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Experimental Investigation and Characterization of Biodiesel from Argemone Ocheroleuca Seed Oil

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Experimental Investigation and Characterization of Biodiesel from Argemone Ocheroleuca Seed Oil

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Experimental Investigation and Characterization of Biodiesel from Argemone Ocheroleuca Seed Oil

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September, 2019
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DECLARATION

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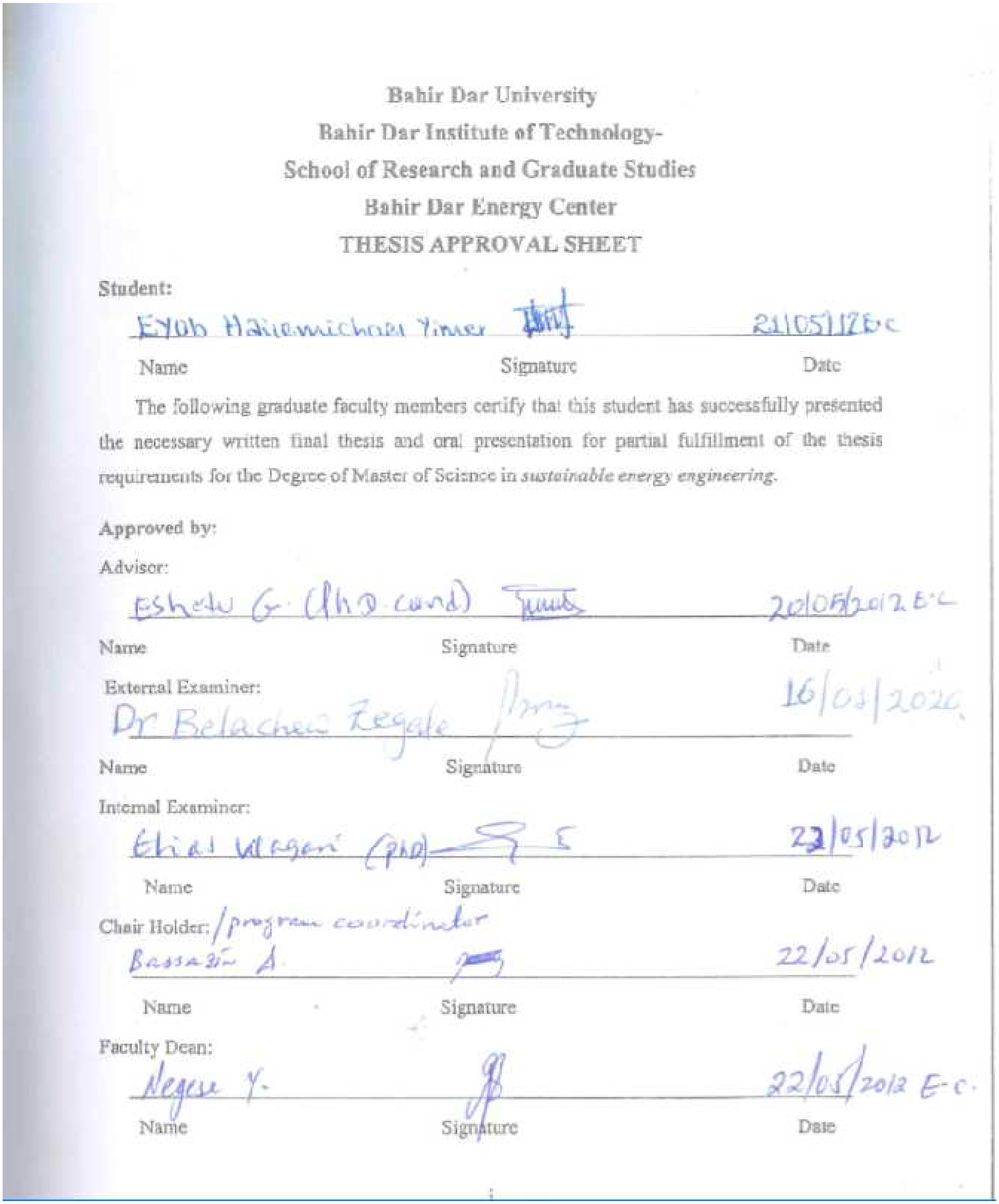

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ABSTRACT

Biodiesel is a renewable bio-fuel derived from natural fats or vegetable oils, and it is an attractive alternative to replace diesel fuels. Currently, the main disadvantage could be the high costs of some types of raw materials. The main purpose of this research is, therefore, to develop the optimum condition biodiesel production method from a low cost of raw material Aregmone Ocheroleuca seed oil and methanol alcohol by transesterification reactions. In the present investigation the effect of acid pretreatment of oil, the effect of catalyst amount, temperature, and alcohol to oil molar ratio. Special attention was paid to the optimization of base-catalyzed on the conversion of fatty acid methyl ester (FAME). The Aregmone Ocheroleuca oil used in the esterification contained 12.5 mg KOH/g of acid and after acid pretreatment; it was possible to bring down the acid value to 1.59 mg KOH/g. After the pretreatment process, to determine the optimum condition for transesterification of Aregmone Ocheroleuca oil using methanol and potassium hydroxide as input, 18 experiments varying methanol-to-oil molar ratio (3:1,4:1 and 6:1), reaction temperature (45,55, and 65^{O}C), and amount of catalyst (0.5 and 1%). Reaction time and mixing intensity were fixed to 2 hrs, and 350 rpm respectively. The optimum conditions found for transesterification were a methanol-to-oil molar ratio of 6:1, a reaction temperature of 55^{O}C and an amount of catalyst of 1%. At the optimum condition obtained a FAME conversion of 93.4% v/v was achieved and a produced biodiesel property has a viscosity of 3.95mm^2/s, Acid value of 0.34, HHV of 41.20 MJ/kg, iodine value of 40.7 gI2/100ml density of 871.8 Kg/m^3, Flashpoint 166.7^{O}C and Cetane number of 54.63.

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LIST OF ABBREVIATIONS

ASTM	American Standards Tests and Materials
AV	Acid Value
BLTV	Blank Level Titration Volume
Cm	Concentration of Mass
CN	Cetane number
EN	European Normalization (European Standards)
FFA	Free Fatty Acid
MS	Mass of Sample
N	Normality
SV	Saponification Value
RF	Reagent factor
TF	Titration Factor
TAG	Triacylglycerides
TV	Titration Volume
V/V	Volume per Volume
V/W	Volume per Weight
W/W	Weight per Weight
FAME	Fatty acid methyl esters

LIST OF SYMBOLS

CI	Compression ignition
CO	Carbon monoxide
CO_2	Carbon dioxide
HC	Hydrocarbon
IC	Internal combustion
NOx	Oxides of nitrogen
PM	Particulate matter
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
H_2SO_4	Sulfuric Acid
NaCl	Sodium chloride

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CHAPTER ONE

1. INTRODUCTION

1.1. Background

Biodiesel, a green alternative source of fuel to diesel engine, it extracts from renewable sources such as vegetable oils, animal fats, and microalgae. Due to its renewability, biodegradability, and non-toxicity properties, biodiesel plays a major role in the energy sector and becoming increasingly important as an alternative fuel for diesel engines as a result of combustion properties similar with petroleum fossil fuels [1][2].

The biofuel production using edible oils such as palm oil, corn, soybean, and maize, is not economical because the land use for the production of edible oil and the price edible plant and vegetable oils is higher than fossil fuel. Moreover, competitive with a source of food forced researchers into finding another source of biodiesel which cost is low and non-food source crops such as the seed of the rubber tree, neem, jatropha, waste oil and animal fat [2][3][4].

Structurally viewed, biodiesel is known to be a fatty acid alkyl ester produced by the reaction of triglycerides with short-chain alcohols (e.g. methanol and ethanol). Biodiesel consists of fatty acid methyl esters (FAME). The most common way to produce biodiesel is esterification triglycerides of vegetable oil, or of the lipid phase obtained from algae. The esterification is performed by reacting the oil with alcohol in the presence of an alkali or acid catalyst [5][6][7]. However, non-edible oil has a high free fatty acid content, which is unfavorable for production of biodiesel because the poor quality of oil react with alkaline catalysts such as sodium hydroxide cause to formation of relatively large amounts of soaps, leading to product loss and difficulty in the separation and purification of the biodiesel produced [8][7].

In order to reduce the impacts of high free fatty acid (FFA) content on purity and yield biodiesel and require a chemical process called transesterification. Through this process, first-step acid-catalyzed esterification used to reduce the FFA content and second-step alkali-catalyzed transesterification is conducted in this step glycerol is removed from the oil and can be used in existing engines. Furthermore, it improved physical and chemical properties, such as viscosity, density, a higher flash point, higher cetane number, sulfur content, better lubricity, and the oil properties are made closer to fossil fuel. It can also be blended with conventional fuel and used in engines without any modifications[3][4] [9][10].

Various studies have been carried out using different oils as the raw material and different parameter that affect the production of biodiesel such as alcohols (methanol, ethanol, butanol) type of catalysts especially homogeneous ones such as sodium alkaline, acid catalyst, and supercritical fluids or enzymes such as lipases. The application transesterification process using heterogeneous catalysts is studied by the researcher to produce biodiesel from high FFA oil, because of their environmental and economic advantages. Argemone ochroleuca is a new potential as the raw material oilseed crop for the production of biodiesel in Ethiopia.

This research, therefore, is intended to show another raw material for the source of biodiesel by setting up a technical insight towards a small-scale biodiesel production from Argemone ochroleuca. Small scale production of biodiesel consists of three steps such as oil extraction, oil purification, and processing of oil. Oil extraction from Argemone ochroleuca seeds can be done by three different methods. These are mechanical extraction using a screw press, solvent extraction method. The selection of the extraction method will be decided by material availability, cost, quality, etc. The purification will be carried out by the degumming process. Then the final step processing of vegetable oil to methyl ester will be conducted using a heterogeneous catalyst.

In the present work, the technical feasibility of Argemone oche ochroleuca biodiesel with the influence of operating conditions, such as methanol to oil molar ratio, amount of catalyst and temperature to the yield and physicochemical properties was studied. The quality assessment of the vegetable oil, pretreated oil and biodiesel will be performed by laboratory tests and comparison with ASTM and EN standards.

1.2. Statement of The Problem

Substituting the demand of fossil fuel by renewable fuel is the alternative way to fulfill the demand of world energy and to reduce the pollutant gas emission, biodiesel production from vegetable oils is one alternative for energy demand and biodiesel has recently attracted much attention all over the world because of its availability, renewability, non-toxicity, better gas emissions, and its biodegradability. Vegetable oils, mostly produced by seed-bearing trees and shrubs can provide an alternative source of biodiesel. Due to low cost for harvesting and inedible for human, the researchers turn attention to different types of oil source like Jatropha curcas, neem, castor seed, palm seed, tobacco (Nicotiana tabacum L.) seed, rubber seed, mahua (Madhuca indica), Karanja (Pongamia pinnata) seeds which used for the production of biodiesel.

Currently, Aregemone ochroleuca is a widely spread weed in farmland, grassland and also grows in any type of soil slightly suited for the agricultural product which is thrown as weed. It is not edible. However, currently, biodiesel from Aregemone ochroleuca oil is not introduced in any markets in Ethiopia; hence Aregemone ochroleuca oil will be new potential to produce biodiesel.

The focus of the research is on the production of biodiesel from these seed oil. Various factors, which affect the yield and quality of biodiesel as well as characterization of the product were studied to completing the research.

1.3. Objectives

1.3.1. General Objective

The main study of the paper was experimental investigation and characterization of biodiesel from Aregmone ochroleuca.

1.3.2. Specific Objectives

The specific objectives of the study were:

To investigate the effect of particle size on the extraction process.

To characterize the physicochemical properties of the seed oil.

To study the effect of molar ratio of oil and methanol on Ester conversion.

To see the effect of reaction temperature on biodiesel production.

To characterize the physicochemical properties of biodiesel extract from the seed oil.

1.4. Scope of the Study

Studies on production of biodiesel from Aregmone ochroleuca needs experimental work for extraction and conversion of oil to fatty acid methyl ester, and characterization of biodiesel to study the quality of biodiesel by comparing with ASTM and EN standards. In this study, the conversion techniques' will be studied by the transesterification process using acid and the base heterogeneous catalyst. The acid catalyst is used for the reduction of a high amount of FFA in oil. After this alkaline catalyst is used to produce methyl ester. The effect of three different parameters, the Molar ratio of methanol to oil in the range of (3:1-6:1), Reaction temperature (45-65^{O}C) and amount catalyst (0.5 and 1%) on conversion process will be studied. Finally, the product of Argemone ochroleuca biodiesel properties will be determined and by comparing it with ASTM and EU biodiesel standard important conclusion will be drawn from both the theoretical and experimental results.

1.5. Significance of the Study

This thesis has great significance in terms of showing the additional source of biodiesel that increasing the production of an alternative form of energy from Aregemone ochroleuca and in the increasing of the potentials of the country in supplying feedstock for biodiesel production. It also will be helpful to produce biodiesel from Aregemone ochroleuca oil using methanol and alkali catalyst, which is locally available, can be abundantly cultivated and grown, non-edible and good for production of biodiesel. This helps to encourage rural communities to cultivate more Aregemone ochroleuca plants to sustain their earnings. In addition, the study will be used as a reference material for researcher studies on biodiesels and company owners who are interested to produce biodiesel from Aregemone ochroleuca oil using methanol with alkali catalysts at small scale.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Introduction

Biodiesel is a diesel fuel that can be produced from a variety of biological sources including vegetable oils, animal fats, and microalgae. The physical and chemical characteristics of biodiesel are equivalent to diesel fuel that can be produced from fossil petroleum oil due to this it can be used in conventional diesel engines either alone or blended with fossil petroleum diesel in any compression-ignition engine without the need for modification [11].

Biodiesel fuel has the significant potential that reduce the level of pollutants such as carbon monoxide, particulate matter, Sulfates, polycyclic aromatic hydrocarbons, and unburned hydrocarbon emissions cause to environmental impact because of pollutant produced after combustion of biodiesel can be recycled by photosynthesis [12]. Unlike petroleum diesel which releases carbon that was stored for a million year in underground biodiesel has better quality exhaust gas emission since the fuel is more oxygenated in the pyramid of fuel component diagram and all of the carbon that makes up biodiesel originates from photosynthetic in the atmosphere and is simply returned to the atmosphere after combustion, thus carbon dioxide produced by combustion process minimizing the impact of biodiesel on the greenhouse effect [13].

Biodiesel can be produced from the fatty acid triglycerides present in vegetable oil, animal fats, used frying oil, waste cooking oil, edible oils, and non-edible oils. The transesterification process is the best way for biodiesel production is carried out by using alcohol and catalyst. The triglycerides are converted into mono-alkyl esters of long-chain fatty acids, Such as fatty acid methyl esters and fatty acid ethyl esters. Fatty esters from vegetable oils have shown potential as alternative diesel fuels as a result of improved viscosity and volatility relative to the triglyceride [14]. There are four basic methods to alkyl esters production from oils and fats: Base-catalyzed transesterification; direct acid-catalyzed transesterification; enzyme catalytic conversion of triglyceride into alkali ester, and non-catalytic transesterification using methanol [15][16].

Currently, biodiesel is generally produced by conventional methods using a homogeneous base catalyst. Because the use of edible oils as the production of ester biodiesel feedstocks competes with their human consumption, exploring new methods to produce biodiesel from low-cost raw materials is the main interest in recent biodiesel research. Many other non-edible oil sources are particularly attractive for potential use as biodiesel feedstocks. The availability and sustainability of sufficient supplies of less expensive feedstock is a vital determinant delivering a competitive biodiesel price[10][17][18]. However, waste cooking oils and non-edible oils usually contain high FFA (mainly free fatty acid content >2%) and it difficult to convert poor quality vegetable oil into biodiesel by a transesterification reaction. Because conversion is complicated if the oil contains large amounts of FFA contained in triglycerides react with the alkaline catalyst it forms soap. The soap can prevent separation of the biodiesel from the glycerine [10]. The process also requires a complex purification step to eliminate saponified product as well as a catalyst, eventually resulting in the lower yield of biodiesel. On the other hand, the major problem associated with the use of pure vegetable oils as direct use oil to be problematic due to their greater viscosity which affecting piston, injector deposits, and oil thickening. Although short-term tests using neat vegetable oil showed promising results, longer tests led to injector coking, more engine deposits, ring sticking, and thickening of the engine lubricant. These experiences led to the use of modified vegetable oil as a fuel [19][20].

2.2. Alternate Feed Stocks for Biodiesel Production

The production of biodiesel starts with the choice of feedstock. Biodiesel, an alternative source of diesel fuel, is mono-alkyl esters of long-chain fatty acids derived from renewable feedstock primarily vegetable oils, animal fats, residual oils, and microalgae. Choice of feedstocks depends on the oil content of the feedstock, process chemistry and economy of the process [21]. Physical and chemical characteristics of feedstock oil affect the potential biodiesel production are free fatty acid (FFA) content, moisture content and other impurities.

2.2.1. Biodiesel from Edible Vegetable Oil

Vegetable oils are becoming a promising alternative to diesel fuel because they are renewable in nature and can be produced locally and environmentally friendly as well. Hence, they essentially help to alleviate the increasing carbon dioxide content in the atmosphere[22]. Biodiesel production from edible Aleurites moluccana, canola, Palm and soybean oil predominantly used in Asia, United State and Europe. However, the edible oil-based biodiesel faced the high price of the feedstock and competition between food and fuel[23][24][25].

The main advantage of edible for biodiesel production due to its lower FFA content manufacturing process required shorter reaction time and less amount of catalyst does not need pretreatment of oil use a strong alkali as a catalyst. Therefore, a strong alkaline catalyst is widely used in the production biodiesel reduce the production cost but the cost of vegetable makes the biodiesel from edible oil higher than the petroleum fuel [1] [23][26] [27].

2.2.2. Biodiesel from Non-edible Oil and Residual Oil

The high value of vegetable oil used as a food consumption makes the production of biodiesel very expensive due to this new finding of new potential to produce biodiesel from low-cost raw materials and plants able to grow in large-scale on non-used for farming marginal lands or wastelands. is the main interest in recent biodiesel research[28]. Many studies have proposed the non-edible vegetable oils which contain high FFA such as Pongamia glabra (Karanja), Karanja (Pongamia pinnata), Jatropha (Jatropha curcas), Rubber (Hevca brasiliensis), Mahua (Madhuca indica), Neem (Azadirachta indica), and waste oils and fats were found to be good viable sources for producing biodiesel [25].

A two-step transesterification process is used to produce biodiesel from high free fatty acid non-edible oils in order to convert the high FFA oils to its mono-esters. The first step used to reduce the amount of high FFA to less than 2% using acid-catalyzed esterification. The second step, alkaline catalyzed transesterification process converts the products of the first step to its mono-esters and glycerol.

Various researches have been tasted out to find out different types of non-food oil and fat for biodiesel production using transesterification reaction, such as waste palm oil using ethanol, waste sunflower oil, rapeseed oil, Syagrus coronata, and Acrocomia aculeata oils, Jojoba oil-wax and other [29][30] [31][32][33].

Biodiesel production from different non-edible vegetable oils using the transesterification process gives yields of about 80–95%. High yield of oil up to 54% is extracted from Cerbera odollam (sea mango) and 83.8% fatty acid methyl esters (FAME) are recovered from this oil using the transesterification reactions using sulfated zirconia catalyst.

Camellia japonica and Vernicia fordii seed oils used for the production of biodiesel as a feedstock. The highest yield of methyl ester is 97.7% and 96.1% respectively evaluated by transesterification reaction with methanol on KOH alkali catalysts.

The maximum yield of oil obtained from Moringa oleifera is 39%. Transesterification of the Moringa oleifera oil in the presence of acid catalyst using H_2SO_4 reduce the FFA below 2% and basic catalysts of NaOH in transesterification produced the highest yields of FAMEs (70% at 4 h) [34].

The potential of fleshing oil for biodiesel production is determined and the yield of the fleshing oil is 64%. The esterification reaction using sulfuric acid to initiate the reaction is conducted at $60^{O}C$ and 1h to contact time the amount FFA level of 12.33% reduced to below 2.5%. 97% conversion of the oil was achieved using potassium hydroxide as a catalyst [33].

2.2.3. Biodiesel from Algae Feed Stock

Recently, microalgae species become an alternative source of renewable energy. They are a photosynthetic organism and grow without much care on waste nutrients does not require fertile land, higher biomass production, non-competitive with food and faster growth compared to other energy crops could be chosen as the best alternative source for biodiesel production[35].

The Lipids are used as storage products of algae. Many species' algae have content around 50–60% of their dry weight of as storage products. The chemical structure of triacylglyceride (TAG) of this lipid is similar to other oilseed crop so, lipids derived from algae was used as making biodiesel fuel using transesterification reaction. However, some factors like costs for drying, extraction, and processing inhibits the processing of algal biomass for biodiesel production in commercial scale[36].

High lipid content (55%) of chlorella protothecoides microalgal study for the production of biodiesel. A large amount of microalgal oil is extracted using n-hexane as a solvent from these heterotrophic cells. Biodiesel production from heterotrophic microalgal oil obtained by acidic transesterification process. The best quality of biodiesel obtained at 56:1 molar ratio of methanol at a temperature of $30^{o}C$, and reduced specific gravity from 0.912 to 0.8637 in 4 h of reaction time.[35]

The lipid content of Nannochloropsis and Chlorella microalgae has 30%-40% by dry weight extracted easily for biodiesel production. Two-step alkali catalyzed transesterification and also high conversion rates have been observed in both samples. Its composition is similar to sunflower oil and the fundamental physiochemical properties close to chosen standard rapeseed oil. The FAME obtained from the algae is not significantly different than those prepared from vegetable oils and meet the requirements of the EN14 214 standard [37].

Biofuel production from two algae samples Cladophora fracta and Chlorella protothecoid is study. The fatty acid methyl esters (biodiesel) are produced by using pyrolysis and the yield of bio-oil from pyrolysis of the samples increased with temperature. The maximum yields fatty acid methyl esters (biodiesel) is 48.2% and 55.3% of the sample for C. fracta and C. protothecoides, respectively.

2.3. Argemone ochroleuca Plant

Argemone Ocheroleuca is a plant in the belongs to the Papveracae (poppy) family, and the species is used as an oilseed. It is commonly known as koshashle in Ethiopia and is found on dry riversides, and in wastelands and fields. The plant has yellow flowers and is a branching herb with yellow juice, and its height varies between 0.12 and 0.3 m [17][38]. The diameter of the seed is 1.5–2.5 mm, spherical shape and dark brown. It is a non-edible, parts of the plant, including the seed, contain toxic alkaloids but it has many medicinal usages and can be applied in the external part of the body. The whole plant is analgesic, antispasmodic, possibly hallucinogenic and sedative. It contains alkaloids similar to those in the opium poppy (Papaver somniferum) and so can be used as a mild pain-killer. The fresh yellow, milky, acrid sap contains protein-dissolving substances and has been used in the cold sores, cutaneous affections, skin diseases, itches, etc. It has also been used to treat cataracts. The root is alterative and has been used in the treatment of chronic skin diseases. The flowers are expectorant and have been used in the treatment of coughs and other chest complaints[18].

Figure 2.1 Aregmone ochroleuca plant

2.4. Seed Oil Extraction Method

There are so many investigations on oil extraction techniques for non-conventional feedstocks of oils that have done in the last few years.

2.4.1. Mechanical Extraction

The technique of oil extraction by using mechanical presses is most applicable in the industrial process. But oil extracted by mechanical presses contains a large amount of gum due to these acids needs further treatment of purification and degumming. One more problem associated with conventional mechanical presses is that their design is suited for some particular seeds, and yield affected for other seeds [39].

The common method used to extract the seed oil from the seed, since this method is effective for a seed that contain 30-70% oil. The mechanical extraction has several advantages compared to the other methods, such as simple equipment and low investment, low operating cost, and the oil does not undergo solvent separation process, etc. For oil extraction using mechanical pressing, oilseed is fed to mechanical presser which exerts high pressure for extracting oil. When pressure is exerted at the required amount, the solid cake is removed in one region; oil and some impurities are collected on a different side. Finally, oil and impurities are separated using centrifuge or gravity settling.

2.4.2. Soxhlet Extraction

Extraction of oil using soxhlet is used particular Soxhlet apparatus consists of a glass extractor, condenser at the top, thimble holder, the round-bottom distillation flask initially contained an extracting solvent and Hot plate. This apparatus allows the extraction of oil from the seed samples using the distillation extraction method. Due to low cost and low toxicity hexane is the most common type of solvent in the soxhlet extraction technique. Initially, the extraction solvent is poured to round-bottom distillation flask and it is heated up. As the solvent vapor goes up to the condenser and condensate returned to the glass container and comes in contact with seeds, as a result, oil filtered out from the seeds due to mass transfer. After 3 and 4 h of the extraction, the mixture was allowed to recover under vacuum at 65 °C with a rotational evaporator for removing solvents, and then dried at 105 °C in an oven to remove the remaining impurities until its weight was constant to calculate the weight of oil obtained. Two replicate experiments were carried out and average values are presented [40] [41].

2.5. Pre-refining of Extracted Oils

The purity of crude vegetable oils or animal fats used for biodiesel production very low because usually exhibit high levels of acidity, phosphorous, trace metal, wax, and gum also content other contaminants that inhibit the quality and yield of biodiesel [42].

High viscosity of the non-edible vegetable oil has to be processed to remove gummy materials to reduce the factors affect the quality of oil for the utilization in the diesel engine. Crude vegetable oils contain over 95% triacylglycerol’s the remaining components is an undesirable substance that causes to increase rate oxidation, undesirable flavor, and color, and shorten the shelf-life of oil also consists of substance like copper which are classified as pro-oxidants. And also contain other substances include phospholipids, free fatty acids (FFAs), pigments, sterols, carbohydrates, proteins, calcium and magnesium and contain traces of other elements such as iron and copper, waxes, oxidation products and color bodies that impact negatively on their suitability for consumption and other uses. The conversion of methyl ester is reduced by 3–5% and generate additional difficulty of separating the glycerol from the esters if the phosphorus content in the oil is above 50 ppm. But all material causes to this problem can be removed by different treatment processes such as water and acid degumming, alkali refining and oil bleaching to produce high-quality oil and resistant to oxidative degradations [43][44].

Direct use of crude plant oil can cause several problems in transesterification reaction and fuel quality problems such as oil rancidity, corrosion, and incomplete combustion when used as fuel. The degumming process might alleviate such problem for the plant oil application in diesel engines and biodiesel fuel production. For example, A lower conversion rate is recorded when using crude plant oils without degumming due to the performance of catalyst inhibits during the transesterification reaction. In addition, emulsification occurs after the transesterification reaction it makes difficult to separate biodiesel and glycerol [11-15].

Degumming is a refining process that tends to remove trace metal and the phospholipids molecules which formed by glycerol with two fatty acids attached, and a phosphoric molecule, to which another base is attached and form complexes with the trace metals. Typically, it is carried out by mixing the crude oil with a water solution containing phosphoric acid or sulphuric acid. Hydratable-phospholipids gum can be removed by the water degumming process, but non-hydratable gums cannot be removed by this method. The Acid degumming process is used to remove the non-hydratable gum by converting them to hydrated gums. However, non-dissociated phosphatidic acid (PA) cannot remove be removed by acid degumming from the oil so to reduce the level of phosphorus content in the oil combination of water and acid degumming shows good result. [46][47].

The effect of the water degumming process can be studied to remove phospholipids and trace metals from crude vegetable oils. The optimal performance of the degumming process is found at 5:1 oil: water ratio. The oil: water mixture is agitated for 60 min at 60–70^{O}C during this a colloidal mixture beneath the oil layer is formed and centrifuge for 30 min at 1000 rpm to render fat-soluble phosphatides insoluble by hydrating. [46] [48] [49].

Degumming process using NaCl is studied to remove fat-soluble impurities (phospholipid lecithin complexed with metals) contained in the crude oil and to increase their shelf life. The ratio of 5 mL of raw oil with 1 ml of the 300 µg/mL NaCl solution was agitated for 60 min at 60°C on magnetic stirrer to form a layer between the oil and colloidal mixture and separate by decanting. Then, other insoluble phosphatides are separated by centrifugation at 1000 rpm for 30 min. The result shows that using 300 mg/mL NaCl solution for degumming process proved to be the most efficient way to reducing the heavy metal levels of the oils [47]

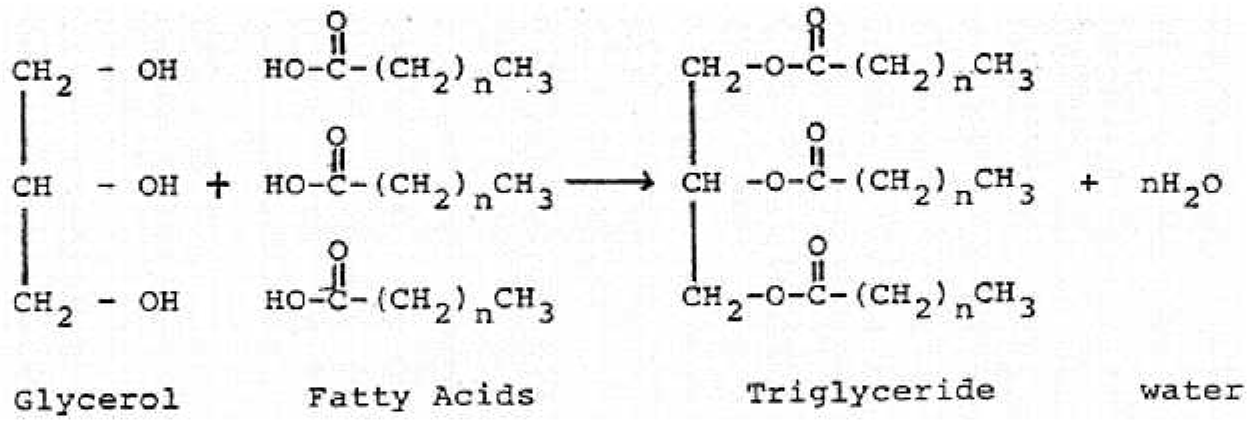
The phospholipids in oil are usually present in hydratable and nonhydratable forms. The hydratable form of phospholipids can utilize water to convert them into hydrated gums but the NHPLs, Mg and Ca remain in the degummed oil and make the degumming process less effective. Therefore, Acid with water degumming process is used to remove the non-hydratable acid is used to remove phospholipids by converting them to hydrated phospholipids and this hydratable form of phospholipids can utilize water to convert them into hydrated gums. then hydrated gums are removed by centrifugation or gravitation [50] [51][52].

The degumming process of crude oil using phosphoric acid and water at different temperatures and ratios of oil and acid solution is studied by numerous researchers. Karanja oil is degummed by 1%, 2%, 3%, 4% and 5% of acid treatment at 40 °C with stirring for 10-min its viscosity is reduced from 43.67 cSt to around 35 cSt by 4% acid 2% hot water treatment. The 20% blends of degummed Karanja oil with diesel give satisfactory engine performance.

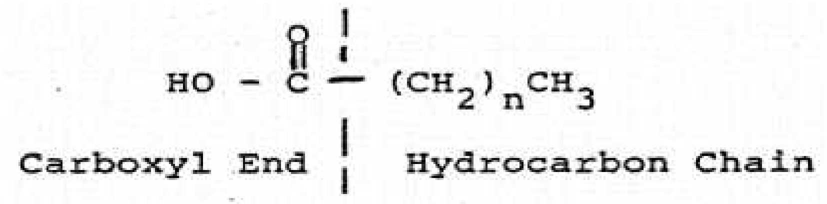
Removal of HPLs and NHPLs tested by using 1%, 2%, 3%, 4% and 5% phosphoric acid at different temperature is studied. Soft water is added to the mixing tank for the formation of an insoluble precipitate from the hydratable phosphatides The optimum operating conditions found to be 65^0C, 4 wt% phosphoric acid with 2% hot water or steam solution and 1600 rpm of centrifugation. Under these conditions, the phospholipid content of the oil was decreased from 1200 ppm to 60 ppm. The process is very efficient due to the water pretreatment and acid degumming due to all types of phospholipids are removed when using acid and water solutions [50][53].

2.6. Fatty Acid Composition

Biodiesel fuel properties and composition derived from different feedstocks are different from their fatty acid profile correspond to that of its parent oil or fat. The major component of (95-98%) of oil is Triglyceride- esters of one molecule of glycerol and 3 molecules of fatty acids.

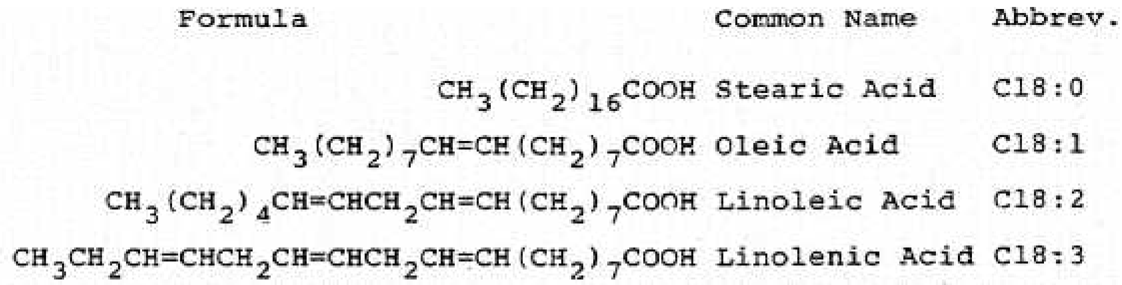


A fatty acid is composed of the carboxyl group and a hydrocarbon chain.


$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_nCH_3$$

The physicochemical properties of a fatty acid alkyl ester molecule are affected by its structural features like chain length and branching of the alkyl group, the length, branching, position, geometric configuration and number of double bonds of the fatty acid chain, and the presence of additional functional groups in the fatty acid chain. Most commercial biodiesel fuels are mainly composed of natural medium- to long-chain (C16-C18) fatty acid methyl esters, for which the main structural difference is consequently the number of double bonds [54].

A straight fatty acid chain palmitic (C16:0) acid, stearic (C18:0) acid, oleic (C18:1) acid, linoleic (C18:2) acid and linolenic (C18:3) acid are the major common fatty acid found biodiesel. Individual fatty acids distinguished from one another by the nature of the hydrocarbon chain and double bonds. The fatty acid hydrocarbon chain varies in length from 4 to 24 carbon atom and can be classified based on a number of double bonds that can be saturated, monounsaturated (one double bond) or polyunsaturated (2 or more double bonds).



Formula	Common Name	Abbrev.
$CH_3(CH_2)_{16}COOH$	Stearic Acid	C18:0
$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	Oleic Acid	C18:1
$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	Linoleic Acid	C18:2
$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$	Linolenic Acid	C18:3

A higher concentration of unsaturated fatty acids is an indicator of the number of double bonds present in its fatty acid chain representing a higher degree of unsaturation which are mainly linoleic acid (18:2) and oleic acid (18:1) [54].

When the degree of unsaturation of oil increases the oxidation of the unsaturated fatty acids component easily occurs and it could lead to degradation of the oil. This is the reason for auto-oxidation is due to with the level of degree of unsaturation of oil the oxygen content increase because of the decrease in the molecular weight associated with the displacement of two hydrogen atoms by each double bond. The degree of unsaturation and the properties of alkyl esters has correlated in a number of ways, while the level degree of unsaturation decrease (monounsaturated fatty acid) excellent quality biodiesel is produced. Biodiesel with low-level unsaturation have excellent characteristics in fuel stability, ignition quality and flow properties at low temperature[39].

The compounds of Argemone ochroleuca seed oil were analyzed using GC-MS. The compounds of this plant detected were (9Z,12Z)-octadeca-9,12-dienoic acid (linoleic acid) 58.72%, (E)-octadeca-9-enoic acid (Oleic acid) 22.35%, Hexadecenoic acid (palmitic acid) 13.48%, Methyl stearate 4.81%, Methyl tetra decanoate 0.26%, 2-Pentanamine 0.19% and 2-(E)-heptanoic acid,(4S)-4-[((S)-alanyl)amino]-6-methyl 0.19 % [55]. This indicates that (9Z,12Z)-octadeca-9,12-dienoic acid (linoleic acid) and Oleic acid remained as a major oil constituent of Argemone ochroleuca seed oil analyzed.

Table 2.1 Fatty acid distribution of animal and vegetable oil sources [56]

Sources	Palmitic 16:0	Palmitoleic 16:1	Stearic 18:0	Oleic 18:1	Linoleic 18:2	Linolenic 18:3
Rape oil	3.5	-	0.9	64.4	22.3	8.2
Olive oil	9.2	0.8	3.4	80.4	4.5	0.6
Sunflower	6.0	-	4.2	18.7	69.3	-
Soybean	10.6	-	4.8	22.5	52.3	8.2
Palm oil	47.9	-	-	4.2	37	9.1
Cottonseed	28.7	-	0.9	13	57.4	-
Poppy seed	12.6	0.1	4.0	22.3	60.2	0.5
Sesame	13.1	-	3.9	52.8	30.2	-
Castor oil	1.1	-	3.1	4.9	1.3	-
Jatropha	13.3	1.0	4.9	32.0	45	0.2
Fleshing oil	27.25	5.10	13.23	42.06	2.04	0.16
Yellow grease	23.2	3.8	13.0	44.3	7.0	0.7
Brown grease	22.8	3.1	12.5	42.4	12.1	0.8
White grease	23.3	3.5	11.0	47.1	11.0	1.0

2.7. Biodiesel Production Process

High viscosity, Fatty Acid (FA) composition and free fatty acids (FFAs) content of Vegetable oils prevent directly use as a fuel in diesel engines. To overcome this issue, the conversion of triglyceride to their respective Fatty Acid Alkyl Esters (FAAE) is widely investigated by several authors in different production processes.

The continuous base-catalyzed process is the most widely used biodiesel process to investigate the possibility of large-scale production further. The continuous base-catalyzed process is divided into four main sections, namely; crude oil degumming, refining, and drying; transesterification reaction, ester washing, and methanol recovery and glycerol refining[57].

Cost of biodiesel still more expensive than fossil fuel petroleum-derived diesel due to the higher feedstock and processing costs. The production cost can be reduced by creating a continuous process, making the price of biodiesel competitive with respect to fossil fuels hence it reduces the overall cost of biodiesel production cost. A continuous process, the feed is sent continuously to a series of equipment, with each piece usually performing a single unit operation. In order to be profitable, their plants need to be large and operate throughout the year, and the storage facilities can be considered to overcome the feedstock availability and seasonal demand but the production cost will increase [58].

A continuous process is not economical for laboratory-scale since it requires high capital as well as operation and energy cost. Hence, to acquire a more effective and efficient process system, and flexible biodiesel production is necessary. The simplest method for producing alcohol esters is to use a batch, stirred tank reactor[31].

A batch process is one in which a finite quantity of product is made during a period of a few hours or days. One advantage of the batch process over continuous is its flexibility and the process needs the use of very low methanol since the methanol vapor can be recycled back to the reactor by the condenser and separate after use once time. The other advantage of batch processes with each piece equipment performing multiple operations and depending on the seasonal demand. Because of the amount of methanol and the small size of equipment catalyst loadings range is varies from 0.3% to about 1.5% the most commonly used catalyst is sodium hydroxide and potassium hydroxide. After Transesterification completion rates of yield in the range of 85 to 95% have been reported[31][58].

2.8. Technologies Used in Biodiesel Production

Direct injection of vegetable oil in diesel engines is restricted by some unfavorable physical properties, particularly their viscosity. The higher viscosity of vegetable oil is caused to poor fuel atomization, incomplete combustion and carbon deposition on the injector and valve seats resulting in serious engine fouling. There are four commonly employed methods to make biodiesel from vegetable oils and animal fats. They are (1) direct use and blending with diesel fuel, (2) emulsification (3) thermal cracking (pyrolysis) by means of heat and (4) transesterification (also called alcoholysis). The most practical technique is transesterification with methanol among these, transesterification of vegetable oils appears to be more suitable because the by-product (glycerol) has commercial value [28].

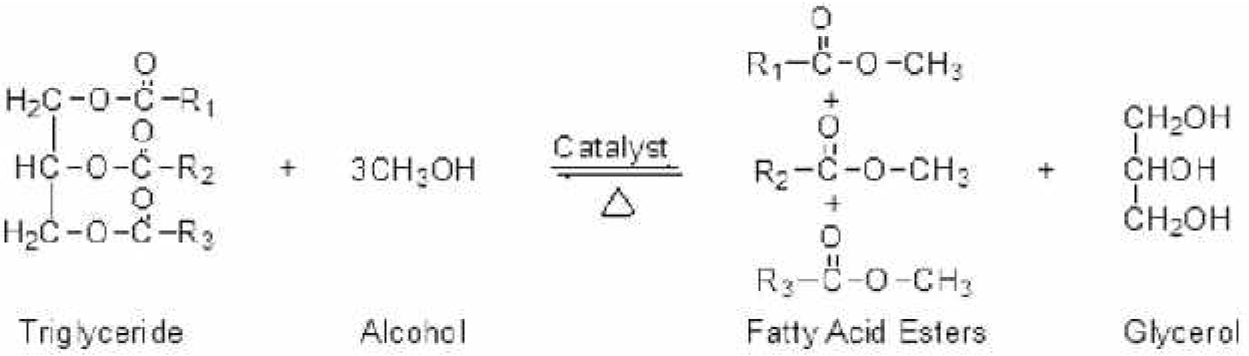
2.8.1. Transesterification

Transesterification of oil is defined as chemically transforming triglycerides into methyl ester and glycerol when vegetable oil reacts with an alcohol in the presence of a strong acid or base. Transesterification converts raw and viscous triacylglycerol’s/free fatty acids to lower molecular weight fatty acid alkyl esters [17]. Due to the high value of acid content in vegetable oil, two-step is needed transesterification to convert the high FFA oils to its mono-esters. First process done with acid catalysts to reduce the higher FFA value in the oil by esterification with methanol and acid catalyst after that that alkali catalyst is used for methyl ester production by chemical reaction occurs between triglyceride and alcohol [59].

Different types of alcohol can be used for the transesterification process but due to economical and efficiency value, Ethanol and methanol are the most suitable for the production process. Ethanol is more renewable alcohol because it can be produced by the fermentation process and also less toxic. Methanol is widely used because more reactive and produces more volatile fatty, cheaper, effectiveness, acid methyl esters, is preferred over ethanol. The reaction rate and yield can be also improved by the use of a suitable catalyst [29].

Transesterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is employed instead of water. Transesterification converts vegetable oil into fatty acid methyl esters (FAME) with the appropriate properties for diesel fuel oil. This process has been widely used to reduce the viscosity of triglycerides, thereby enhancing the physical properties of renewable fuels to improve engine performance. Thus, fatty acid methyl esters (known as biodiesel fuel) obtained by transesterification can be used as an alternative fuel for diesel engines [60].

The transesterification process consists of a sequence of three consecutive reversible reactions. That is, conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. The glycerides are converted into glycerol and yielding one ester molecule in each step. The properties of these esters are comparable to that of diesel. The overall transesterification reaction can be represented by the following reaction scheme.



1 Supercritical transesterification

The transesterification reaction can be proceeded in supercritical methanol without any catalysts, uses supercritical alcohol at high temperatures and pressures in a continuous process. In the supercritical state, the oil and ethanol are in a single phase, and the reaction occurs spontaneously and rapidly. To produce biodiesel by supercritical methods is a much simpler process, particularly in the purification step because the catalyst removal step is eliminated. The process can tolerate water in the feedstock and free fatty acids are converted to esters instead of soap, so a wide variety of feedstock can be used. As high temperature and pressure are required, cost energy production is higher [61].

2. Lipase catalyzed transesterification

Using enzymes as a catalyst for the transesterification is verified by many researchers as good yield could be obtained from crude and used oils using lipases. The use of lipases makes the reaction less sensitive to high FFA content which is a problem with the standard biodiesel process. One problem with the lipase reaction is that ethanol cannot be used because it inactivates the lipase catalyst after one batch [60].

3. Homogeneous alkali-catalyzed transesterification

Commercial biodiesel from plant oils is produced mostly by using very effective homogeneous catalysts such as alkali or acid. Alkalis used for transesterification include NaOH, KOH, carbonates, and alkoxides such as sodium methoxide, sodium ethoxide, and sodium butoxide. Alkali-catalyzed transesterification proceeds approximately 4000 times faster than that catalyzed by the same amount of an acidic catalyst. Sodium hydroxide and potassium hydroxide are more effective alkali catalysts [60].

4. Homogeneous acid-catalyzed transesterification

Acids used for transesterification include sulfuric, phosphoric, hydrochloric, and organic sulfonic acids. Although transesterification by acid catalysis is much slower than that by alkali catalysis, acid-catalyzed transesterification is more suitable for glycerides that have relatively high free fatty acid contents and more water as it prevents the formation of soap stock. Conversely, the addition of an excessive amount of catalyst gives rise to the formation of an emulsion, which increases the viscosity and leads to the formation of gels. These hinder the glycerol separation process and, reduce the apparent ester yield [60]. In general, the ethyl esters of monounsaturated or short-chain fatty acids with 2% sulfuric acid should make good alternative fuels.

5. Heterogeneous acid and base-catalyzed transesterification

Acid catalysts can be used in combination with a base catalyst (two-stage process). High fatty acid-containing low-cost feedstock like waste oil can be processed by this two-stage method. In the first stage, free fatty acids are converted to methyl esters by the acid catalyst, and then base catalyst converts the leftover triglycerides to methyl esters [14] [62].

2.9. Variables Affecting Alkaline Catalyzed Transesterification Reaction

The main factors affecting transesterification are the amount of alcohol and catalyst; reaction temperature, pressure and time; the contents of free fatty acid (FFAs) and water in oils.

2.9.1. Molar Ratio of Alcohol to Oil

The most common primary alcohol used in biodiesel production is methanol, although other alcohols, such as ethanol, isopropanol, and butyl, can be used. Three-mole alcohol and 1-mole triglyceride stoichiometric ratio require for transesterification reaction require to produce 3-mole fatty acid methyl ester and 1-mole glycerol. But in practice, three mole of alcohol is not sufficient to produce the theoretical amount of methyl ester in a shorter time due to different reason. Therefore, a higher amount of molar ratio is required to increase the miscibility and to enhance the contact between the alcohol molecule and the triglyceride it shifts the reaction toward completion to improve the yield of product [63]. However, the level of purity of alcohol is crucial for its successful application in the production of biodiesel. This is because the soap formation and poor yield happen due to the presence of water in alcohol it causes hydrolysis of triglycerides to free fatty acids during transesterification reaction.[64].

The effect of molar ratio on conversion efficiency has been studied by several scholars on the transesterification of different sources of biodiesel. The effects of the methanol to oil ratio on the esterification of rubber seed oil, jatropha oil, Jatropha curcas, Sterculia foetida, and Ceiba pentandra was conducted within 6:1, 8:1, 10:1, 12:1 and 15:1 methanol to oil ratio for 3 h. The maximum conversion efficiency is obtained very close to the molar ratio of 9:1. However the use of molar ratios above 9:1 the conversion efficiency more or less remains the same because the excess methanol moves over the ester layer and it makes difficult to the separation of glycerol. Excess methanol in the ester decreases the flashpoint of the biodiesel [65].

In the transesterification of Soybean, sunflower, peanut, Karanja and cottonseed oils with alcohol, the highest conversion being achieved at 6:1 molar ratio than a ratio of studied the effect of molar ratios (from 1:1 to 24:1) on ester conversion of vegetable oils[66][67]. Transesterified vegetable oil at different temperatures and an organic solvent as a catalyst and found that the conversion increased with increasing molar ratios of methanol to oil. Thus, a molar ration of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% on a weight basis. As the molar ratio decreased to the theoretical ratio of 3:1, the percentage of ester decreased to 82% [14][60].

The conversion of FFA from waste cooking oil is studied at different molar ratios from 3:1 to 9:1. When molar ratio 3:1 at 3 h 91.6% methyl ester is extracted from crude oil. The conversion of FFA to FAME in the same reaction time was increased when the excess amount of methanol added. However, after a 7:1 molar ratio increment of conversion was relatively slow [68][39].

2.9.2. Alkali Catalyst Amount

A catalyst is needed to improve the transesterification reaction and amount of yield production. Since alcohol and triglycerides are immiscible at room temperature, it avoids the mass transfer and limits the performing of reaction under intrinsic kinetics. Because an emulsion is very quickly formed which is then broken down into two phases, that is, an upper phase constituted by methyl esters and a lower one formed by glycerol. When alkaline is used as catalyst, it dissolves into the alcohol and then triglycerides diffuse through this mixture, and so the reaction is initially mass transfer controlled. As a result of less corrosive to industrial equipment, alkaline catalysts such as sodium hydroxide and potassium hydroxide are most widely preferred in industrial processes.

The amount of FFA content affects the purity of the oil, So FFA content different non-edible vegetable oil was studied to be decreased with an acid catalyst to obtain maximum product by use of the different methanol-oil ratios and acid catalyst concentrations. Acid-catalyzed alcoholysis can be used when the raw materials are low-grade oil or have a high free fatty acid content; because direct use of alkaline base catalyst for transesterification reaction reduces the conversion rate as a result of high content of fatty acids cause to deactivate or neutralize an alkaline catalyst and the high content of FFA may induce the saponification during transesterification. The different experiment shows that 1% of sulphuric acid with an increasing amount of methanol ratio decreased FFA content effectively[6][63][69].

The concentration effect in the range of 0.3–2w % sodium hydroxide alkaline catalyst is studied, to see the conversion efficiency of different vegetable oil. The maximum conversion of methyl ester up to 98.01% is achieved at 1% of NaOH. However, the conversion amount of methyl ester decreased to 89.33%, when the amount of catalyst is decreased within the range of 0.5–0.75 wt.%. Because esterification does not take place for an insufficient amount of NaOH due low amount of catalyst is not well reacted with oil completely. After a 1% conversion rate is an insignificant improvement. Further increase in catalyst concentration does not affect the conversion but adds to extra cost, as the catalyst needs to be removed from the reaction mixture after completion of the reaction [14] [10] [70] [26][71].

The effect of excess amount of catalyst in transesterification reaction on different oilseed is studied. High concentration effect of catalyst is not only decreasing the yield of methyl ester but also rise to the formation of an emulsion, which increased the viscosity and led to the formation of gels. The methyl ester yield decreases after concentration 1.25 wt.% of NaOH catalyst and 12:1 M ratio because the high amount of NaOH catalyst will cause insolubility to oil and methanol this cause to heterogonous phase for ester yield due to the formation of emulsion and saponification formation [64][72] [73].

The effect of catalyst concentration on Methanolysis of Karanja oil is carried out with KOH at a concentration of 0.25–1.5% wt. with different temperature and molar ratio of oil and alcohol. However, compared to 1% KOH the lower catalytic concentration i.e. 0.25% of KOH the effectiveness of catalyst is insignificant to accomplish the reaction. At 1% KOH the optimal reaction is completed in 3h in with a yield of 96% and the reaction was completed 86.4% in 10min. It also observed that an increase in catalyst concentration beyond 1 % w/v of KOH results in a decrease in the yield of methyl esters due to the formation of soap and increased the viscosity of the reactants in presence of a high amount of catalysts [67].

Production biodiesel from Nigerian Mango Seed Oil at different catalyst concentration is studied. The percentage conversion of methyl ester increases from 0.33 to 1 %w/v, and thereafter the yield gradually decreases above this concentration (1 % w/v of KOH). Hence the result shows that yield at 1.17 % w/v was lower than the yield obtained at 0.33 % w/v. This can be clearly explained that the excess amounts of catalysts cause the reversible of transesterification reaction[6].

2.9.3. Reaction Time and Temperature

The study on the effect of temperature is extremely imperative for any chemical reaction. Since alcohol and triglycerides are immiscible at room temperature, as the temperature increase in the transesterification reaction, the conversion rate of the oil also increases. Increase temperature causes the decrease of oil viscosity, improving the contact between reactants and hence, in general, the higher temperature the better the performance [56].

Temperature had a positive influence on methanolysis high temperatures favor reactions with higher activation energy, and low temperatures those with lower activation energy i.e. the energy required to derive the chemical reaction is gained from the temperature. It was observed in various vegetable oil transesterification reactions.

The reaction temperatures maintained by most researchers ranged from 45–70 °C. Due to higher temperature, the volume of MeOH would be lowered, for economic efficiency and effectiveness, 60 °C at 1 h can be considered a suitable condition for the transesterification of vegetable oils [74].

The maximum conversion of FFA to FAME was 93.87% and 95 % from palm and Castor oil was achieved at the optimum reaction temperature of 60°C. At this temperature, the FFA content was reduced from 23.2% to below 2%. It was also observed that the conversion of FFA to FAME decreased with an increase in reaction temperature higher than 60 °C [72] [74][75].

The effect of temperature in the range 34–64 ^{0}C on biodiesel conversions from jatropha oil at a feed molar ratio of 1:1.5 and at a speed of agitation 550 rpm was studied. The conversions obtained at 34 ^{o}C, 44 ^{o}C, 54 ^{o}C and 64 ^{o}C were found to be 98.01%, 98.11%, 98.24% and 98.38%. It is clearly observed the conversion of methyl ester temperature effect very small. The increment of temperature does not show much significant change in the yield [76].

The effect of reaction time on the yield of methyl esters is studied for methanol/oil molar ratio of 6:1 after 3h was 97% whereas the same yield was obtained with the molar ratio of 24:1 in 30min. It was found that the reaction was faster with a higher molar ratio of methanol to oil whereas longer time was required for lower molar ratio (6:1) to get the same conversion [67].

2.9.4. Free Fatty Acid and Moisture Content

The conversion of methyl ester is affected by different factors from this to the high level of FFA above 1% in the triglyceride. The FFA amount of different oil will vary and depend on the quality of feedstock. In the transesterification process, the vegetable oil should have an acid value less than one and all materials should be substantially anhydrous to complete the reaction unless the amount of acid value is greater than one, the effectiveness alkaline catalyst NaOH or KOH is reduced because free fatty acids consume and neutralized the base catalyst. [20][69].

Alkaline catalytic trans-esterification is the most common industrial biodiesel production. The presence of FFA in the oil/fat can lead to an increase in the use of catalysts, and complicate phase separation and product neutralization due to the soap formation. In order to avoid soap formation, normally, acid catalytic trans-esterification or acid pretreated alkaline catalytic trans-esterification has to be performed when FFA content is greater than 0.5% (w/w) [37].

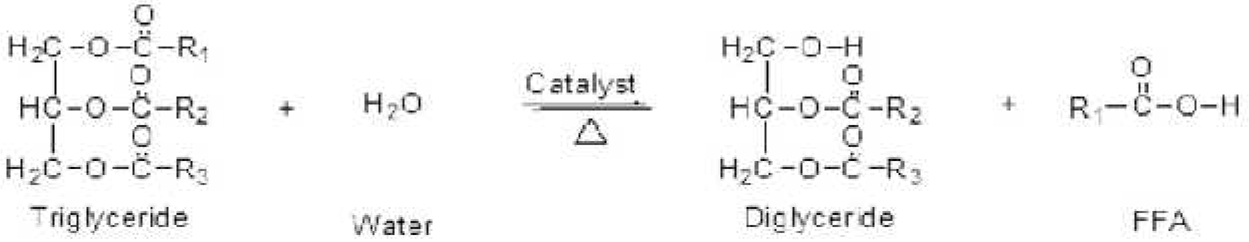
For alkali catalyzed transesterification, the water must be removed from glycerides and alcohol because water causes the formation of FFA this causes partial reaction change to saponification, which produces soap. The soap consumes the catalyst and reduces the catalytic efficiency, as well as causing an increase in viscosity, the formation of gels, and difficulty in achieving separation of glycerol. 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, diminishing their effectiveness [60].

2.10. Side-reaction Affecting the Yield of Fatty Acid Ester from Transesterified Oils

In the conventional transesterification of animal fats and vegetable oils for biodiesel production, free fatty acids and water always produce negative effects, since the presence of free fatty acids and water causes soap formation, consumes catalyst and reduces catalyst effectiveness, all of which resulting in a low conversion.

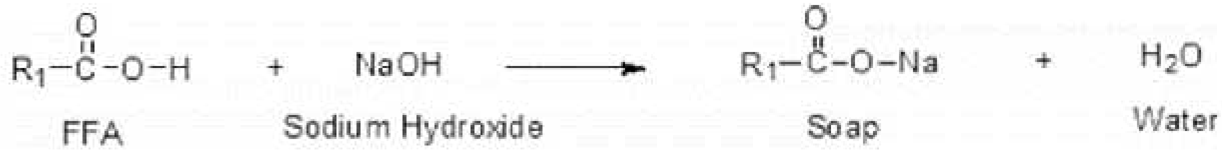
2.10.1. Hydrolysis

The higher moisture content of reactants either from (i) water formed during saponification reaction; or (ii) from the moisture content of the reactants start hydrolysis reaction. During hydrolysis, triglycerides are hydrolyzed into diglycerides and FFA formation takes place. Hydrolysis reaction retards the transesterification reaction as well. Moreover, the presence of water could also cause emulsions. Therefore, when the water content is greater than 0.05% (w/w), the water removing step is required[37][77].



2.10.2. Saponification

In presence of an alkali catalyst, FFAs present in the vegetable oils undergoes saponification reaction in preference to transesterification. Saponification is an undesirable reaction because the formation of soap lowers biodiesel yields significantly and inhibits separation of esters from glycerol. Saponification reaction also consumes the catalyst hence lowers the ester yield, thus increasing catalyst requirement.



$$R_1-\overset{O}{\overset{\|}{C}}-O-H + NaOH \longrightarrow R_1-\overset{O}{\overset{\|}{C}}-O-Na + H_2O$$

where R represents fatty acid chains.

An Index of the average size and weight of fatty acids. Fatty acid methyl esters with a carbon chain length from 12 to 20 are considered as biodiesel. The saponification value indicates the chain length of triglycerides. Shorter chain length leads to higher SV [37].

2.11. Characteristics and Specification of Biodiesel

Fuel characterization data show some similarities and differences between biodiesel fuels and diesel. The industrial value of a particular oil or fat depends upon its physical and chemical characteristics. The biodiesel was characterized by determining its viscosity, density, cetane number, cloud and pour points, flash and combustion points, the chemical composition of fatty acids, and higher heating value according to ASTM standards.

2.11.1. Viscosity

Viscosity is a measure of the internal fluid friction or resistance of oil to flow, which tends to oppose any dynamic change in the fluid motion. As the temperature of the oil is increased its viscosity decreases and it is, therefore, able to flow more readily. The lower the viscosity of the oil, the easier it is to pump and atomize and achieve finer droplets.

It is the most important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors.

2.11.2. Density

Density is an important property of biofuel. Density is the mass per unit volume of any liquid at a given temperature is another important property of biofuel. Density has importance in diesel engine performance since fuel injection operates on a volume metering system. Also, the density of the liquid product is required for the estimation of the Cetane index. Specific gravity is the ratio of the density of a liquid to the density of water.

2.11.3. Flash Points and Fire Points

The flashpoint and fire point temperature of liquid fuel are defined as the lowest and highest temperatures for the vapors above the liquid to be ignited when exposed to a flame. The flashpoint temperature of biodiesel fuel is the minimum temperature at which the fuel will ignite (flash) on the application of an ignition source [78].

Flashpoint varies inversely with the fuel's volatility. Minimum flashpoint temperatures are required for proper safety and handling of diesel fuel. The flashpoints of bio-oils are usually measured with closed-cup testers and vary in the range of 40–70^{O}C or above 100 ^{O}C, depending on the contents of the light organic volatiles. It is usually difficult to measure the flashpoints at 70–100 ^{O}C, due to vigorous evaporation of water, which will inhibit the ignition of the fuel vapors. The flashpoint and fire point of the sample is determined with an open cup tester. Fuels having high flash points, have lower volatilities, causes delayed ignition, arising difficulties during the startup of the engine [79].

Fire point is the lowest temperature at which a specimen will sustain burning for 5 seconds. These two parameters have great importance while determining the fire hazard (temperature at which fuel will give off inflammable vapor).

2.11.4. Iodine Value

Iodine number is a measure of the degree of unsaturation of the fuel. The unsaturation in the fatty acid chain is the main source of thermal instability and reason for causing carbon deposits due to burning [79]. Iodine value measured in grams, that is taken up by 100 grams when formally adding iodine to the double bonds of sample [80]. Saturated sample of oil takes up no iodine; therefore, their iodine value is zero; but unsaturated sample of fuel takes up iodine. (Unsaturated compounds contain molecules with double or triple bonds, which are very reactive toward iodine). The fatty acid composition will affect the iodine value whereas the higher iodine value leads to rapid deterioration of lubricant oil [39].

2.11.5. Cetane Number (CN)

The physical and chemical properties of fuel play a very important role in ignition quality or ignition delay. Cetane number (CN) of the fuel is one such important parameter which is responsible for the delay period is related to the time required for a liquid fuel to ignite after injection into a compression ignition engine. Fuel of a higher cetane number gives a lower delay period and provides smoother engine operation. Biodiesel has a higher CN than petrol-diesel because of its higher oxygen content [78]. Having higher cetane numbers and producing lower carbon monoxide and hydrocarbon emissions. They also present some technical challenges such as low volatility, high pour and cloud points and cold filter plugging temperature. They contain essentially no sulfur; therefore, they greatly reduce sulfur dioxide emissions from diesel vehicles.[54]

Cetane number (CN) of biodiesel samples is determined according to ASTM D 975. This test method measures the ignition delay and utilizes a constant volume combustion chamber with direct fuel injection into heated, compressed air [54].

2.11.6. Saponification Value

The saponification value is used as an indicator of fatty acid chain length. The saponification value can be defined as the amount of ml of KOH required to complete the hydrolysis of one gram of oil. The critical part of the diesel engine may be damaged by corrosion due to the high saponification value of oil. The range of saponification values for various types of bio-oils is 160– 190 mg KOH/g [79] [81].

2.11.7. Heating Value of a Fuel

The suitable properties of methyl ester from vegetable oil used as an alternative source of diesel fuel also investigate by its heating value. It measures the energy content in fuel when the fuel is burned completely the temperature reaches its maximum point and the products of combustion are cooled back to the initial temperature it shows the thermal energy released per unit quantity of fuel. A bomb calorimeter according to ASTMD240 standard method was used to measure the calorific value of vegetable oils and their methyl esters [78].

2.11.8. Water Contents

The water content of biodiesel is one of the indicators of the purity and quality biodiesel. Excess water in biodiesel influences the accurately measure the net volume of actual fuel in taxation, sales, exchanges, and custody transfer. High water content limits the shelf-life of biodiesel due to oxidation stability [82]. Evaporation methods rely on measuring the mass of water in a known mass of the sample. The moisture content is determined by measuring the mass of a fuel sample before and after the water is removed by evaporation.

Table 2.2 An international standard requirement for biodiesel characterization [83]

Property	Units	Diesel	Biodiesel standards	
			ASTM D 6751-02	DIN EN 14214
Density at 15°C	kg/m^3	850	-	860-900
Viscosity 40°C	mm^2/s	2.60	1.9-6.0	3.5-5.0
Flash point	°C	68	>130	>120
Cetane number	-	51	51.0	-
Acid value	mg KOH/g	-	<0.8	<0.5
Iodine value	-	-	-	120
HHV	MJ/kg	42	-	-
Ash	wt%	0.01	<0.02	<0.02
Water content	mg/kg	0.02	<0.03	<0.05

2.12. Chapter Summary

From the study of works of literature, many researchers have been searching for different experimental investigations for cheaper and non-edible oils to be used as an alternative feedstock for biodiesel production. Few sources have been identified such as waste cooking oil and oils from non-edible oil-producing plants such as Jatropha curcas, Pongamia pinnata, Calophyllum inophyllum, cottonseed, rubber seeds, and tobacco seeds. Nevertheless, the world biodiesel feedstock should never be too dependent on certain sources as it could bring a detrimental effect in the long run. The worlds' dependence on crude petroleum is a perfect example. Therefore, biodiesel feedstock should be as diversified as possible, depending on geographical locations in the world.

CHAPTER THREE

3. MATERIALS AND METHODS

In this chapter, material selection and preparation and methodology used production process biodiesel was developed. Experimental set-up for laboratory and experimental design for the reaction for different run by changing the parameter was established to obtain the maximum conversion rate and best quality parameter for production of biodiesel from Aregmone ochroleuca seeds oil. The different type of characterization method and equipment used for the test of biodiesel properties was designated. Finally, the separation and purification method of biodiesel from glycerol has been drawn.

3.1. Materials

Materials that were used for biodiesel production were Aregmone ochroleuca seeds oil, methanol alcohol, potassium hydroxide catalyst, Sulfuric acid, property test study chemicals as shown in Table 3.1. The Aregmone ochroleuca seeds were collected from South Wollo, Tenta waste Land. Chemicals were bought from Private Limited Company; in Addis Ababa. Additional materials were used for this research: reactor, flask, beaker, measuring cylinder, separatory funnel, protective equipment, thermometer, PH meter, hot plate with magnetic stirrer, digital balance and glassware.

Table 3.1 Chemicals used for biodiesel production

Activities	Chemicals used
Acid value test	Potassium hydroxide, ethanol alcohol, phenolphthalein, and distilled water.
Saponification value test	Potassium hydroxide, hydrochloric acid, ethanol alcohol, phenolphthalein, and distilled water
Iodine value test	Chloroform, glyceryl acetic acid, Iodine, potassium iodide, starch indicator, sodium thiosulphate
Oil degumming and Neutralization	distilled water and sodium chloride
Biodiesel production	Methanol alcohol, sulfuric acid, and Potassium hydroxide

3.2. Methods

The methodology of the research was the batch laboratory-scale production of biodiesel from argemone oil, methanol, and potassium hydroxide catalysis through transesterification methods and the characteristics of argemone biodiesel were compared with ASTM and EUROPEAN Biodiesel standard.

3.2.1. Experimental Set up for Biodiesel Production

Figure 3.1 illustrates a schematic diagram of experiments that were conducted in a laboratory-scale setup which consists mainly of a three-necked round bottom flask (250 mL), equipped with a thermometer and a coil condenser. The large necke in the middle of the flask was connected to a reflux condenser, a thermometer was placed in one of the two side necks, and the third neck was reserved for sampling during extraction process period. The flask was submerged in an adjusted temperature water bath with a magnetic stirrer. After the required reaction time, the reaction mixture was carefully transferred to a suitable separating funnel [33][84].

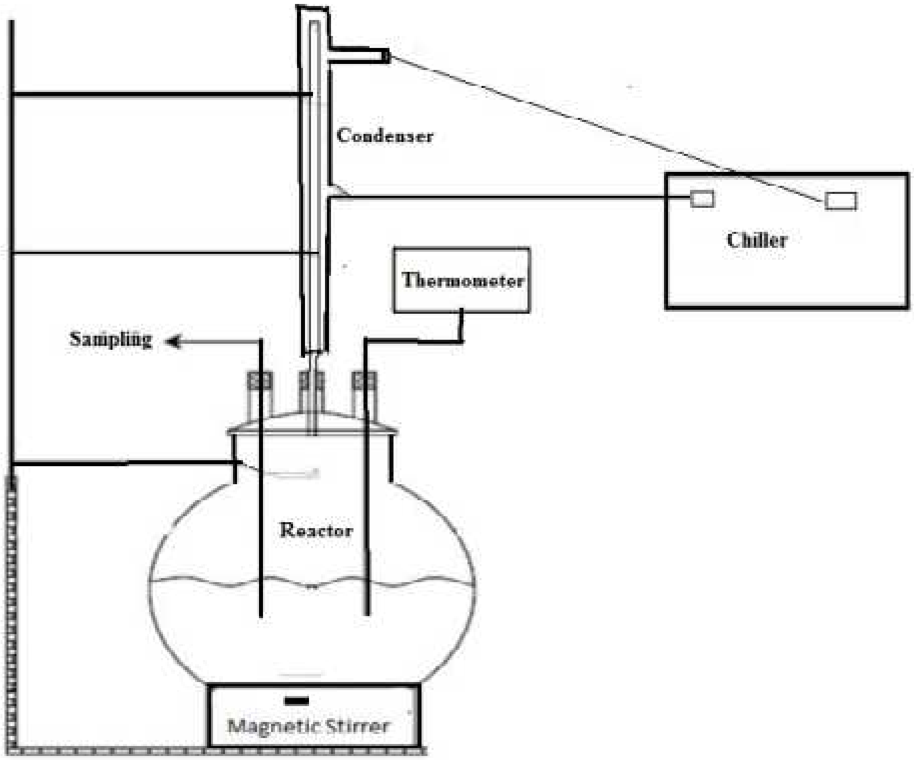


Figure 3.1 Experimental set up for biodiesel production in laboratory-scale

3.2.2. Experimental Work Design

The pretreatment (Acid catalyze) esterification process selection parameter levels were based on previous research work maximum yield giving molar ratio of (9:1). Increasing the methanol amount was no significant effect on the acid value or FFA concentration reduction. It was due to the effect of water produced during the esterification of FFA. In practically, the esterification process might be improved by water removal in the mixture continuously. Therefore, there was an optimum quantity of methanol required to complete the esterification process of all FFA in vegetable oil [71]. The, reaction temperature (60^oC), amount of catalyst (0.5,1,1.25,1.5%v/v) H_2SO_4 for the reaction time of 2 hours was conducting to reduce the amount of FFA below 2 % [64][75].

An optimization for percentage yield of biodiesel was designed for three selected factors: Methanol to Argemone oil molar ratio, Amount of catalyst and reaction temperature. The selection of parameter levels was based on previous research works and practical considerations. The upper-temperature level was (65°C) almost equal to the theoretical boiling point of methanol, the amount of catalyst varies in the range of 0.5 and 1% weight of oil was based on literature data [75]. The lower molar ratio (3:1) was the theoretically declared maximum yield giving molar ratio, and the upper molar ratio (6:1) was based on previous research [60]. The reaction time was fixed at 2 hours for all experimental runs. The order for conducting the 18*2 replica experimental runs was presented in table 3.2 by different combinations of three factors reaction temperature, the molar ratio of Methanol to Oil, and KOH concentration. The feed ratio of the experiment varies depend on the parameter evaluated at each specific experiment. The calculation used to determine the amount of the reactant involved for each run was established in Appendix 3-A;

Table 3.2 Order for conducting experimental runs

Run number	Factors		
	Methanol to oil ratio	Operating temperature (^{O}C)	Catalyst (%wt. of oil)
1	3:1	45	0.5
2			1
3		55	0.5
4			1
5		65	0.5
6			1
7	4:1	45	0.5
8			1
9		55	0.5
10			1
11		65	0.5
12			1
13	6:1	45	0.5
14			1
15		55	0.5
16			1
17		65	0.5
18			1

3.2.3. General Method to Conduct the Experiment

This research was conducted mainly based on the following experimental procedures [59].

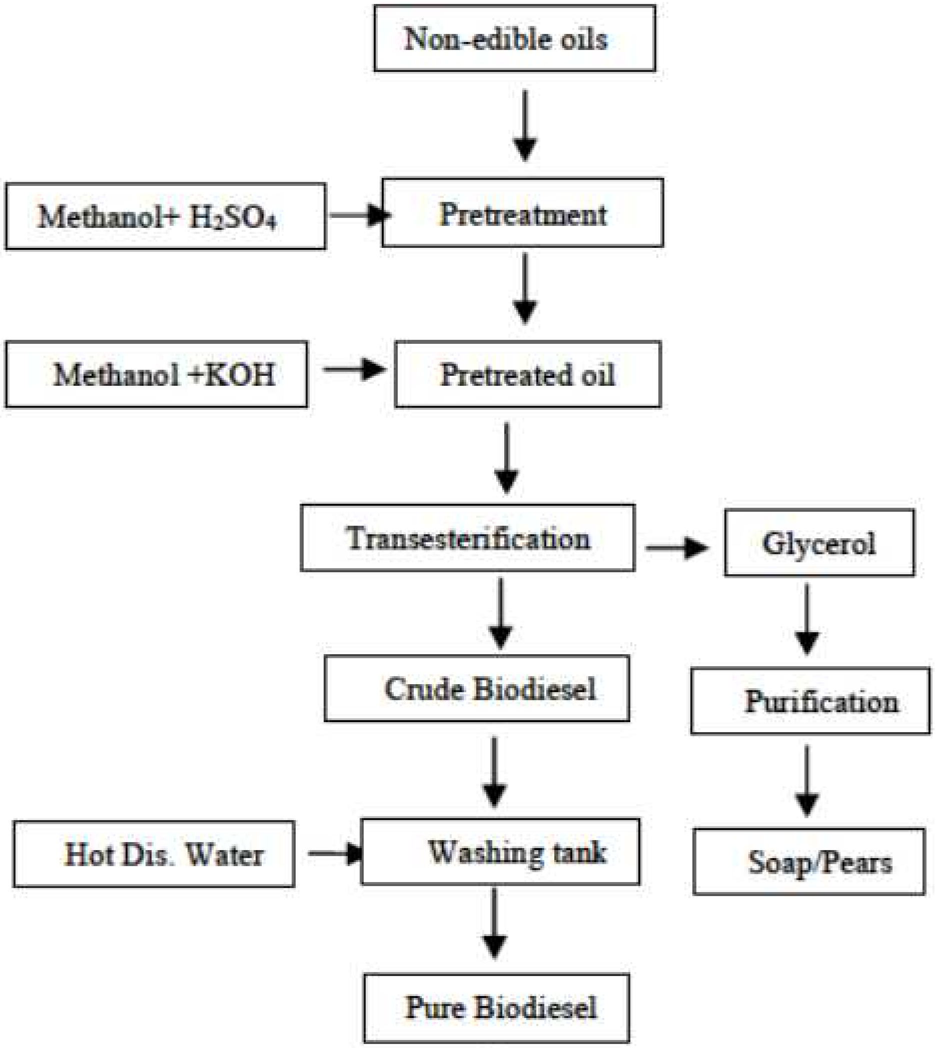


Figure 3.2 Production process of biodiesel

3.2.4. Argemone ochroleuca Oil Extraction

For extracting the oil, the samples of Argemone ochroleuca seeds were cleaned and dried at 50°C to remove some moisture from the seed. The method used to extract the oil was soxhlet extraction and mechanical pressing extraction methods.

3.2.4.1. Oil Extraction Using Soxhlet

200ml of normal hexane was poured into a round bottom flask. 50g of the sample was placed in the thimble and was inserted in the center of the extractor. The Soxhlet was heated for two hours. The experiment was repeated by placing the same amount of the sample into the thimble again by varying particle sizes (0.1-0.5mm, 0.5-0.841mm and 0.841-1.4mm). The weight of oil extracted was determined for each run particle size. At the end of the extraction, the resulting mixture containing the oil was heated to recover the solvent from the oil [27]. After extraction, the solids and the solvent oil mixtures were separated by a settling followed by vacuum filtration. The solvent and oil were separated in a rotary evaporator at a temperature of 70°C. The solvent was recovered using condenser for reusing in the extraction of oil.

Figure 3.3 Soxhlet extraction setup

The yield of oil extracted was calculated by Equation 3.1.

$$\% O \quad = \frac{m \qquad o \quad o}{i \qquad m \qquad o \quad s} * 100 \tag{3.1}$$

3.2.4.2. Oil Extraction Using Mechanical Pressing

The method used to extract the oil was a mechanical pressing of the Aregmone seed by an electrically operated mechanical pressing machine which is available in the workshop of the chemical department at Bahir Dar Institute of technology.

Figure 3.4 Mechanical press oil extraction machine

3.2.5. Purification of the Crude Aregemone Ocheroleuca Oil

For refining, the oil Sedimentation and degumming process methods were applied [45].

1. Sedimentation: This is the easiest way to get clear oil, but it takes about a week until the sediment is reduced to 20-25% of the raw oil volume.

2. Degumming; Gum contains phosphate, protein, carbohydrate, water residue and resin. In order to improve the oxidization stability of the final product, the oil is separated from the gums through the degumming process. In this process, Distilled water 3% (v/v) of oil at 60^{o}C and 0.3% sodium chloride (v/v) of oil were mixed with the oil which was heated at 60^{o}C. The oil and NaCl solution mixture was agitated for 60 min at 60 °C on magnetic stirrer to render fat-soluble phosphatides insoluble. After that, this mixture was separated by density separation process using a separating funnel for at least 4 h in which the phosphate compounds resided at the bottom. Other impurities were separated using a centrifuge at a speed of 1500 rpm for 20 minutes.

Figure 3.5 Degummed oil

3.2.6. Physicochemical Properties Determinations

The physical properties of the degummed oil, pretreated and biodiesel were measured that includes the Acid value, Saponification value, Iodine value, HHV, Cetane Number (CN), kinematic viscosity, Moisture Content, Specific Gravity, Flashing point and an ash content of the oil. The measured properties were then compared with international standards.

3.2.6.1. Acid Value

Acid value (neutralization number) is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number is a measure of the number of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds.

The acid value was determined by titration (EN14104), firstly, a titration solution of 0.1N of KOH in distilled water was prepared. Subsequently, mix 25ml of anhydrous ethanol and 1ml of phenolphthalein solution (1%) and was added to the 250ml conical flask titration beaker and Dissolve 2.5 g of oil in the mixed solvent. Then the oil sample was mixed with 25ml of ethanol and 1ml 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 [82].

First, 0.1N KOH solution preparation in 100 ml of distilled water.

$$N = M = \frac{n}{V_L} \tag{3.2}$$

$$n = \frac{m}{M} \tag{3.3}$$

$$m = MM_w V_{(l)}$$

Substituting values in the above equation gives the acid value

$$A \quad = \frac{M * M \quad * T}{M} \tag{3.4}$$

Where;

M=The molar concentration of titrant (N)

Mm=is the molecular weight of KOH

Tv=is the difference in the volume of titrant (ml) consumed by the oil sample and Blank solutions.

Ms.=is the mass of the sample in grams

3.2.6.2. Saponification Value

The saponification value is the amount of potassium hydroxide required in milligrams to saponify 1g of oil under the conditions specified. It is a measure of the average molecular weight (or chain length) of all the fatty acids present.

To determine the saponification value of the oil, initially, 0.5mol/l potassium hydroxide in anhydrous ethanol (99.5%w/w) and 0.5mol/l hydrochloric acid solution in distilled water was prepared. Then, a 2 g sample was placed in a 250ml conical flask. Next, a 25ml of 0.5mol/l potassium hydroxide in ethanol solution was added. The flask was heated at a temperature of 70^oC and shaken when adjusting the heat so that backflow ethanol did not reach the top of the cooling pipe. After that, the sample was heated for 30 minutes and it was cooled immediately. 5 drops of phenolphthalein were added as an indicator. Finally, the sample was titrated with

0.5mol/l hydrochloric acid solution before the test liquid solidified. The titration was stopped and the value was recorded when the color change was observed. A blank level test was also performed in parallel using all the above procedures without the oil sample addition [85].

Figure 3.6 Saponification value determination

$$S \qquad v \quad ,^{m} \qquad /_{g} = \frac{(V_0 - V_1) \times N \times 56.1}{m} \tag{3.5}$$

Where: Vo= is the blank level titration volume

m= is the mass of the sample

N= is normality of the HCl

V= is the titration volume

3.2.6.3. Iodine Value

Iodine value was measured by Hannus method (EN 14111) [82]. The iodine value determination was done by measuring one gram of biodiesel/oil and dissolving it in 10ml of chloroform. 25ml of Hanus solution (which was prepared by dissolving 13.6g of iodine in 825ml glacial acetic acid by adding 6ml of bromine liquid) and allowed it in dark place for 30min. 10ml of 15% KI (15g of KI dissolved in100 ml) added. The solution was titrated against 0.1N sodium thiosulphate until a yellow solution turns in to almost colorless [54][80][85].

$$I| = \frac{(V_O - V_1)\times N \times 1\ .7}{m} \tag{3.6}$$

Where; Vo= ml of Thiosulphate for blank

V= ml of Thiosulphate for sample

m = weight of the sample

3.2.6.4. Higher Heating Value

Higher Heating Value is the amount of heat released during the combustion of one gram of fuel to produce CO_2 and H_2O at its initial temperature and pressure. The determination of HHV was conducted using empirical equations available. Equations were developed for the calculation of the Higher Heating Value of vegetable oils and biodiesel from their viscosity (ν), density (ρ) and flash point (FP) [86].

The equations between density and higher heating values for biodiesel are

$$H \quad he \quad H \qquad V \qquad (H \quad) = -0.0259\rho + 63.776 \tag{3.9}$$

Where; HHV is Higher Heating Value (MJ/kg) and ρ is density (g/L)

3.2.6.5. Cetane number

Cetane number determination was done using the mathematical relationship between viscosity, density, calorific value, flash point and cetane number (CN) developed by Sivaramakrishnan and P. Ravikumar. An equation was developed relating the cetane number and thermal properties [78].

The CN was calculated using a relation between cetane number and properties of biodiesel so a correlation was developed which is given as Equation 3.8.

$$\text{Cetane Number } (C \quad) = K5 + K4V + K3H \qquad + K2F \quad + K1\rho \tag{3.8}$$

Where *K1, K2, K3, K4, K5* are constants and ν is kinematic viscosity (mm^2/sec), HHV is a heating value (MJ/kg), FP is flashpoint (°C), ρ is density (kg/L).

The values of coefficients for vegetable oils, vegetable oil methyl esters, Karanja blends, jatropha blends are given in Table 3.3

Table 3.3 The value of the constants of the model equation [78]

K1	K2	K3	K4	K5	Types of oil
-132.94	0.0258	-2.556	0.0165	254.4344	For all vegetable oils
-42.13	0.005	-15.855	12.856	556.92	For all vegetable oils methyl esters
152.43	-0.021	0.108	0.3423	-80.866	Karanja biodiesel
-31.44	0.292	0.299	-1.435	52.593	Jatropha biodiesel

3.2.6.6. Kinematic Viscosity

A Brookfield Viscometer was used to determine the viscosity of oil, and the sample was kept in the water thermostat bath until it reaches the equilibrium temperature of 40°C. After maintaining the equilibrium temperature, the appropriate spindle size at a specified speed was inserted to the sample and the reading was taken from the controller[87].

Figure 3.7 Rotating-Viscometer

3.2.6.7. Moisture Content Determination

The empty dish was weighed with and without the amount of seed and dried in an oven at105°C for 8hr, weighing each 2hr till constant weight is obtained and finally the weight was taken and compared with the initially recorded weight. The percentage weight in the seed was calculated using the formula [72]:

$$\text{Moisture content}(w/w) = \frac{w_1 - w_2}{w1} * 100\% \tag{3.9}$$

Where; w_1 = Original weight of the sample before drying

w_2 = Weight of the sample after drying

3.2.6.8. Determination of Specific Gravity

The density of the oil is determined by multiplying the density of water with the specific gravity of the oil. The sample was filled into a graduated cylinder (50 ml) and insert a hydrometer to measure the specific gravity of the oil at 20°C [33].

3.2.6.9. Ash Content

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 that adjusted at a temperature of 500°C for 1 hour and after burning the residue sample was weighted and ash content was calculated [24].

Ash content of oil was determined by;

$$\text{Ash content}\%(^{w}/_{w}) = \frac{\text{The final mass of oil after burning}}{\text{The initial mass of a sample}} \times 100\% \tag{3.10}$$

3.2.6.10. Flash Point

For determining the flashpoint of the samples automated Pensky-Martens closed cup apparatus were used to measure in different temperature range according to (ASTM D93)[78][88]

3.2.7. Separation and Purification of Biodiesel from By-Products

After the transesterification process, the product was transfer to the separating funnel and allowed to settle down overnight. After a time two distinct liquid phases crude ester phase at the top and glycerol phase at the bottom would occur. The bottom glycerol phase was removed from the funnel from top ester phase (biodiesel) and transferring to a clean 250mL conical flask.

The biodiesel was then purified by washing with hot distilled water. Hot water can prevent the formation of an emulsion during the performing washing action. The volume of hot water added for washing, 50% v/v (50 ml/100 ml biodiesel sample) warm distilled water (50^oC) was used for the product to remove all the residual by-products like excess catalysts, alcohol, soap, and glycerine. The flask was shaken gently for 1 minute and allow settle down until the biodiesel separate from water. After separation, the biodiesel was transferred to a clean conical flask. The washing process was for several times until the washed water became clear. The clean biodiesel was dried with anhydrous calcium chloride ($CaCl_2$) to remove remaining water and stored at room temperature (28^0C) [82].

CHAPTER FOUR

4. RESULTS AND DISCUSSION

In this chapter, discusses the result obtained from the three steps of the experimental run on the argemone seed oil. The first step an experimental run was conducted to see the effect of particle size on the yield of extraction of oil and physicochemical properties of crude oil were determined. In the second step of the experimental process, the crude oil was pretreated using sulfuric acid to reduce the acid value of crude oil and the experimental run was performed so as to determine the physicochemical properties of pretreated oil. Several experimental runs were conducted under the third step so as to determine the best yield giving parameter combinations and the physicochemical properties of biodiesel obtained by the experimental method are compared with the ASTM and EU standard of biodiesel. Finally, useful conclusions have been drawn from both the experimental and standard results.

4.1. Percentage Yield of Oil and Crude Extracts

From the Soxhlet successive extraction of different particle size of seed of Argemone ochroleuca using the solvent of n-hexane, the yields are tabulated with the percentage in Table 4.1.

Table 4.1 Total %yield for soxhlet extractor for different particle size using n-hexane

Particle size	Extracted oil(g)	Extractedoil (g) replica	Average extracted oil (g)	%yield
0.841-1.4mm	17.249	17.511	17.38	34.76
0.5-0.841mm	18.13	18.406	18.27	36.53
<0.5mm	18.80	19.25	19.03	38.05

The Maximum seed oil yield of Argemone ochroleuca collected from Wollo, Ethiopia, was obtained by Soxhlet extraction from the smaller particle size of the ripe seeds and the yield was 38.05%. The yield of oil reduced by 2% compared to similar species of Argemone Mexicana seed oil (40%) extracted by Soxhlet and collected found in India. It was almost yellowish color, it is an indication of freshness and flavor quality oil because the good quality of oil has a yellowish color and slightly transparent liquid with a characteristic, refreshing and pleasant odor.

Figure 4.1 Oil extracted from Argemone ochroleuca

4.1.1. Effect of particle size on percent yield of oil

Figure 4.2 shows that particle size plays a great role in the yield of Aregmone oil. From the smaller particle size high yield of oil obtained while the particle size was increased the yield of oil decreased gradually. That means less oil was extracted from the larger particles (>0.841 mm) compared to the small size of the particles. The discrepancy in results observed is due to the reason of smaller contact surface area solvent and larger particles this resisted the ingress of solvent to the particle and oil diffusion towards the solvent. Therefore, less amount of oil was transferred from inside the larger particles to the surrounding solution in comparison with the smaller ones. The second aspects relate to the cover of oilseed by nature the cover of argemone ochroleuca seed is tough, it against the ingress solvent through the seed. Thus, an increase in particle size decreased the oil yield.

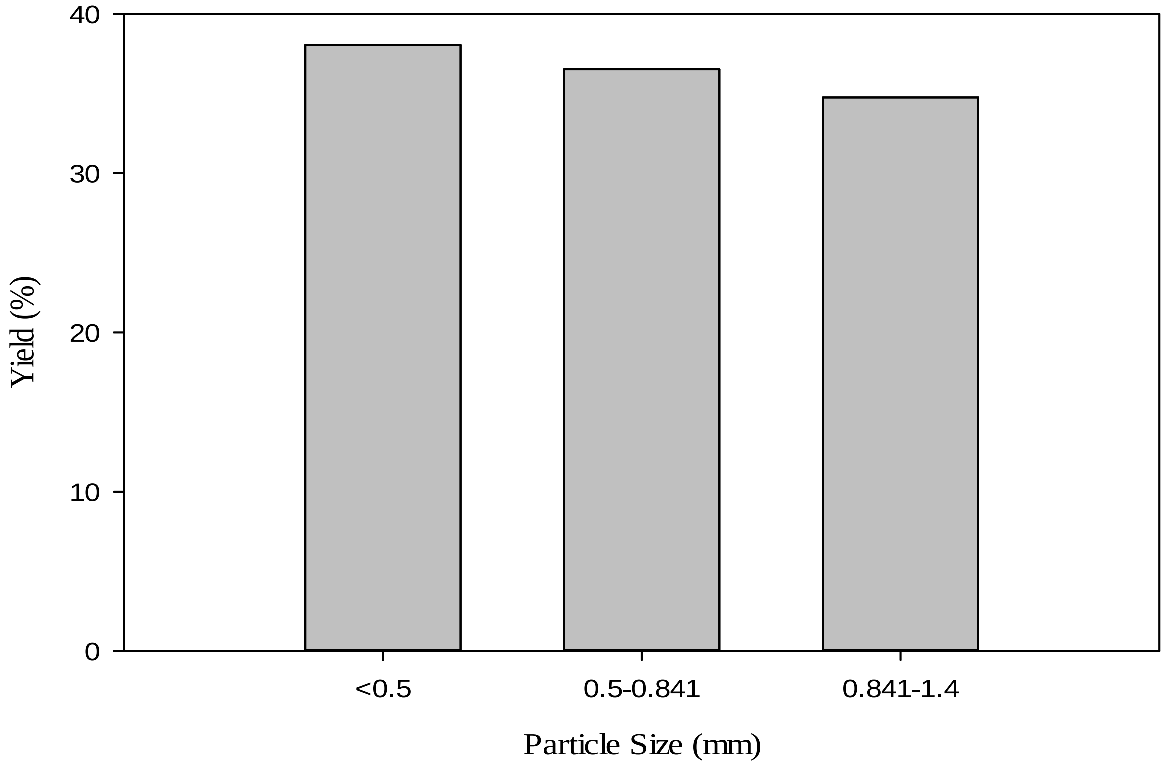


Figure 4.2 Effect of particle size on percent yield of oil

4.2. Physicochemical Properties of Oil

The test results obtained to determine the properties of produced oil were given in Table 4.2.

Table 4.2 Physicochemical properties of the oil

Physicochemical properties	Units	Values
Acid value	mg KOH/g	12.506
Free fatty acid	mg KOH/g	6.253
Saponification value	mg KOH/g	91.34
Specific Gravity	-	0.92
Density @ 20°C	kg/m^3	920
Kinematics viscosity @ 40°C	mm^2/s	33
Ash content	% (w/w)	0.04

As discussed in chapter two FFA and moisture contents have undesirable effects on the transesterification of glycerides with alcohol using a catalyst. Total acid number (AV) indicates the level of free fatty acids (FFAs) present in Aregmone oil. The FFA value of oil is half of experimental result acidic value. From the obtained AV as tabulated in Table 4.2 the FFA value was 6.25%. The high content of free fatty acids (FFAs) oil reduces the biodiesel yield as result during transesterification vegetable oil undergo saponification reaction. The high FFA content (>1 wt%) neutralizes the alkaline catalyst, resulting in reducing the amount of catalyst needed to initiate the conversion of triglyceride to methyl ester. The second problem form soap when a homogenous base catalyst (for example, KOH) is used, resulting in difficulty in separating products and causing a low biodiesel yield. The other effect of higher FFA and unsaturated fatty acid in seed oil made it easier suspectable to oxidation. Therefore, the amount of FFA value must be reduced to less than 1% by using acid-catalyzed esterification of the oil to reduce its effect on biodiesel production. So, the two-step transesterification process of the vegetable oil was carried out for feedstock having the high FFA content argemone ochroleuca oil for better yield of biodiesel.

Saponification value of the studied oil was 91.34 mg KOH/g. The range of saponification values for various types of bio-oils is 160– 190 mg KOH/g [79]. High saponification value very useful in the production of liquid soap and shampoo industries as a result of oils are normal triglycerides [81]. The biodiesel production from higher SV oils require more methanol and produce more glycerol but less biodiesel than longer chain oils. Oils with high SV impart high foamability (e.g. palm kernel, coconut and babassu oils). The high saponification value is associated with corrosion problems to the critical parts of a diesel engine. The saponification value of argemone oil was very low compared to many vegetable oils but similar to Jojoba Oil. A low saponification value indicated its average molecular weight of triglyceride in the oil. A low saponification value (91.34) of the oil indicated that the triglyceride has a long carbon chain. The longer the carbon chain of fatty acid, the less fatty acid content in the oil [39].

Density is mass per unit volume. The density of argemone oil was 920 kg/m^3, it is higher than the standard value of biodiesel. The higher density of oil indicated that for the same volume of oil more mass is entering into cylinder and cause to incomplete combustion and imbalance of air to fuel ratio occurs as a result of more fuel entering into cylinder causes to it increased of CO_2

and NOx emission values. The oil density is closely related to the calorific value and the power generated per unit volume. So, the greater the density, the heating value and the power generated were also greater. Higher density generally means higher viscosity, to large density value could increase viscosity that causes difficulties for oil to burn in the diesel combustion chamber[89].

Viscosity defined as resistance liquid to flow it indicated the thickness of the oil. The kinematic viscosity of the Aregmone oil is measured by viscometer and the value was 33 mm/s^2. Nevertheless, viscosity values can be very different for oil produced from different oils seed and fats produced with different techniques. Also, the value viscosity is directly related to molecular weight and inversely proportional to temperature and unsaturated level of oil. The viscosity of the Aregmone oil was minimum compared with Jatropha oilseed of 42.88mm/s^2 [81]. The viscosity of Aregmone oil can be reduced for biodiesel application since the kinematic viscosity of biodiesel is very low compared to vegetable oils. High viscosity of the Aregmone oilseed was not suitable if its use directly as engine fuel, often results in operational problems such as carbon deposits due to incomplete combustion, flow resistance increased with higher viscosity causes to a reduced power output of engine.

4.3. Biodiesel Production and Experimental Analysis

4.3.1. Esterification Reaction

The acid-catalyzed esterification reaction was carried out to get the low content of FFA treated argemone ochroleuca oils through the process conditions such as the temperature at $60^{O}C$, 2h contact time, the Molar ratio of 9:1 and effects acid catalyst variety’s in four parameters (0.5,1,1.25and1.5% v/v). Sulfuric acid-catalyzed was used to initiate the esterification reaction. The purpose of the pretreatment process was to reduce the free fatty acids (FFA) content from high content FFA (6.25%) the argemone oils to a minimum level for biodiesel production (<1%). The results showed that the FFA of argemone oils was reduced from 6.25% to less than 1% FFA using 1% v/v of sulphuric acid with the molar ratio of methanol to oil of 9:1 for 2h reaction time at 60 °C.

4.3.1.1. Effect of sulfuric acid dosage on esterification reaction

Figure 4.3 shows the effect of different dosages of sulfuric acid on the acid value and the FFA content of Aregmone oil. The acid value decreased gradually from 12.9 mg KOH/g-oil to 1.59 mg KOH/g-oil. The FFA content decreased from 6.25% to less than 1% in the dosages of

1% of sulfuric acid until it was 0.79%. The results showed that sulphuric acid was an effective catalyst to reduce the high FFA value in the esterification process. However, when the dosage of sulfuric acid 0.5%v/v the FFA value was greater than the limit of 1% because an insufficient amount of catalysts resulted in low resistance of the catalyst and incapability to provide enough catalytic activity to reduce the acid value. When the dosage of sulfuric acid 1%v/v gave the lowest percentage of FFA 0.7953% in temperature of 60^{O}C,2h contact time and Molar ratio of 9:1. And also observed that the acid value was negligible change when the dosage of sulfuric acid is increased from1% v/v to 1.5%. The excessive dosage of sulfuric acid did not show a significant variation on the acid value. As a result, increasing the volume of the catalyst after 1%v/v has no effect on the reduction of acid value, but rather it causes extra cost.

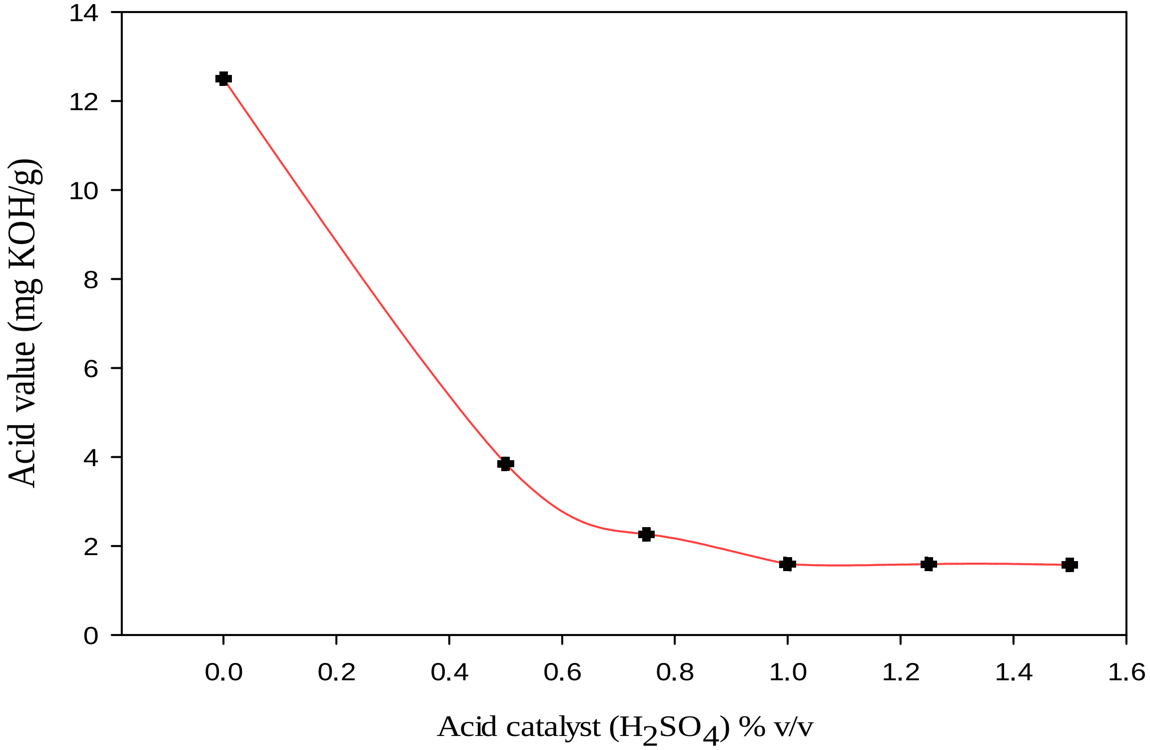


Figure 4.3 The effect of acid-catalyst (H_2SO_4 anhydrous) concentration on esterification

4.3.2. Physicochemical Properties of Pretreated Oil

The major physicochemical properties to determine properties of pretreated oil were given in Table 4.3.

Table 4.3 Physicochemical properties of the pretreated oil

Physicochemical properties	Units	Values
Acid value	mg KOH/g	1.5906
Free fatty acid	mg KOH/g	0.7953
Saponification value	mg KOH/g	80.17
Specific Gravity	-	0.91
Density @ 20^oC	kg/m^3	910
Kinematics viscosity @ 40^oC	mm^2/s	23

The FFA content of the raw oil determined the yield of biodiesel. From Table 4.3, the FFA of pretreated argemone oil was 0.795%; due to this low content of FFA we expect high yield of biodiesel. The expectation of high biodiesel yield is due to the following reasons; The lower value of FFA content (<1 wt%) effectively uses the catalyst needed to initiate the conversion of triglyceride to methyl ester. The alkali-catalyzed process is sensitive to both water and FFA content due to the occurrence of saponification reaction under alkaline conditions.

Viscosity is an important property of biodiesel the pretreated Aregmone oil (23mm/s^2) was lower than the crude oil. But still, the viscosity is much higher than the standard value of biodiesel. Improper viscosity causes the poor-quality biodiesel leads to poor combustion, which results in loss of power and excessive exhaust smoke. Higher viscosity is also not desirable as too viscous fuel increases pumping losses in injectors which reduce injection pressure resulting in poor atomization and insufficient mixing with air ultimately affecting the combustion process.

4.3.3. Experimental Result of Physicochemical properties and Yield Biodiesel for Experimental Runs

The transesterification reaction is normally a sequence of three consecutive reversible reactions. In this process, triglyceride is converted stepwise into diglyceride, monoglyceride, and, finally, glycerol in which 1 mol of alkyl esters is formed in each step. As shown in Table 4.4 and 4.5 effects of three-factor, including the type of catalyst (alkaline), alcohol/vegetable oil molar ratio, and temperature on the yield and physicochemical properties was investigated on the transesterification rates.

Table 4.4 Physicochemical properties and yield of prepared biodiesel (Average)

Run	Molar Ratio	Temperature (^{O}C)	Catalyst(%wt oil)	Kinematic Viscosity (mm^2/s)	Density (Kg/m^3)	Acidic Value (mg KOH/mg oil)	Iodine Value (gI$_2$/100 ml)	Flashpoint (^{O}C)	Higher Heating Value (MJ/Kg)	Cetane Number	FAME yield (%)
1	3:1	45	0.5	9.1	880.5	0.61	37.02	178.1	40.97	56.805	69.5
2	3:1	45	1	7.7	879	0.58	38.115	174.3	41.5	56.575	78.6
3	3:1	55	0.5	7.05	876.6	0.665	38.805	170.7	41.1	55.84	72.58
4	3:1	55	1	6.45	877.5	0.67	44.83	168.3	41.545	56.045	85.1
5	3:1	65	0.5	6.1	876.5	0.5	32.54	169.5	41.03	55.73	74.1
6	3:1	65	1	5.65	874.7	0.48	35.7	166.4	41.11	55.345	88.6
7	4:1	45	0.5	5.85	878	0.57	33.49	173	41.035	55.77	77
8	4:1	45	1	5.75	879.8	0.41	48.755	171	40.985	56.04	84.6
9	4:1	55	0.5	5.3	880.2	0.47	44.09	165.3	40.97	56.035	87.35
10	4:1	55	1	4.65	875	0.485	47.22	164.7	41.13	55.08	91.1
11	4:1	65	0.5	5.4	876.25	0.38	36.735	165.9	41.075	55.415	87.5
12	4:1	65	1	4.05	875	0.32	40.03	162.3	41.13	54.96	91.5
13	6:1	45	0.5	5.15	876.5	0.45	33.63	170.6	41.07	57.25	81.7
14	6:1	45	1	4.7	879.5	0.415	43.31	166.5	40.99	55.445	86.5
15	6:1	55	0.5	4.1	879.9	0.39	38.755	161	40.985	55.7	89.3
16	6:1	55	1	3.95	871.8	0.34	40.7	166.7	41.20	54.635	93.4
17	6:1	65	0.5	4.55	874.5	0.37	47.655	161.6	41.10	54.98	90.4
18	6:1	65	1	4.35	874	0.53	48.24	160	41.14	54.885	93.8

4.3.3.1. Effect of Reaction Temperature on Biodiesel Production

The effect of reaction temperature on oil conversion was studied at three temperatures (45, 55, and 65 °C). Fig. 4.4 and Fig. 4.5 presents the effect of the reaction temperature on the conversion of oil to FAME at different catalyst amount. At lower reaction temperature, the yield is lower for lower methanol to oil molar ratio. As the reaction temperature increased by 10 ^{O}C the yield increased irrespective of the change in a molar ratio (refer Fig.4.4 and Fig.4.5). The yield of biodiesel was increased simultaneously with the reaction temperature when it increased from 45^{O}C to 65^{O}C. In this study, it was found that the optimum reaction temperature was 65^{O}C. As can be seen from the figure, the methyl ester conversion was 93.8%. This is due to the fact that temperature was the basic factor in chemical reaction kinetics. Therefore, high temperature promotes the kinetic energy of the molecules and hence increases the methyl ester conversion.

But the graph shows that yield starting decreased after the temperature reached 60^{O}C, this is due to the fact that the actual boiling point of methanol is around 65^{O}C indicated that the formation of methanol bubbles due to its boiling point limits the mass transfer on the three-phase interfaces since methanol vaporizes, the reactant methanol exists in gas phase whereas the oil and the catalyst are still in the liquid phase. Thus, due to the limited amount of methanol (below the stoichiometric amount) in the liquid phase, the reaction may be stopped ultimately decrease the conversion. The reaction temperature above the boiling point of alcohol is avoided since at this temperature the saponification is high by alkaline catalyst this hinders the separation of glycerol [67].

The results were similar with the several types of research noted that those obtained the most favorable reaction conditions for optimum biodiesel yield from vegetable oil using alkali-catalyzed methanolysis was: reaction temperature of 65^{O}C, alkaline catalyst concentration of 1.00% (w/w) and methanol to oil molar ratio, 6:1 [30-33].

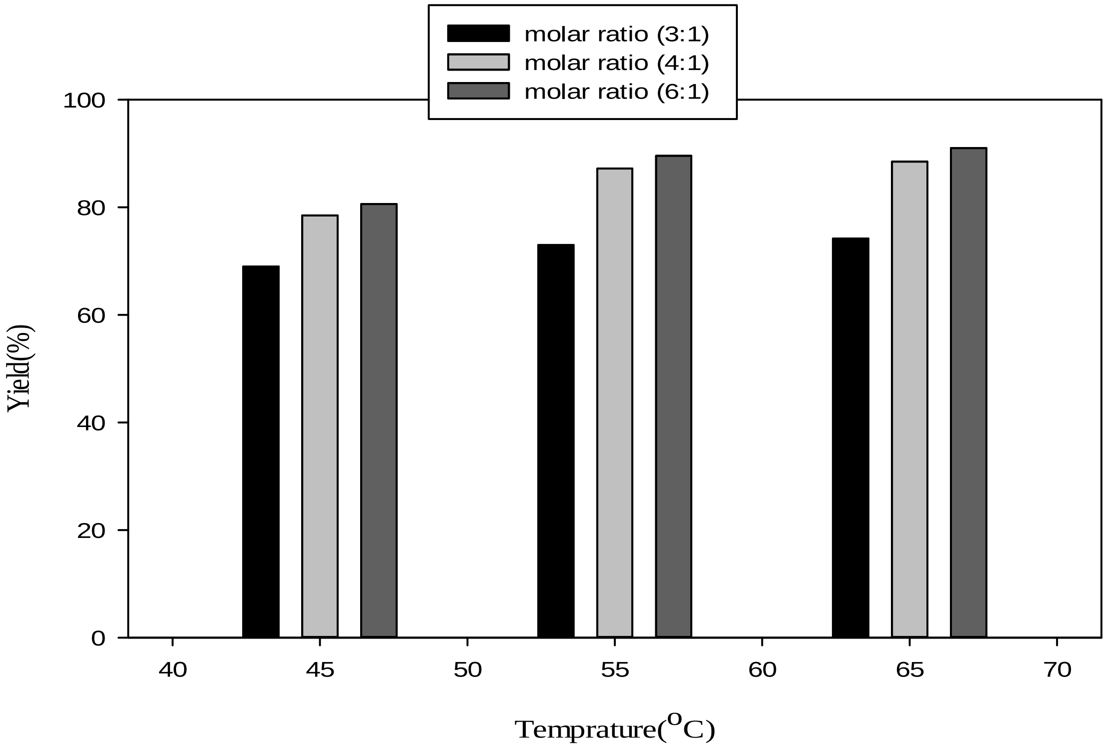


Figure 4.4 Effect of temperature on the yield of biodiesel for 0.5% catalyst concentration

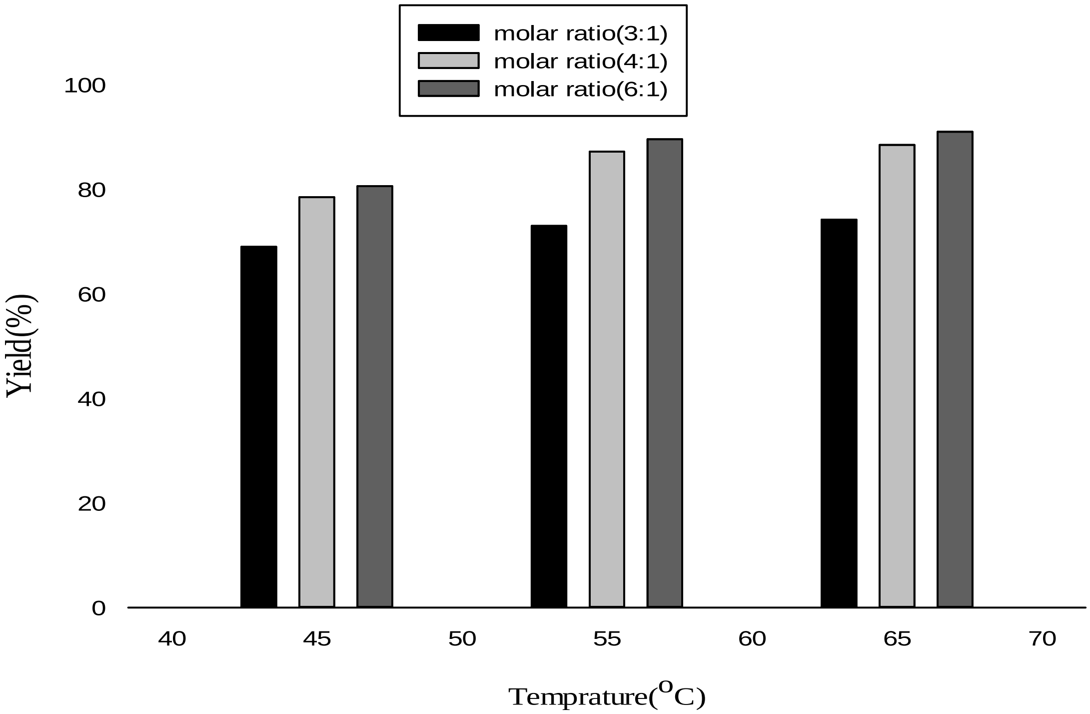


Figure 4.5 Effect of temperature on the yield of biodiesel for 1% catalyst concentration

4.3.3.2. Effect of Catalyst Concentrations on Biodiesel Production

Fig.4.4 and Fig.4.5 showed that the mean yield increased when the catalyst amount was increased from 0.5 to 1.0wt%. Similarly, many researchers declared that biodiesel yield was directly proportional to the catalyst amount up to 1.0wt% and inversely proportional to beyond 1.125w %. The reasons may be offered to explain why catalyst amount 0.5% resulted in lower mean yield Aregmone oil contains some amount of FFA. During the transesterification reaction, some of the catalysts were neutralized by FFA, as a result, the amount of catalyst needed to initiate the reaction is insufficient due to that the yield of biodiesel was minimum compared to 1%wt catalyst. Therefore, increasing the amount of catalyst used can improve the yield. This might explain why the mean yield was only 90.4 % when 0.5 %wt. of the catalyst was used and why the mean yield increased to 93.8 % when catalyst amount was increased from 0.5 to 1.0 wt%. The result was comparable with earlier findings that catalyst amount is the significant factor on the yield of biodiesel, and the maximum yield levels are 1.0 wt%. Above the optimum amount of base catalysts presence in the reaction mixture influences soap formation, emulsion, ester yield reduction and complicating separation of final products (biodiesel and glycerol) [77].

4.3.3.3. Effect of Different Oil to Methanol Molar Ratio on Biodiesel Yield

The effect of the molar ratio of alcohol to the oil of 3:1, 4:1, and 6:1 for 0.5 and 1%wt. catalyst, on the yield of biodiesel displayed in Fig.4.6 and Fig.4.7. Oil to methanol molar ratio of 3:1 gave the lowest yield of biodiesel and the yield was increased with the molar ratio of alcohol to oil. To maximize the fatty acid ester from vegetable oil it is needed an extra amount of methanol than stoichiometric ratio (3:1) required for transesterification of triglyceride. In experimental practice when molar ratio increased from (3:1) to (6:1) the recorded result was simultaneously increased in methyl ester production. The greater amount of methanol in the transesterification reaction required to increase the miscibility and to enhance the contact between the alcohol molecule and the triglyceride in a short time, as a result, the reaction shifts toward completion and the yield of biodiesel also improved. So, an additional excess amount of methanol was required to break the glycerin–fatty acid linkages during transesterification of triglycerides to biodiesel to improve the yield and purity of methyl ester.

Therefore, from the experimental result, the maximum yield of biodiesel was obtained at 6:1 methanol to oil molar ratio. For 1% wt. alkali-catalyzed and 65^{O}C temperature, the 6:1molar ratio produces a 93.8 % yield of methyl ester. The result was harmonized with many researchers results found that the optimum methanol to oil molar ratio was 6:1 is employed to have enough amount of alcohol to break the fatty acid-glycerol linkages [64]. For alkali-catalyzed transesterification, the 6:1 molar ratio of methanol to oil to produce the optimum biodiesel yield more than 90w/w% yield. However, this relationship is not linear because after the molar ratio of 6:1 does not increase yield because of the microscopic equilibrium reached in the reaction rather it could hinder glycerol separation process and saponification may occur due to its water content of alcohol.

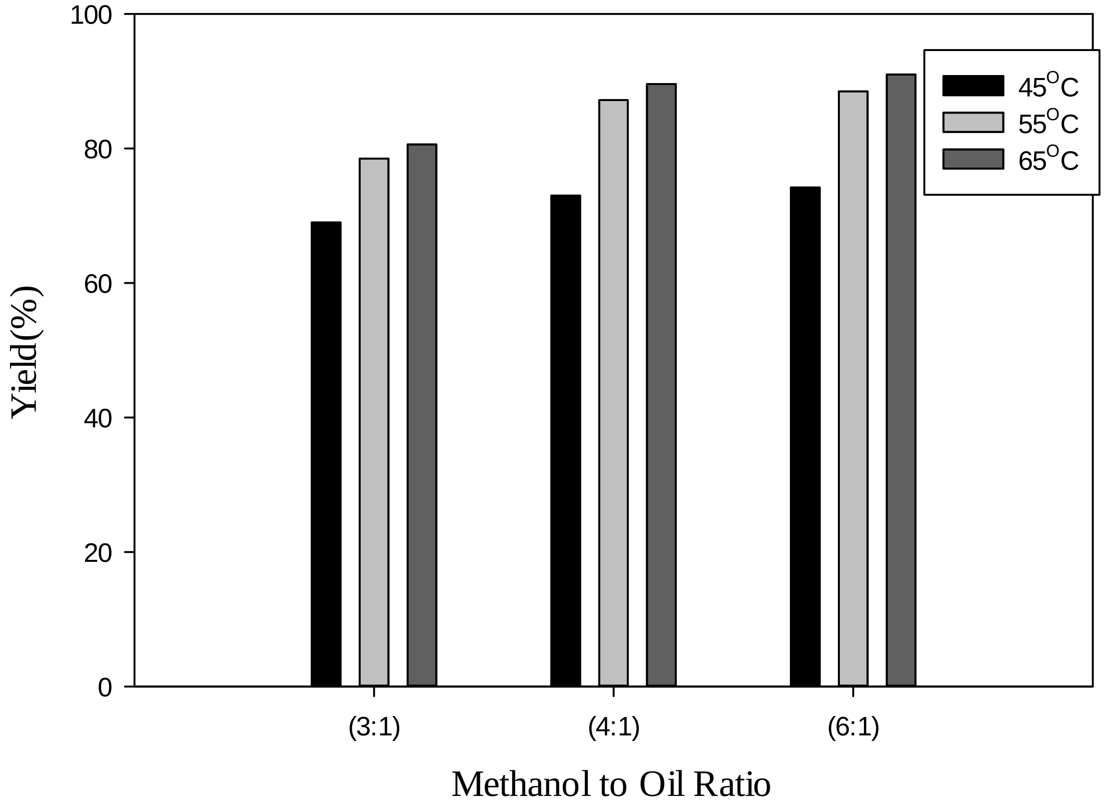


Figure 4.6 Effect of different methanol to oil molar ratio on biodiesel production for 0.5 % catalyst concentration

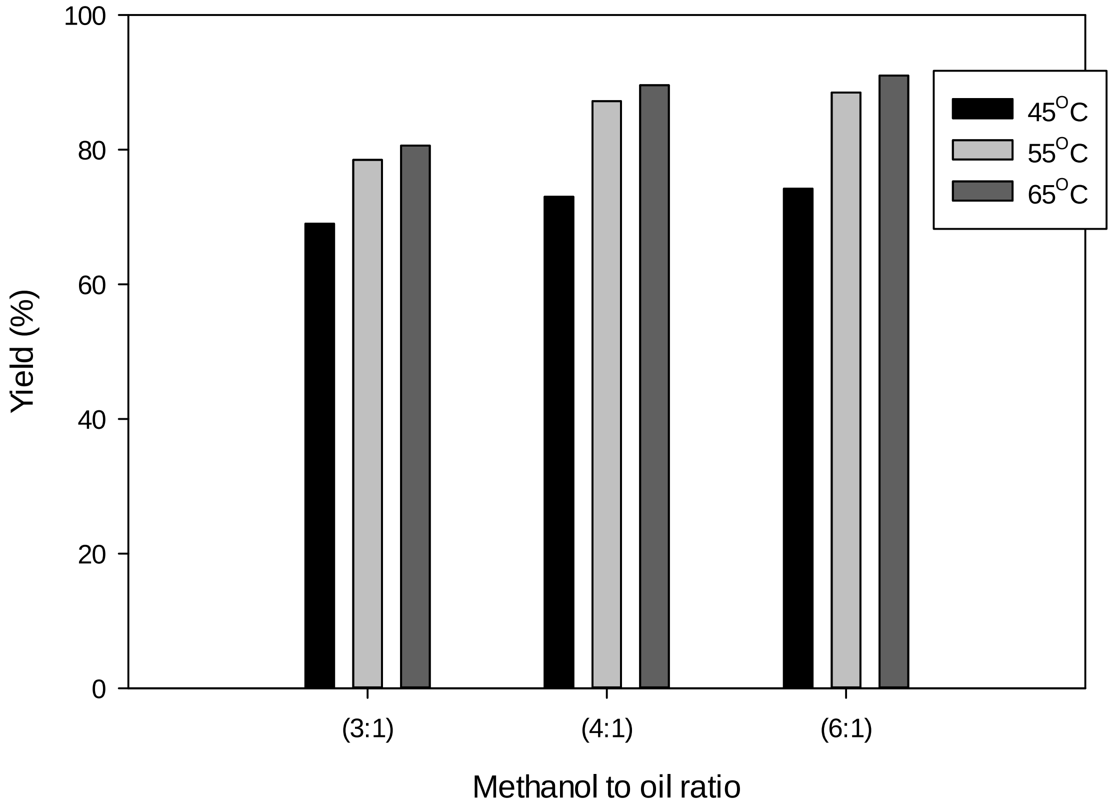


Figure 4.7 Effect of different methanol to oil molar ratio on biodiesel production for 1% catalyst concentration

4.4. Physicochemical Properties of Biodiesel

The quality of biodiesel is very substantial for the performance and emission characteristics of a diesel engine. The physicochemical properties of argemone ochroleuca biodiesel produced were tested for quality testing and to examine the relationship with the yield the biodiesel samples. The characterization was performed for the seven properties namely density, kinematic viscosity, acid value, flash point, iodine value, higher heating value and, cetane number. These properties were selected for two main reasons. One because they are the defining properties of biodiesel and the other is because of the limitation of resources to perform other tests. Table 4.4 depicts the result of biodiesel quality assessment.

The acid value for the experiments was found to be between 0.32, and 0.61 mg KOH/gm respectively. It is clear to see from the result that the methanolysis process successfully reduces the acid value of the initial oil. The maximum level of AV for pure biodiesel, as specified in ASTM standard D6751 is 0.8 mgKOH/g. Thus, the acid value of the produce biodiesel was lower than the ASTM standard and agree with another source of biodiesel acid value.

The kinematic viscosity measured for the biodiesel measured for all experiments. The kinematic viscosity of the original and pretreated oil at 40^{O}C was 33 and 23 mm^2/s respectively. After the transesterification process, the viscosity of argemone ochroleuca methyl ester significantly reduce. The viscosity result obtained from the experiment as shown in Table 4.4 some results were slightly higher than the standard value but several results were between (3.95-9.1mm/s^2) the result was agreed with the limit of the ASTM specification i.e. (1.9 – 6.0 mm^2/s). The obtained methyl ester result was reasonable value for the diesel engine operation. The variation of viscosity values of esters originated from the same type of feedstock argemone oil was due to the influence of experimental conditions such as insufficient alcohol, catalyst and temperature reduce the conversion efficiency. The purification method biodiesel from glycerol also affects the viscosity of the product.

High viscous of biodiesel affect the performance of the fuel supply system including fuel pump, fuel filters, and air-fuel mixing behavior. High values of viscosity reduce the performance of engine because incomplete combustion was occurring due to the volume flow and injection spray quality, the size of the particles (drops), and the quality of the fuel-air mixture. High viscous oil will form blue smoke because the formation of big drop causes reduces the temperature of the cylinder it interrupts the complete combustion and the deposit due to incomplete combustion also reduce the power of the engine. The fuel with a too low viscosity causes operational problems because some part of the engine is lubricated by the fuel so low viscous biodiesel cause abnormal wear and injectors and injector pump leakage. provides a very fine spray, the drops having a very low mass and speed. This leads to insufficient penetration and the formation of black smoke specific to combustion in the absence of oxygen (near the injector). Fuel atomization is also affected by fuel viscosity. Diesel fuels with high viscosity tend to form larger droplets on injection which can cause poor combustion, increased exhaust smoke and emissions [3] [87].

From the physicochemical point of view, viscosity means the resistance of one part of the fluid to move relative to another one. Therefore, viscosity must be closely correlated with the structural parameters of the fluid particles. The viscosity slightly decreases with an increased degree of unsaturation and rapidly increases with polymerization. The viscosity almost linearly decreases as the iodine value increases [86]. The figure shows that more the number of unsaturation number present in the fuel and the viscosity of the oil is reduced.

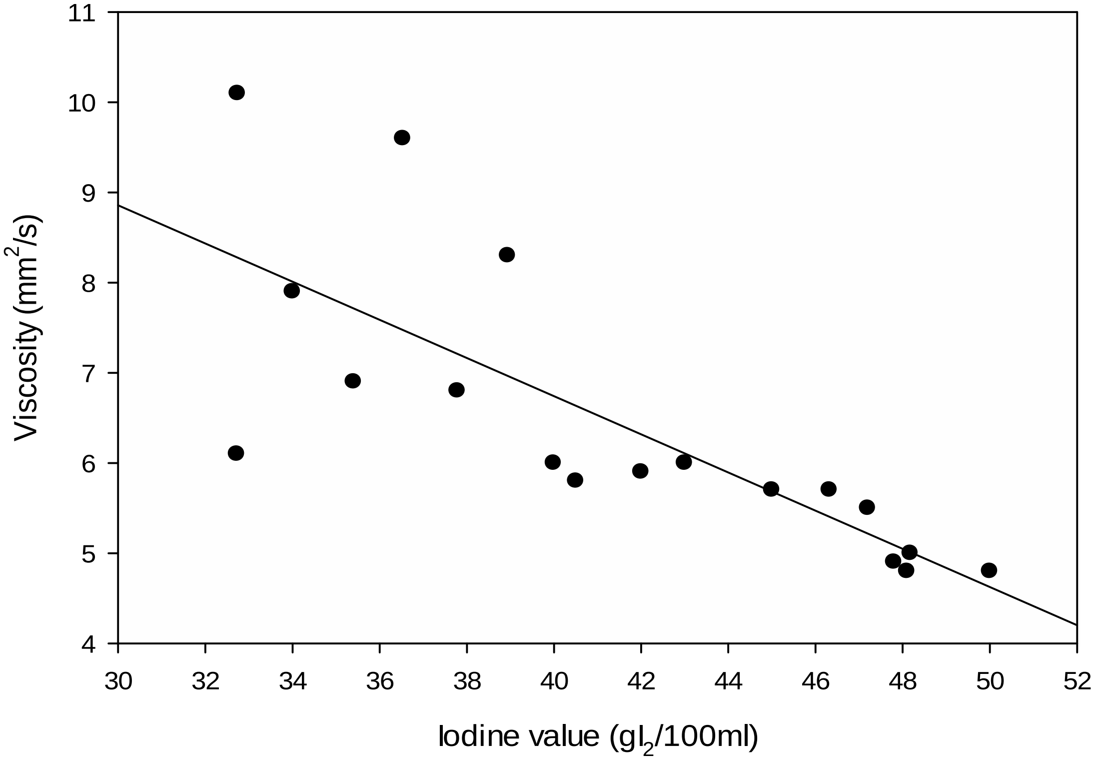


Figure 4.8 Correlation between viscosity and Iodine value for methyl ester

The iodine value is one parameter of methyl ester used for the determination of the unsaturation of fats and oils. Higher iodine value indicated that higher unsaturation of fats and oils. As it can be observed in Table 4.4, the iodine value of the produced biodiesel was in the range (32.54-48.755) g I_2/100ml, the maximum standard iodine value for biodiesel is 120 gI_2/100ml for Europe's EN 14214 specification. This value was lower than the standard limit indicated that the quality of biodiesel produced in this work is in good agreement with Europe's standard and another literature standard [1][33]. High degrees of unsaturation are generally not desirable for fuels because the oxidation reactions occur at high temperatures during combustion this higher temperature causes the polymerization of glycerides unsaturated fatty acid [27]. This polymerized product can lead to the formation of deposits or to worsening of the lubricity of the fuel. The higher the value of unsaturated value causes to more iodine is attached, the higher is the iodine value, and the more reactive, less stable, softer, and more susceptible to oxidation and acidification is the fuel. The result of this work of agreed with agree with several samples of biodiesel obtained from edible oil have iodine number is less than 100 gI_2/100 ml it indicates that argemone oil was a good source of raw material for biodiesel production in terms of iodine value [6]. The unsaturation in the fatty acid chain is the main source of thermal instability and reason for causing carbon deposits due to burning[79].

The density of a material is defined as the measurement of its mass per unit volume. The density of the fuel is very important in diesel engines because the fuel injection system (the pump and the injectors) operates on a volume metering basis. As a result, the mass fuel with the same volume that reaches the combustion chamber is determined by density oil as a result high amount of mass of oil injected with the same volume due to a higher density of oil. It altering the fuel/air ratio and the engine's power because fuel injection pumps meter fuel by volume not by the mass so the extra mass of fuel reduces engine power due to incomplete combustion and great emission of smoke to the environment [90]. The argemone seed oil density decreased from 920 to 871.8Kg/m^3 through a transesterification reaction. All the experimental result was still within the ASTM standard value which is between 871.8 and 880.5 Kg/m^3. This value also agrees with works of literature conducted by different authors [39] [91]. Fig 4.9 shows the effect of density on the quantity of energy released when the fuel burn in the combustion chamber. The graph shows that the higher heating value of oil linearly increases when the density of fuel decreases.

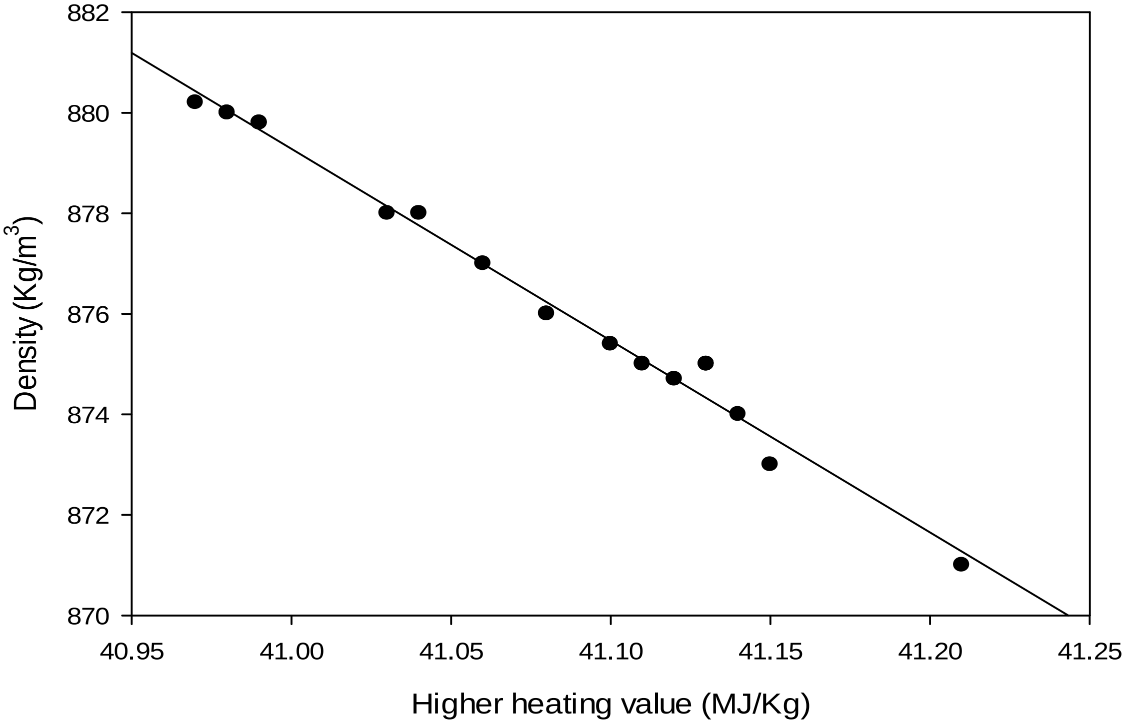


Figure 4.9 Effect of density on Higher heating value for methyl ester

The Heat of combustion (heating value) refers to the measure of energy content in the fuel. It measures the quantity of heat/energy liberated when a unit amount of fuel is burned in oxygen. So, the lower heating value of biodiesel is attributed to the decrease in engine power. The HHV of argemone ochroleuca biodiesel of this work ranged from 40.97 to 41.545 MJ/kg and is slightly lower when compared those of Petro-diesel (43 MJ/kg), and petroleum (42 MJ/kg), because methyl esters contain higher amount of oxygen than Petro-diesel. Due to the presence of oxygen in the biodiesel complete combustion of fuel was held in the engine this helps reduce the amount of carbon emission to the environment. The heating value of argemone ochroleuca biodiesel was higher than castor oil and linseed oil biodiesel which is 38.34 and 39.86 MJ/kg respectively. This is due to a reason of Heating value increases with increasing chain length and decreases with increasing unsaturation of methyl esters, the iodine value of linseed oil biodiesel is (185.4 g of I_2/100 g) significantly higher than that of the maximum iodine value argemone ochroleuca oil biodiesel (48.755 g of I_2/100 g) and it is important for estimating the fuel consumption, the greater the calorific value the lower the fuel consumption [54] [72]. The mass heating value of unsaturated esters is lower than that of saturated esters, but due to their higher density, the volume heating value of unsaturated esters is higher than that of saturated esters. [78] [80].

The flashpoint of a fuel is not directly related to engine performance. This parameter reflects a fuel's safety, the minimum temperature at which the air-vapor mixture start ignition. The higher the flashpoint reduces the possibility of starting the ignition of fuel accidentally before injection to the combustion chamber. The flashpoint biodiesel has higher when compared to diesel fuel. The flammability of biodiesel fuel is very low due to the less flash point than diesel and therefore safer from the risk of fire during storage, handling, and transportation of fuel. Both ASTM and EN standards specified that 130^{O}C is a minimum flash point of biodiesel. The observed flashpoints this work of argemone ochroleuca biodiesel test was in the range of 160 and 178.1^{O}C. The value indicates that the purity of biodiesel, which was free from excess methanol residue. This is because even a small amount of methanol can reduce the flash point reasonably and also negatively affects diesel engine parts such as fuel pumps, seals and elastomers. The reduction of viscosity resulting from transesterification of vegetable oil consequently causes a significant decrease in the flashpoint of the fuel produced.

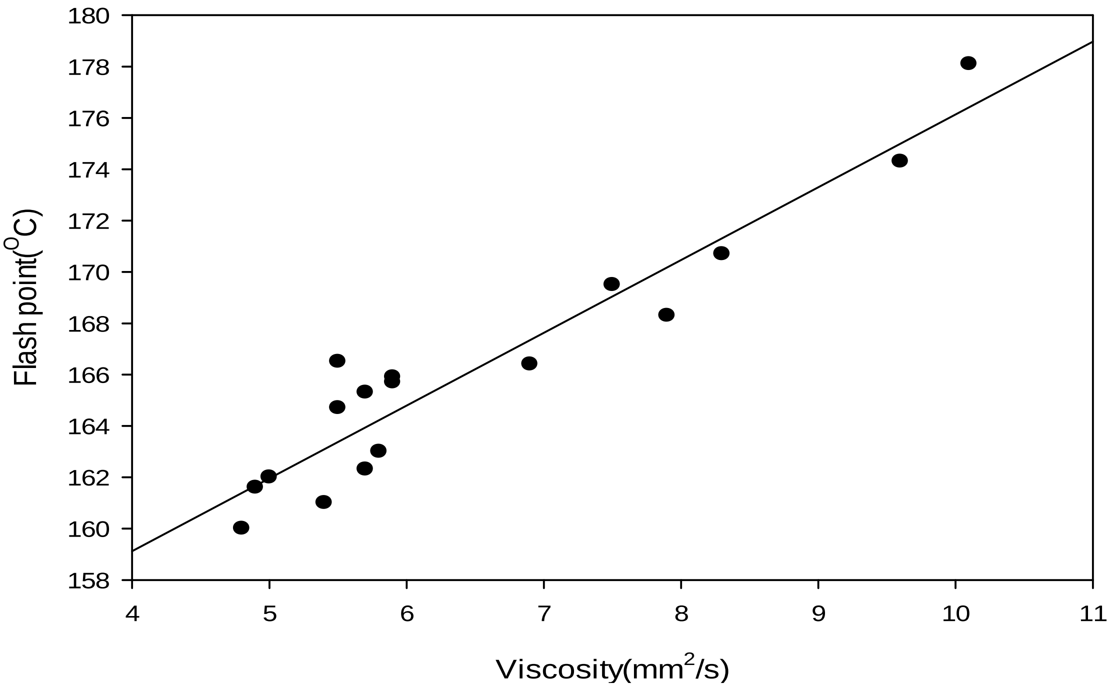


Figure 4.10 Effect of viscosity on Flashpoint of methyl ester

Cetane number (CN) is a dimensionless value that indicates the ignition quality of fuels, the easy of self-ignition for compression ignition engines. The higher cetane number fuel will good ignition quality (ignite easily) when it injected into the engine. When the cetane number is high the ignition delay period between the start of fuel injection and the onset of auto-ignition is short. But the ignition will start before the proper mix of air and fuel due to the very high value of the cetane number of biodiesels it causes to incomplete combustion and the increase the amount of exhaust smoke that causes environmental pollution. Oppositely, a very low value of cetane number also causes the operational problem to the engine at low temperature difficult to start or operate of engine unevenly and noisily without combustion and also incomplete because it warms very slowly [6]. This work indicates the maximum and minimum value of cetane numbers was found to be 57.25 and 54.635 respectively. Biodiesel records high CN values; these values are higher than that of diesel fuel with CN of 52 [78]. The obtained result was higher than the minimum standard value of CN for diesel oil is 40 in the USA (ASTM D 975) and 51 in Europe (EN 590). The value of the cetane number was a good agreement with other methyl ester products.

4.5. Comparison of the Optimum Quality Argemone Ocheroleuca Oil Biodiesel with ASTM and EN Standards

The comparison of the produced biodiesels in this experiment with international standards was done by selecting one optimum operating conditions of the experiment result from the total run using the yield and physicochemical property of the biodiesel. As it can be seen in Table 4.6, run 16 experiment was selected as an optimum operating condition due to the physicochemical properties of the Argemone ochroleuca oil biodiesel were in good agreement of the international standards and its highest yield. The proximate transesterification reaction yield was 93.4% at optimum operating conditions 6:1 molar ratio, 55^{O}C, and 1% catalyst and a produced biodiesel has a viscosity of 3.95mm^2/s, Acid value of 0.34, HHV of 41.20 MJ/kg, iodine value of 40.7 gI2/100ml density of 871.8 Kg/m^3, Flashpoint 166.7^{O}C and Cetane number of 54.63, which are in the range of international standards.

Table 4.5 Comparison of experimental biodiesel with standards

Property	Unit	EN standard	ASTM standard	Diesel	Experimental Biodiesel
Viscosity	mm^2/s	3.5-5.0	1.9-6.0	1.9-3.8	3.95
Density	Kg/m^3	860-900	-	840-860	871.8
Acid value	mg KOH/g	<0.5	<0.8	-	0.34
HHV	MJ/kg	42	-	43.3-46.7	41.20
Iodine value	gI_2/100g	<120	-	-	40.7
Flash point	^{O}C	>120	>130	68	166.7
Cetane number	-	-	46-70	47-55	54.36

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATION

5.1. Conclusion

In this research, biodiesel was prepared at different reaction parameters from argemone ochroleuca oil and methanol alcohol with a potassium hydroxide catalyst on a laboratory scale. Reaction temperature, amount of catalyst and methanol to oil molar ratio were the considered parameters for the optimization investigation. Under this investigation, two parameters with three levels and one parameter with two-level were considered. From the experimentation, it was found that maximum biodiesel yield of 94.1 % was obtained by using reaction parameters such as methanol to oil molar ratio of 6:1, 1 % KOH catalyst, reaction temperature of 65 C and reaction time of 120 minutes. The optimum quality result using transesterification reaction yield was 93.8% at optimum operating conditions 6:1 molar ratio, 55^{O}C and 1% catalyst and a produced biodiesel has a viscosity of 3.9mm^{2}/s, Acid value of 0.33, HHV of 41.21 MJ/kg, iodine value of 40.5 gI2/100ml density of 871 Kg/m^{3}, Flashpoint 161^{O}C and Cetane number of 54.36.

After the production is completed the physicochemical properties of biodiesel prepared were tested to check whether the products could satisfy the international standard or not. The tested physicochemical properties for the selected were found to be within the ASTM specified limit. From the lab-scale production of biodiesel, from the methanolysis process, the obtained value was similar in yield and properties with the value reported by other researchers. To increase the conversion efficiency of methyl ester, it was necessary to purify the crude oil by degumming process using NaCl to remove the phospholipids and undesirable substance that causes to increase rate oxidation causes to and also pretreatment of purified oil to reduce the higher amount of acid value that inhibits the performance of the catalyst.

Generally, from this research one can say that ‘It is possible to produce biodiesel from non-edible plant argemone ochroleuca seed oil using heterogeneous catalyst under transesterification reaction that can meet international standards.

5.2. Recommendations

Since Ethiopia has a high potential of argemone ochroleuca seed it grows on wasteland since, it is highly recommended to use these seed resources as additional sources for the production of biodiesel, an eco-friendly fuel, that can substitute a fossil-based Petro diesel. This research confirmed the possibility of producing biodiesel from those local resources. Even though the result of this study was satisfactory, on the basis of producing biodiesel from those local resources and meeting an international standard, the yield of every experimental run as good as expected.

Biodiesel was produced using heterogeneous catalyzed transesterification reaction that results in the high cost for purification. Although, production of biodiesel using methanol and acid-catalyzed, enzymatic catalyzed or supercritical catalyzed transesterification reaction should be explored. Biodiesel production was done in the batch process system; but, the cost of a batch process system is higher due to energy consumption production should be conducted in a continuous process system.

The present study was only focused on to evaluate the experimental investigation and characterization of argemone ochroleuca biodiesel. However, for a better understanding of the performance of the fuels with different ratio Petro diesel blends and its physicochemical properties of the fuels that determine the quality should be analyzed.

The property of glycerol was not determined, but glycerol has relevance in cosmetics and soap industries. Consequently, the property of glycerol should be analyzed and purified for further applications.

6. REFERENCES

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APPENDIXES

Appendix 3.1-A Feed Material Requirement for Biodiesel Production

The feed ratio of the experiment varies depend on the parameter evaluated at each specific experiment. This calculation made to determine the amount of the reactant involved for;

The molar ratio of Methanol/Oil 3:1-6:1

Operating Temperatures 45-65^{O}C

Catalyst KOH, Ratio 0.5 and 1% by weight of the oil.

The raw material of Argemone oil is composed of different free fatty acid in different composition but linoleic acid (58.72%), is a major free fatty acid in Argemone oil. Linoleic acid and Oleic acid were chosen to represent Aregmone oil.

Molar mass=817.43 g/mol

to mass of methanol=32.04 g/mol

Liquid density of oil = 0.92g/ml

Density of methanol= 0.791 g/ml, at 20^{O}C

For 3:1 Methanol Ratio

For every run 100ml of purified Argemone oil was used. Hence, the amount of methanol and catalyst were calculated as follows using the process parameters. The amount of methanol required when the molar ratio of ethanol to oil ratio 3:1;

Mass one mol of oil =1mol*817.43 g/mol=817.43g

Mass of 3 moles of methanol=3moles*32.04g/mol=96.12 g of methanol

From this,96.12g of methanol is needed for 817.43 g of oil involved in the reaction. For each run 100ml of oil used for transesterification so,

Mass of 100ml oil=density of oil*Volume of oil

=0.92g/ml*100ml

=92g of oil

Therefore the amount of methanol needed is, 10.4 g of methanol.

The volume of methanol required is, 13.5 ml.

The catalyst required for this experiment is 1% by weight of the oil.

=0.92 g of KOH

Similar procedures have been done for the other methanol ratio.

Appendix 3.2-A Acid value of oil

First, 0.1N KOH solution preparation in 100 ml of distilled water.

$$N = M = \frac{n}{V_L}$$

$$n = \frac{m}{M}$$

$$m = MM_wV_{(l)}=0.1*56*0.1$$

$$= 0.56 \text{ g in 100ml}$$

1% Phenolphthalein solution is prepared by dissolving 1g of phenolphthalein powder with 50 ml of ethanol and 50 ml of distilled water

Table A: Determination of acid value of oil

Oil Sample (titrants)	Weight(g)	Initial value(ml)	Final value(ml)	Difference (titration volume)
Blank	0	0	0.1	0.1
Oil 1	2.5063	0.2	5.3	5.3
Oil 2	2.5245	5.6	11.5	5.9
Oil 3	2.5054	11.5	17.4	5.9
Average value	2.512			5.7

$$A \quad = \frac{M * M \quad * T}{M}$$

Substituting the following values in the above equation gives the acid value

Acid value $= \frac{0.1m \quad /_{l} *^{5} \quad .1g /_{m} \quad *5.7*1 \quad ^{-3}l}{2.5 \quad g}$ =12.506

Therefore, the acid value was 12.506 mg KOH/g of oil.

Thus, the free fatty acid content of the oil is half of the acid value which is equal to 6.253 mg /g of oil.

Appendix 3.3-A Saponification value of oil

Preparation of 0.5N KOH-Ethanol (Ethanolic potassium hydroxide): to prepare 0.5N of Ethanolic KOH solution,7gm of KOH dissolved in 250ml of ethanol.

C_m is the mass concentration of KOH = 0.5mol/l×56g/mol×0.25l=7gKOH

Preparation of 0.5N of HCl: to prepare this solution, 4.42ml of HCl poured on 100ml of distilled water.

$$M_1 = \frac{s \quad .g \times c \quad\quad o \quad H \quad \times 1000m}{m \quad\quad m \quad o \quad H}$$

$$M_1 = \frac{1.18 \times 35 \times 10}{36.46} = 11.32$$

$$M_1V_1 = M_2V_2$$

$$V_1 = \frac{0.5 \times 1}{1 \quad .3} = 4.42m \quad o \quad H \quad d \quad\quad i \quad 100m \quad o \quad d \quad\quad w$$

Table B: Blank experiment observation table (KOH Vs HCl)

The volume of KOH solution in ml	Burette reading		The volume of HCl solution in ml (Titer V_O)
	Initial	Final	
50	0	47.5	47.5

Table C: Original experiment observation table (sample oil + KOH Vs HCl)

The volume of sample oil +50ml KOH solution	Burette reading		The volume of HCl solution in ml (Titer V_1)
	Initial	Final	
5.0112g oil	0	31.3	31.3
5.0074g oil	0	29.5	29.5
5.0255g oil	0	32.7	32.7
Average=5.0147			31.17

The saponification value was calculated as follows;

$$Sc \qquad v \qquad ,^{m} \qquad /g = \frac{(V_0 - V_1) \times N \times 56.1}{m}$$

Where;

V_0 = the volume of the solution used for the blank test; V_1 = the volume of the solution used for determination S.V; N = Actual normality of the HCl used; m = Mass of the sample.

$$S \qquad v \qquad m \qquad /g = \frac{(47.5 - 31.17) \times 0.5 \times 56.1}{5.0147g}$$

Thus, the saponification value of the oil was about 91.34mgKOH/g Oil.

Appendix 3.4-A Laboratory work images

Figure A: Oil extraction using mechanical press machine

Figure B: Extracted oil after the degumming process

Figure C: Tranesterfication process laboratory set-up

Figure D:separation of biodiesel and glycerol

Figure E: Separation of Oil from methanol and catalyst using rotary vapor

Figure F: Viscosity measurement using viscometer

Figure G: Iodine value test using Hannu"s method

Figure H: Saponification value determination using titration

Figure H: Acid value determination using titration

Figure I: Specific gravity measurement using a hydrometer