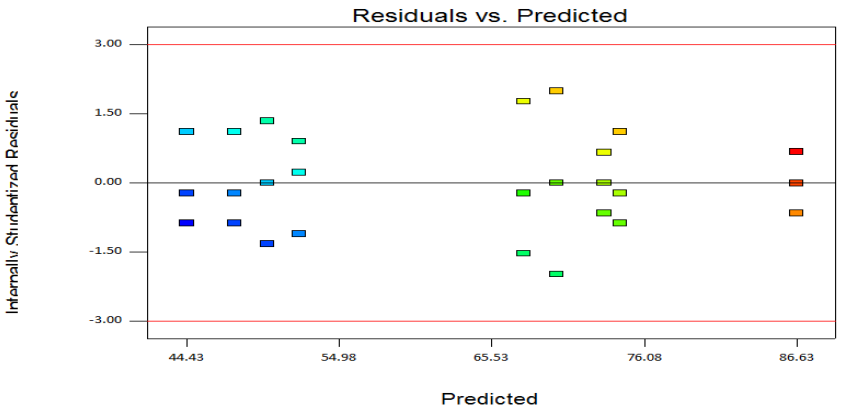

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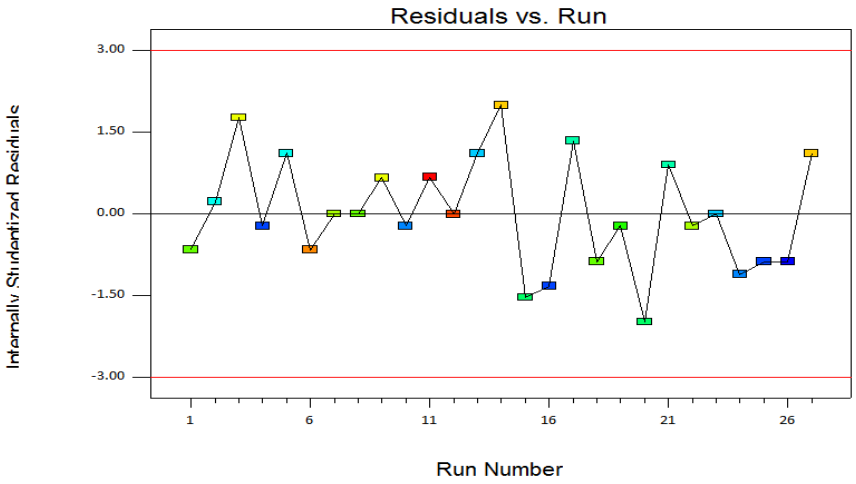

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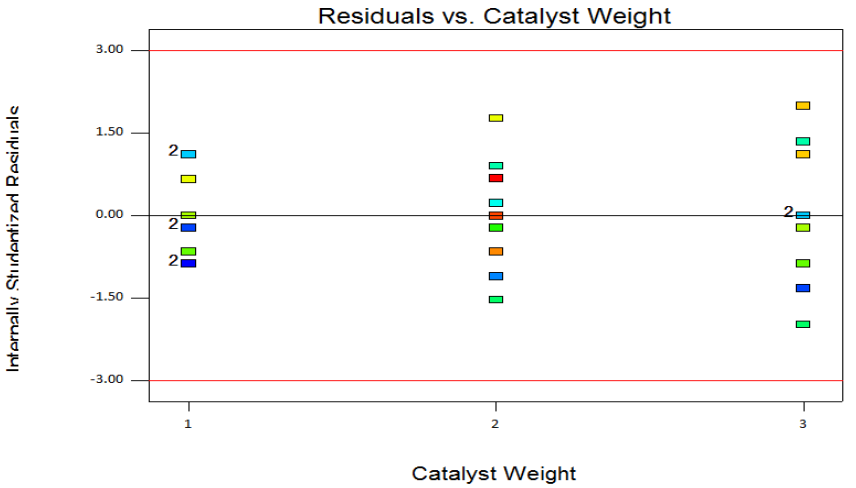

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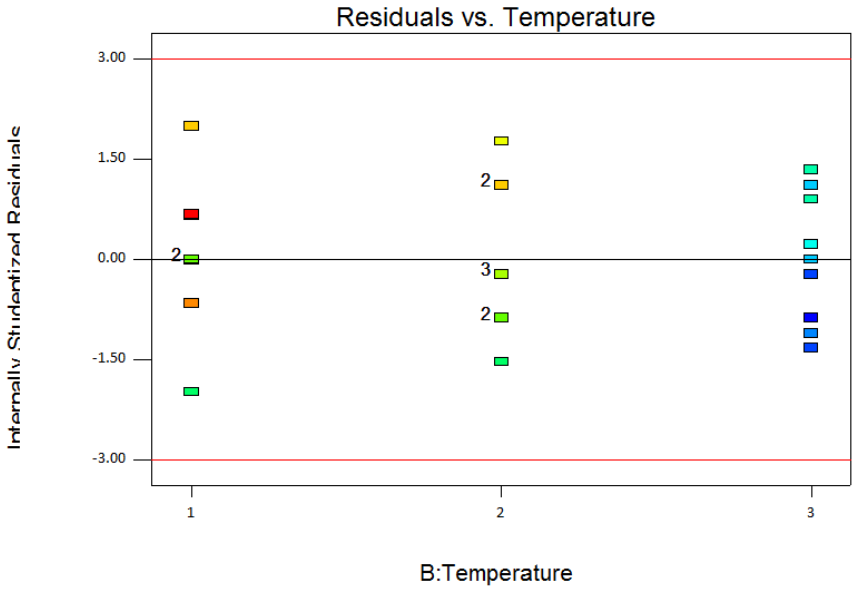

Appendix D

Biodiesel properties

property	unit	Jatropha	soybean	Oil palm	WCO	Biodiesel standards ASTM D 6751-02	DIN EN 14214	Diesel fuel
Density at 20 c^{o}	Kg/m^{3}	880	885	880	884	870-900	875-900	850
Viscosity at 40 c^{o}	Mm^{2}/s	2.37	4.5	5.7	4.5	1.9 - 6.0	3.5-5.0	2.60
Cloud point	C^{o}	--	1	13	1	--	--	4
Flash point	C^{o}	135	178	164	180	130	120	68
Pour point	C^{o}	2	-7	12	-5.0	-15 to 10	-15 to 10	-20
Water	%	0.025	-	-	0.4	0.03	0.05	0.02
Sulfur	PPM	-	-	-		50	50	500
Carbon residue	Wt.%	0.20	-	-	0.3	-	0.3	0.17
Cetane number	--	61	45	62	57.2	48 - 60	49	49
Calorific value	Mj/kg	39.2	33.5	33.5	32.9	-	-	42

Extraction yield of moringa stenopetala seed oil

$$\% \text{ yield} = \frac{W_1 - W_2}{W_1} \times 100\%$$

W_1= 30gm W_2= 17gm

$$\% \text{ yield} = \frac{30-17}{30} \times 100\% = \mathbf{43.3\%}$$

Extraction yield of Neem seed oil

W_1 =30 W_2=15.5

$$\% \text{ yield} = \frac{30-15.5}{30} \times 100\% = \mathbf{48.3\%}$$

Degumming

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

= 60 ml

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

= 2 litre * 0.02

= 40 ml

Petroleum diesel versus biodiesel

Fuel Property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM D6751
Fuel composition	C10-C21 HC[b]	C12-C22 FAME[c]
Kinematic viscosity, mm^2/s (at 40 °C)	1.3 – 4.1	1.9 – 6.0
Specific gravity	0.85	0.88
Boiling point, °C	188–343	182 – 338
Flash point, °C	60 – 80	100 –170
Cloud point, °C	-15 to 5	-3 to 12
Pour point, °C	-35 to –15	-15 to 10
Cetane number (ignition quality)	40 – 55	48 – 65
Stoichiometric air/fuel ratio (AFR)	15	13.8

[a] (Kiss et al., 2008); HC [b] , Hydrocarbons; FAME[c] , fatty acid methyl esters.