# *CHARACTERIZATION AND OPTIMIZATION OF BIODIESEL PRODUCTION FROM MEXICAN POPPY (ARGEMONE MEXICANA)*

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# ABSTRACT

Biodiesel production has generated heated debate on energy security for food crisis. This debate has changed the direction of biodiesel research into the use of non-edible oil sources referred to as second generation biodiesel feedstock. Ethiopia despite having high potential of various non-edible oily plant species, only very few non edible sources of biodiesel are known compared to the number of non-edible oily plant species identified. Thus, exploration of cheap and non-edible sources of biodiesel such as *Argemone Mexicana* can help to increase the production and use of biodiesel. This plant has invaded many ecosystems and communities in Ethiopia.

However, due to lack of research and skill, there was a gap to find optimum conditions and properties of newly identified non-edible oil plant of oil methyl ester. Therefore, the objectives of the present study was to find a way of converting this invasive plant to useable form for the society which was affected by *A. Mexicana* by converting the seed oil to biodiesel production, characterization of the oil and fatty acid methyl ester (FAME). After the seed samples were collected and purified, the physicochemical and instrumental parameters were determined. The biodiesel was produced by heterogeneous CaO catalyst from A. mexicana oil through transesterification method. Experimental design using design expert 7.0.0 software were implemented to identify the oil yield, the effects of different process parameters for FAME production and to find the optimum conditions to maximize the yield of FAME. A total of 40 % yield of oil was extracted and converted into methyl ester by the process of transesterification. The physicochemical studies and the comparisons revealed that transesterification improved the important fuel properties. The best performance result was obtained at a catalyst concentration of 1.0%, molar ratio 9:1 and reaction time of 1 hr, while the reaction temperature and agitation speed was set at $60^0$C and 600 rpm. The FAME yield obtained from transesterification process ranged from 56.3 to 91.2% while the optimum result was found 93% from the design expert software. The results showed that transesterification improved the important fuel properties testes which were relatively closer value with the ASTM and EN standards.

**Key words:** *Biodiesel production, Argemone Mexican , transesterification, FAME*

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# LIST OF SYMBOLS AND ABBREVIATIONS

| | |
|---|---|
| AN | Acid number |
| ANOVA | Analysis of variance |
| ASTM | American Society for Testing and Material |
| BDF | Bio Diesel Fuel |
| CCD | Central composite design |
| CN | Cetane number |
| EtOH | Ethanol |
| EN | European committee for standardization |
| FAME | Fatty acid methyl ester |
| FFAs | Free fatty acids |
| FP | Flash point |
| IV | Iodine value |
| AMO | A. mexicana oil |
| KV | Kinematic viscosity |
| MeOH | Methanol |
| RSM | Response surface methodology |
| SG | Specific gravity |
| SN | Saponification number |
| ºC | Degree Celsius |
| % | percentage |
| Wt. % | Weight Percentage |
| ml | millilitre |
| g | gram |
| h | hour |
| K | kelvin |
| Kg | kilogram |

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# CHAPTER ONE

## 1. Introduction

### 1.1 Background

Our world is in need of energy more than it is using now, so that the demand for energy is increasing from time to time due to the expanding urbanization, better living standards and increasing population. Fossil fuel takes a great share in the energy consumption of the world development. However, in view of the depletion of the world's fossil fuel reserves, the escalating energy crisis and environmental concern such as emission and serious regulations on exhaust emissions; it has become apparent that biodiesel is destined to make a substantial contribution to the future energy demands of the domestic and industrial economies.

The rapid growth of human population and industrialization leads to great demand for alternative and sustainable energy sources, Alternative energy sources include hydropower, wind, solar, geothermal, hydrogen, nuclear, and biomass. Among these alternative energy sources, biofuel derived from non-edible biomass which are known as the second generation feedstocks such as methane, ethanol and BDF have attracted much attention as green energy for the mitigation of global warming due to the advantage of carbon neutrality of biomass. However, many scientists have been warning against the effectiveness of biomass energy and recommended the potential of converting non-edible biomass oil into biodiesel must be well examined [1].

The term biofuel refers to solid (bio-char), liquid (ethanol and biodiesel), or gaseous (biogas, biohydrogen and biosynthetic gas) fuels that are predominantly produced from biomass. The most popular biofuels such as ethanol from sugar cane, corn, wheat or cassava and biodiesel from sunflower, soybean, and canola are produced from food crops that require good quality land for plantation [1]. However, the use of edible biomass oil has been created concerns such as food versus fuel debate that might cause food insecurity especially in the developing countries and environmental problems caused by utilizing much of the available arable land, chemical fertilizers and deforestation for search of arable land.

Biodiesel is a renewable fuel, non-toxic and biodegradable. It is a good alternative for conventional fossil diesel fuel due to the following properties, reduction of greenhouse gas emissions, and reduction of tailpipe emissions and improves engine operation [2].

Biodiesel production has generated heated debate of energy security for food crisis. This debate has changed the direction of biodiesel research into the use of non-edible oil sources referred to as second generation biodiesel feedstock such as Jatropha oil, Pongamia oil, Rapeseed Oil, Mahua oil, Olive oil, Rice Bran oil, Linseed oil, Soya bean oil, Palm oil, Cotton seed oil, Beef Tallow, Lard, Guang-Pietc and others which are easily available in developing countries and are very economical comparable to edible oils. Biomass of non-edible oil plants are well adapted to low fertility and moisture demand to grow, as well as no competition with human food, so that seed cake after oil expelling may be used as fertilizer for soil enrichment [3]. However, the yield and properties of biodiesel products produced from different feedstocks would be quite different from each other, so that choosing a right feedstock and optimum extraction methods through experimental verification was strongly needed.

In many research publications, biodiesel is produced from the refined edible oil using methanol and alkaline catalysts [4]. Alkaline hydroxides are the most effective transesterification catalysts as compared to acid catalysts. However, the problem with alkaline catalyzed transesterification of vegetable oils is possible only if the acid value of oil is less than four [4]. High percentage of free fatty acid in the oil reduces the yield of esterification process; such oils are mainly used for making low cost soap. Therefore, it is considerably more costly to separate the catalyst from the produced monoesters. It is difficult to transesterify these higher FFA vegetable oils using common alkaline catalysts. This indicated that the potential of converting non-edible oil like A. mexicana oil into biodiesel and find optimum conditions and properties of A. mexicana oil methyl ester must be well examined. This is because physical and chemical properties of biodiesel produced from A. mexicana feedstock must comply with the limits of international specifications for biodiesel fuels.

One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids. The availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial determinant delivering a competitive biodiesel price. Thus, nonedible oil sources are preferred as feed stock for the production of biodiesel. The use of non-edible oils as alternative feedstock is picking up as the demand for biodiesel is expected to increase sharply in the near future. Currently, only very few non edible sources of biodiesel are known compared to the number of non-edible oily plant species identified, so that exploration of cheap and non-edible sources of biodiesel such as *Argemone mexicana* , can help to increase the production and use of biodiesel in the developing countries particularly in Ethiopia since this plant affects and invaded many ecosystems and communities in Ethiopia [4].

Therefore, the present work utilized *A. mexicana* plant seed oil, calcined CaO as a catalyst and methanol was used for the production of biodiesel. The effect of different process parameters (reaction time, alcohol to oil molar ratio, and catalyst concentration) were investigated and characterization of the extracted oil and produced biodiesel was conducted.

## 1.2 Problem of Statement

The issue of energy security resulting from the depletion of world petroleum reserves, increase of petroleum price and environmental concerns has stimulated governments and researchers to look for alternative renewable energy sources that are technically feasible, economically competitive and environmentally acceptable. Due to this problem the world is engaged on searching alternative, renewable and sustainable energy technologies to transfer for the next generation.

To this effect, the government of Ethiopia has developed wide range of development programs to ensure supply of modern energy services and biofuel development is one of the priorities given to be implemented. There are, however, several issues that need to be considered before large scale commercial biofuel development is encouraged such as selection of non-edible crops, testing the oil yield of the potential non edible crops, characterization and quality determination of the extracted oil, availability of technology and skilled human resources.

The need to search a convenient biofuel crops to lower the energy requirement and production costs of biodiesel such as to use the non-edible products as a potential source of energy. One of the cheaper feed stock is A. mexicana which can be a good candidate since the plant has large availability in Ethiopia and grow on non-arable lands with high seed production and oil content that ranges between 22-36%, although oil content and properties obtained from the Ethiopian A. mexicana was not known.

A. mexicana invaded many ecosystems and communities in Ethiopia in general, Farta, Gondar and Bahir Dar zuria districts in particular disrupting ecosystem structure, function and reducing native biodiversity (plants and animals). When the distribution and abundance of A. mexicana increased the abundance and distribution of native plant species decreased [4].

Therefore, the present thesis characterized and optimized the parameters that mainly affect the production of biodiesel and introduced A. mexicana to Ethiopian scientific community for considering in the proposal for further studies in biofuel production.

## 1.3 Objectives of the Research

### 1.3.1 General objective

The general objective of the present work was to produce, characterize and optimize biodiesel from the A. mexicana seed oil, calcined CaO and methanol by transesterification process.

### 1.3.2 Specific Objectives

- To extract and determine the physicochemical properties of A.Mexicana seed oil.
- To investigate the effect of different process parameters such as reaction temperature, alcohol to oil molar ratio and catalyst loading wt/wt on biodiesel yield by keeping reaction temperature and agitating speed constant.
- To characterize the physicochemical properties of the maximum biodiesel yield.
- To identify statistically the optimum process parameters to obtain higher fatty acid methyl ester (FAME) yield by employing response surface methodology of design expert software.

## 1.4 Significance of the Study

This thesis has great significance on the current sustainable development of our community/country, assuring the production of an alternative form of energy from A. mexicana seed oil and determine the potentials of the country in feedstock for biodiesel production.It will be helpful to produce biodiesel from A. mexicana oil using methanol and alkali catalyst, by locally available seed which is abundantly cultivated, grown, nonedible and good for production of biodiesel.Biodiesel production from A. Mexicana will minimize the trade gap by reducing imported petroleum, it will be a means of income generation for the farmers by selling the seed which were unwanted to the farm, and also it can be used for soil enricher for crops - after slashing and create job opportunity to the farmer on the process of cultivation. In addition, this study will be used as a reference for further studies on A. mexicana plant cultivation owners who are interested to produce biodiesel plant and also this study shows achievability of biodiesel production from A. mexicana seed oil using methanol with CaO catalyst at small scale.

# CHAPTER TWO

## 2. Literature Review

## 2.1 General Overview

Biodiesel fuel produced by alcoholysis of edible, non-edible and waste cooking oil is viewed as a promising renewable fuel source [5]. Transesterification of vegetable oils was conducted as early as 1853 by Scientists, E. Duffy and J. Patrick, many years before the first diesel engine became functional. Rudolf Diesel‛s (1858– 1913) prime model, a single 3 m (10 ft) iron cylinder with a fly wheel at its base, run on its power for the first time in Augsburg, Germany, on August 10, 1893. In remembrance of this event, August 10 has been declared ―International Biodiesel Day [6]. Diesel later demonstrated his engine and received the Grand Prix (highest prize) at the World Fair in Paris, France in 1900.This engine stood as an example of Diesel‛s vision because it was powered by peanut oil a biofuel, though not biodiesel, since it was not transesterified. Research into the use of transesterified sunflower oil, and refining it to diesel fuel standards, was initiated in South Africa in 1979. By 1983, the process of producing fuel-quality, engine-tested biodiesel was completed and published internationally.

The first industrial-scale plant was erected in April 1989 (with a capacity of 30,000 tons of rapeseed per annum). Throughout the 1990s, plants were opened in many European countries, including the Czech Republic, Germany and Sweden. France launched local production of biodiesel fuel (referred to as diester) from rapeseed oil, which is mixed into regular diesel fuel at a level of 5%, and into the diesel fuel used by some captive fleets (e.g. public transportation) at a level of 30%. Renault, Peugeot and other manufacturers have certified truck engines for use with up to that level of partial biodiesel; experiment with 50% biodiesel are underway. During the same period, nations in other parts of the world also saw local production of biodiesel starting up; by 1998, the Austrian Biofuel Institute had identified 21 countries with commercial bio diesel projects In September 2005, Minnesota became the first U.S state to mandate that all diesel fuel sold in the state contain part biodiesel, requiring a content of at least 2% biodiesel.

For strengthening the quality control requirements of engine and equipment manufacturers, and allowing further companies to issue biodiesel engine warranties for the use of biodiesel fuels, a series of biodiesel standards were issued in succession, such as DIN 51606 (Germany), EN 14214 (Europe), ASTM D6751 (USA and Canada). In 2008, the current version of EN 14214 and ASTM D6751 were published, and superseded previous standards. With the quick development of biodiesel industry, biodiesel is playing a more and more important role in global primary energy.

## 2.2 Biodiesel Feedstock

Biodiesel can be produced from a variety of biolipids. Selecting the right feedstock for biodiesel production depends on oil composition, availability, climate and local soil conditions of the resource.

Mostly, the raw materials of biodiesel are soybean oil, sunflower oil, cottonseed oil, palm oil, palm kernel oil, coconut oil (copra), groundnut oil, rapeseed oil and canola oil. Beef and sheep tallow and poultry oil from animal sources as well as waste cooking oil are also sources of raw materials. Other biodiesel feedstock sources include: neem seed, Jatropha, almond, barley, camelina (Camelina sativa), fish oil, karanja (Pongamia glabra), laurel, oat, poppy seed, okra seed, rice bran, sesame, sorghum and wheat.

Most biodiesels are produced from food grade oils and are referred to as ‘first generation’ biodiesel and accounts for more than 95% of the world total production [7]. For instance, in countries where abundant fertile lands and water resources are easily accessible, first generation biodiesel e.g. soybean and sunflower biodiesels seems to be economically sustainable [8].

Biodiesel will lose its competitive advantage due to high price coupled with problems associated with the impacts on food security and land change. To mitigate these challenges, scientists are developing a new generation of biodiesel feedstocks of varying type, quality, and cost to help avoid such problems.

These feedstocks may include soapstocks, acid oils, tall oils, used cooking oils, and waste restaurant greases, various animal fats, non-food vegetable oils, and oils obtained from trees and microorganisms such as algae. Also, genetic modification is employed to obtain favorable traits of biodiesel crops, such as higher yields or the ability to grow on non-arable land.

Conventionally, biofuels including biodiesel are classified based on their feedstock and production technologies into four different generations. These generations include biofuels produced from, 1. Edible oil seeds, 2. Non-food oil crops and wastes, 3. Algae, and 4. The genetically engineered oil crops. Indeed, the most important challenging and limiting issue in biodiesel production is feedstock supply, accounting for over 70–80% of the total biodiesel production cost which is a serious threat to the economic viability of the biodiesel industry [9, 10].

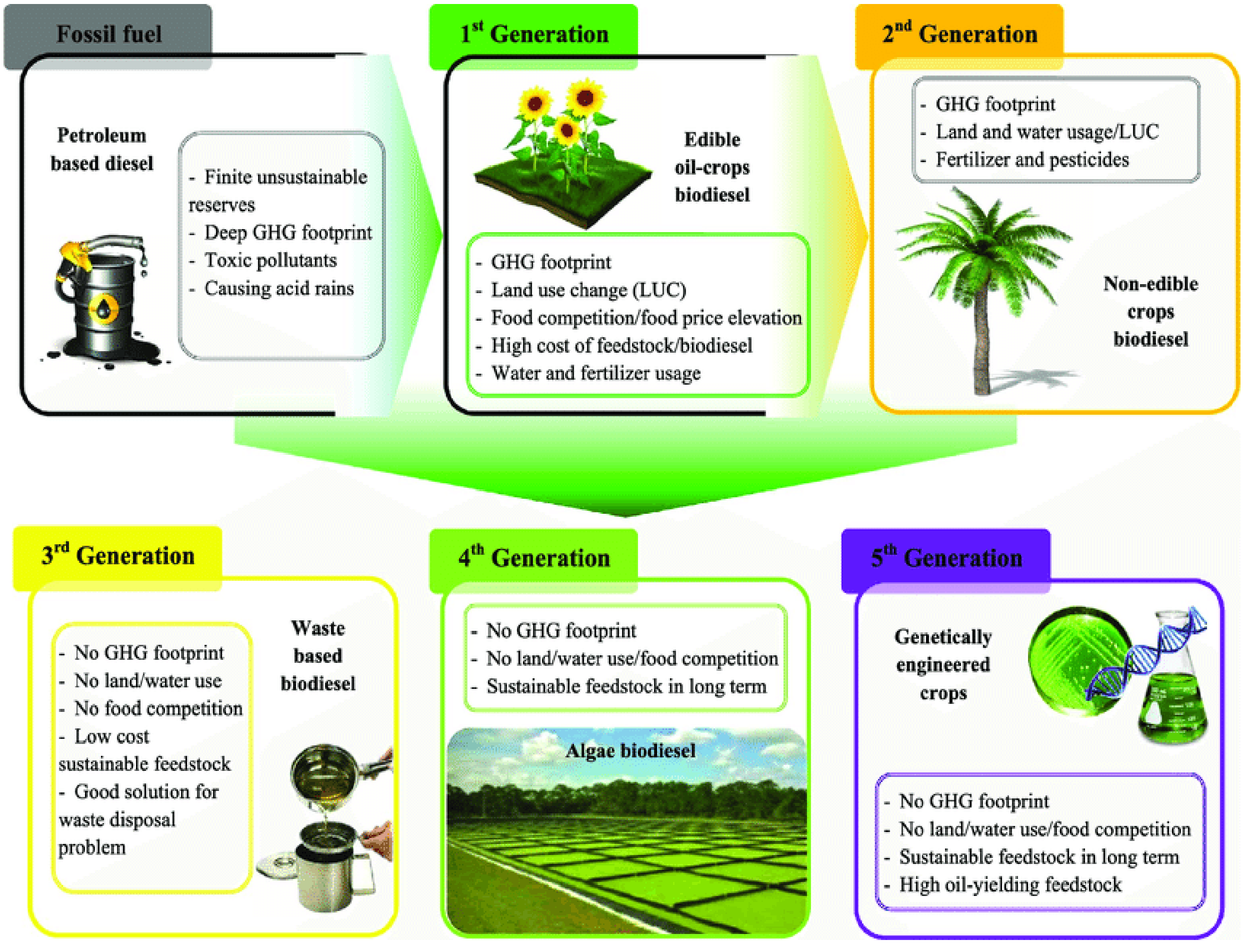

*Figure 2. 1 New classification of biodiesel feedstocks based on the sustainability issue*

### 2.2.1 Biodiesel Production from edible oil seeds

Over the last few years, there has been increasing amounts of research and interest in the different edible feedstocks that can be used to make biodiesel and the effects of the different feedstocks on the quality of the biodiesel [5]. Currently, biodiesel is produced from different crops such as, Jojoba oil, palm oil, soybean oil, canola, rice bran, sunflower, coconut, rapeseed, soybean and sunflower oil [11]. The major difference between various edible oils is the type of fatty acids attached in the triglyceride molecule. Fatty acid composition effects the yield percentage, reaction temperature, FFA content and molar ratio of the biodiesel oil [12]. The fatty acid composition of the triglyceride used for the production of biodiesel determines the physical and chemical properties of the fatty acid methyl or ethyl esters produced.

### 2.2.2 Biodiesel Production from Waste Vegetable Oil and Non Edible Oilseeds

The production of biodiesel from different non-edible oilseed crops and waste vegetable oil has been extensively investigated over the last few years.  Oil extracted from non-edible seeds cannot be directly used as fuel in automobile engine due to higher viscosities of oils. Moreover problems like injector coking, more engine deposits, ring sticking and thickening of engine lubricant are observed using straight vegetable oil as fuel. There are many ways and procedures to convert seed oil in diesel like fuel but trans-esterification is the one of the best process for production of biodiesel.

Today, cheap feedstocks are needed to make the production of biofuels profitable. The use of food crops as a resource for biodiesel is not economically competitive with petroleum-based diesel fuel. Fortunately, around the world large amounts of inedible oil plants are widely available. Non-edible vegetable oils are not suitable for human food due to the presence of some toxic components in them. However, this doesn’t affect the biofuel production. The conversion rate of non-edible oil into biodiesel is comparable to the one of edible oils in terms of production and quality. In this process, also useful by-products are generated which can be used in other chemical processes or burned for heat and power generation. For instance, the seed cakes after oil expelling can be used as fertilizers for soil enrichment.

In a non-edible vegetables oils evaluation, researchers listed more than 50 useful plants for biofuel production, ranging from all over the world. Additionally the necessity of such non-edible seeds is that it must be able to cultivate it on large scale on non-cropped marginal lands and waste lands. The Listed of some non-edible oilseed crops have been used to produce biodiesel [13].

Argemone mexicana
Azadirachta indica
Ricinus communis
Pongamia pinnata
Jatropha curcas
Putranjiva roxburghii
Schleichera triguga
Thevatia peruviana
Madhuca indica
Simmondsia chinensis
Melia azedarach
Cerbera odollam
Calophyllum inophyllum
Sapindus mukorossi
Hevea brasiliensis

***Figure 2. 2: some of non-edible oilseed crops have been used to produce biodiesel***

The above non edible oil seed crops can be listed as potential nonedible feedstock’s and this plants grow naturally without the aid of human effort Moreover, the production of algae can be achieved almost anywhere, even on sewage or salt water, and does not require fertile land or food crops, and processing requires less energy [14].

Waste vegetable oils are defined the used oils generated by the food industry, restaurants and households and are no longer to be consumed from humans [15]. Waste cooking oils have not strictly defined properties. This is because waste cooking oils are usually derived from a mixture of oils and/ or animal fats with different physical and chemical characteristics.

The quality of waste cooking oils is expected to vary as it depends on the type of vegetable oil used, the different culinary practices and the systems for collection and storage of waste oils. Additionally, different oils are used under the same conditions high and long exposure time frying temperatures resulting to different characteristics. During frying, vegetable oils are used at very high temperatures [15].

This process causes several chemical reactions such as hydrolysis, polymerization and oxidation. Therefore, physical and chemical properties of the oil change during frying. The free fatty acids percentage has be found to increase because of oxidation and hydrolysis of triglycerides in the presence of moisture in food. Increase in viscosity has been also referred because of polymerization, which leads to the formation of high molecular weight compounds. Other observations are related to the increase in acid number, density and saponification index in fried oil and a decrease in iodine value. Almost all the triglycerides, even from poor quality, can be converted into high quality biodiesel fuel, without significant pre-treatment. According to literature, the conversion yield of waste cooking oil into biodiesel has been reported to be around 80 – 90%, depending on the quality of waste cooking oil, the process for refining, technology and practices used during transesterification [15].

### 2. 2. 3 A. mexicana Description

Scientific Name with Author Arg mexicana L. Argemone is a genus of flowering plants in the family Papaveraceae commonly known as prickly poppies [1]. There are about 32 species native to the Americas and Hawaii [2]. The generic name originated as αργεμωνη in Greek and was applied by Dioscorides to a poppy-like plant used to treat cataracts [16]. A. mexicana has been accorded research and development attention it is found in Mexico and now widely naturalized in many parts of the world. An extremely hardy pioneer plant, it is tolerant of drought and poor soil, often being the only cover on new road cuttings or verges. It has bright yellow latex, and though poisonous to grazing animals, is rarely eaten, but has been used medicinally by many people including those in its native area, the Natives of the western US and parts of Mexico [17].

A. mexicana (also called Mexican poppy) is a species of poppy originally found in Mexico and at present widely distributed in many parts of the world. It is an herb with pale yellow flower and a height of 0.3 to 0.6 meters. It grows abundantly on dry soil and can tolerate drought [18]. The seeds of this plant are blackish brown, round and apparently have close resemblance with mustard (Brassica nigra) seeds. As a result, mustard is often adulterated by argemone seeds. A. mexicana seeds contain 22–36% of a pale yellow non-edible oil, called argemone oil or katkar oil, which contains the toxic alkaloids sanguinarine and dihydrosanguinarine. Four quaternary isoquinoline alkaloids, dehydrocorydalmine, jatrorrhizine, columbamine, and oxyberberine, have been isolated from the whole plant of A. mexicana [8]. Several significant instances of Argemone oil poisoning have been reported in India and some other countries such as Fiji and South Africa. Even little (1%) adulteration of mustard oil with Argemone oil has been shown to cause clinical disease. When mixed with mustard oil, it causes the disease “dropsy” with symptoms of swelling of the legs [19]. As the argemone seeds are rich in oil and its extraction from the seed is easy and economical, an attempt has been made in the present study to convert the oil to Fatty Acid Methyl Ester (FAME) through transesterification and to explore the potential for its use as a biodiesel [10].

#### ***2. 2. 3. 1 Botanical description***

A. mexicana is an annual herb, growing up to 150 cm with a slightly branched tap root. Its stem is branched and usually extremely prickly. It exudes a yellow juice when cut. It has showy yellow flowers. Leaves are thistle-like and alternate, without leaf stalks (petioles), toothed (serrate) and the margins are spiny. The grey-white veins stand out against the bluish - green upper leaf surface. The stem is oblong in cross-section.

Flowers are at the tips of the branches (are terminal) and solitary, yellow and of 2.5- 5 cm diameter. Fruit is a prickly oblong or egg -shaped (ovoid) capsule. Seeds are very numerous, nearly spherical, covered in a fine network of veins, brownish black and about 1 mm in diameter [20].

### *2. 2. 3. 1 Origin and Distribution in Ethiopia*

A.Mexicana is native in Mexico and the West Indies, but has become pantropical after accidental introduction or introduction as an ornamental. It is naturalized in most African countries, from Cape Verde east to Somalia, and south to South Africa (Bosch, 2008). Distribution: Africa, Northeast Tropical Africa, Ethiopia, Socotra Asia-Temperate, Arabian Peninsula, North Yemen, Oman, Saudi Arabia, South Yemen Europe, Middle Europe, Austria, Germany, Switzerland , Southeastern Europe, Bulgaria , Southwestern Europe, France, Portugal, Spain Southern America, Brazil, Piaui , Northern South America, Venezuela , S outhern South America, Paraguay , Western South America, Bolivia, Colombia, Ecuador Besides being competitive weeds in agriculture, A. mexicana is toxic. Seeds confused with those of mustard and if consumed can lead to illness and even death [21].

A.mexicana invaded many ecosystems and communities in Ethiopia in general, Farta, Gondar and Bahir Dar zuria districts in particular disrupting ecosystem structure, function and reducing native biodiversity (plants and animals). When the distribution and abundance of A. mexicana increased the abundance and distribution of native plant species decreased. A. mexicana shown excellent potential of antibiotic activity towards the bacteria S. aureus, S. agalectiae and E. coli and inhibits its growth.

Argemone has aflatoxins that often occur in crops in the field prior to harvest. Post-harvest contamination can occur if crop drying is delayed and during storage of the crop if water is allowed to exceed critical values for the mould growth Milk, eggs, and meat products are sometimes contaminated because of the animal consumption of aflatoxin-contaminated feed. Therefore, the health of the animals are at risk as the distribution increases besides it biodiversity destruction.

Biodiesel is a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, called B100. Production of biodiesel from nonedible plants is taking great picture of the current world development different plants can be mentioned from this A. mexicana can be listed in world wide. A. mexicana a source for biodiesel or it can be used to treat non healing wounds, constipation, Malaria, chronic fever etc. It is also used in Virechana Panchakarma treatment.

In our country A. mexicana is being used around the rural places for food preparation (enjera baking) and also tanners around rural palaces used it for their works. A. mexicana tends to grow along roadsides, in fallow and cultivated lands, riverbanks, disturbed areas, and on floodplains. It competes with and replaces native species in some cases and is also a significant crop weed and fertilized with Urea, N.P.K., and P2O5 [22].

A. mexicana is an ornamental plant and is sometimes used as a soil enricher for crops - after slashing. Plant extracts can be used as an insecticide and medicinal properties have been attributed to the sap and oil from the seed. However, these uses cannot compensate for this plant's overall negative impact.

A. mexicana is a serious agricultural weed. Where over-grazing reduces grass cover this can favour unpalatable species including A. mexicana. This plant is toxic to animals and cattle avoid grazing it. Harmful allelopathic effects of A. mexicana are recorded on germination and seedling vigour of wheat, mustard, fenugreek, sorghum, finger millet, tomato, cucumber etc. The allelochemicals cinnamic and benzoic acid are identified as harmful chemicals responsible for inhibition of germination and seedling vigour.

Edible vegetable oil either accidentally or deliberately contaminated with A. mexicana has resulted in epidemic dropsy in India. An epidemic occurred in South Africa following the contamination of wheat flour with A. mexicana . Harvesting crops in field infested with A. mexicana can be painful as the plant is poisonous and a skin irritant.

A. mexicana has been listed as noxious weed in South Africa (prohibited plants that must be controlled. They serve no economic purpose and possess characteristics that are harmful to humans, animals or the environment) and in states in Australia (New South Wales and Western Australia). Given abundant nature, drought tolerance and high oil content A.Mexican need high attention for future career in country to consider as a priority crop to alleviate energy source and reduce poverty. However, A. mexicana is one of the forgotten plant in Ethiopia.


a) b)

*Figure 2. 3: A. mexicana (a) plant and (b) seed*

## 2.3 Oil Extraction Methods

Various methods can be used in the extraction of oil. The method is normally dependent on the type of botanical material and seed size. These methods include;

### 2.3.1. Oil Extraction using Solvent

Solvent extraction with n-hexane can produce about high yield by weight of oil per kilogram of the seed. To extract oil using solvent, the seed will be crushed at the required size (powder).

The powdered seeds and hexane at different ratio are fed to soxhlet apparatus by the help of to extract oil. The extraction temperature is near to the boiling point of hexane. The solid cake and mixture of oil and hexane are separated using vacuum filter. Hexane and oil are separated using distillation at a temperature of slightly higher than the boiling temperature of hexane, which is recovered again for further extraction with fresh hexane. Percolation and maceration is other type of extraction method that are recommended for powdered seed.

### 2.3.2. Mechanical Pressing Oil Extraction

For oil extraction using mechanical pressing, seeds will be fed to mechanical presser which exerts high pressure for extracting oil. When pressure is exerted at the required amount, the oil will be separated from the solid cake. For farther purification the impurities will be separated by using centrifuge or gravity settling.

## 2.4 Biodiesel Production Methods

In the production process there are different methods that can be direct use or blending vegetable oil, thermal cracking, micro-emulsification and transesterification.

### 2. 4.1 Direct Use and Blending of Vegetable Oil

The direct use of vegetable oils in diesel engine is not favorable and problematic because it has many inherent failings. Even though the vegetable oils have familiar properties as biodiesel fuel, it required some chemical modification before it can be used into the engine. It has been researched extensively, although some diesel engine can run pure vegetable oils, turbocharged direct injection engine such as trucks are prone to many problems [23]. Energy consumption with the use of pure vegetable oils was found to be similar to that of diesel fuel. [23] Direct use of vegetable oils and/or the use of blends of the vegetable oils have generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems [24].

Heating and blending of vegetable oils may reduce the viscosity and improve volatility of vegetable oils but its molecular structure remains unchanged, hence polyunsaturated character remains [25]. The use of vegetable oils in diesel engines requires significant engine modifications, including changing of piping and injector construction materials, otherwise engine running times are decreased, maintenance costs are increased due to higher wear, and the danger of engine failure is increased.

### 2.4.2 Thermal Cracking (Pyrolysis)

Pyrolysis is the conversion of one organic substance into another by means of heat or by heat with the aid of a catalyst [26]. The pyrolyzed material can be vegetable oil, animal fat, natural fatty acids or methyl esters of fatty acids [27]. Conversion of vegetable oils and animal fats composed mostly of triglycerides using thermal cracking reactions represents a promising technology for the production of biodiesel [28]. This technology is especially promising in areas where the hydro processing industry is well established because the technology is very similar to that of conventional petroleum refining [28]. The fuel properties of the liquid product fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. Many researchers have reported the pyrolysis of triglycerides to obtain products suitable for diesel engines [28, 29]. The research on pyrolysis of triglycerides is divided into catalytic and non-catalytic processes [28]. The pyrolysis reactions of soybean, palm, and castor oils have been studied in an investigation. The adequate choice of distillation temperature (DT) ranges made it possible to isolate fuels with physical and chemical properties comparable to those specified for petroleum based fuels [29]. The equipment for thermal cracking and pyrolysis is expensive for modest throughputs. In addition, while the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produces some low value materials and, sometimes, more gasoline than diesel fuel [30].

### 2.4.3 Micro-Emulsification

Micro-emulsification is the formation of microemulsions (co-solvency) which is a potential solution for solving the problem of high vegetable oil viscosity.

A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid micro-structures with dimensions generally in the 1–150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles [30]. Micro-emulsion-based fuels are sometimes also termed ‘‘hybrid fuels’’,although blends of conventional diesel fuel with vegetable oils have also been called hybrid fuels [31]. Microemulsions are clear, stable isotropic fluids with three components: an oil phase, an aqueous phase and a surfactant. For this purpose, micro-emulsions with solvents such as methanol, ethanol and 1-butanol have been studied.

All micro-emulsions with butanol, hexanol and octanol can meet the maximum viscosity limitation for diesel engines. A microemulsion prepared by blending soybean oil, methanol, 2 octanol and cetane improver in the ratio of 52.7:13.3:33.3:1.0 has passed the 200 h EMA test. Micro-emulsion of vegetable oils lowered the viscosity of the oil but resulted in irregular injector needle sticking, heavy cabon deposits and incomplete combustion during 200 h laboratory screening endurance test [32].

### 2.4.4 Transesterification

Transesterification is a chemical reaction that involves triglyceride and alcohol in the presence of a catalyst to form esters with glycerol as the backbone [33]. The fatty acid composition of the triglyceride used for the production of biodiesel determines the physical and chemical properties of the fatty acid methyl or ethyl esters produced. More than 10 million tons of biodiesel fuel (BDF) have been produced in the world from the transesterification of vegetable oil with methanol by using acid catalysts (sulfuric acid, H2SO4), alkaline catalysts (sodium hydroxide, NaOH or potassium hydroxide, KOH), solid catalysts and enzymes [32].

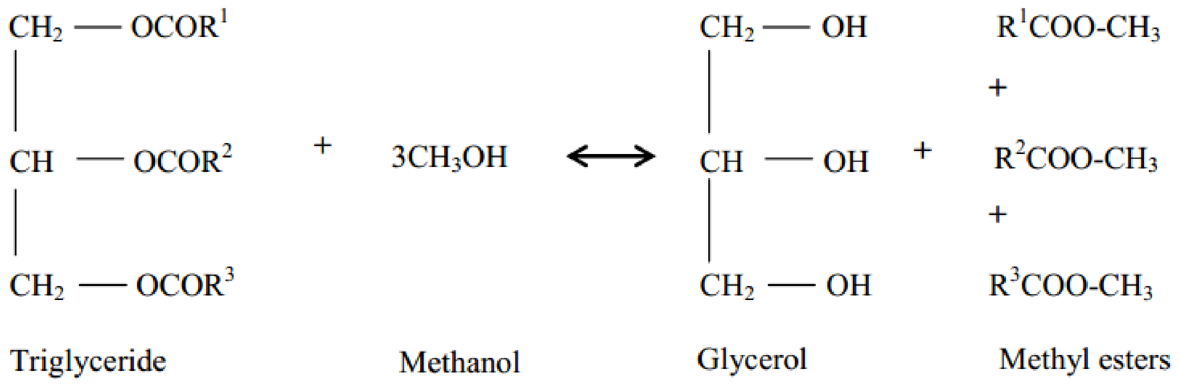

***Figure 2. 4 Over all transesterification reaction***

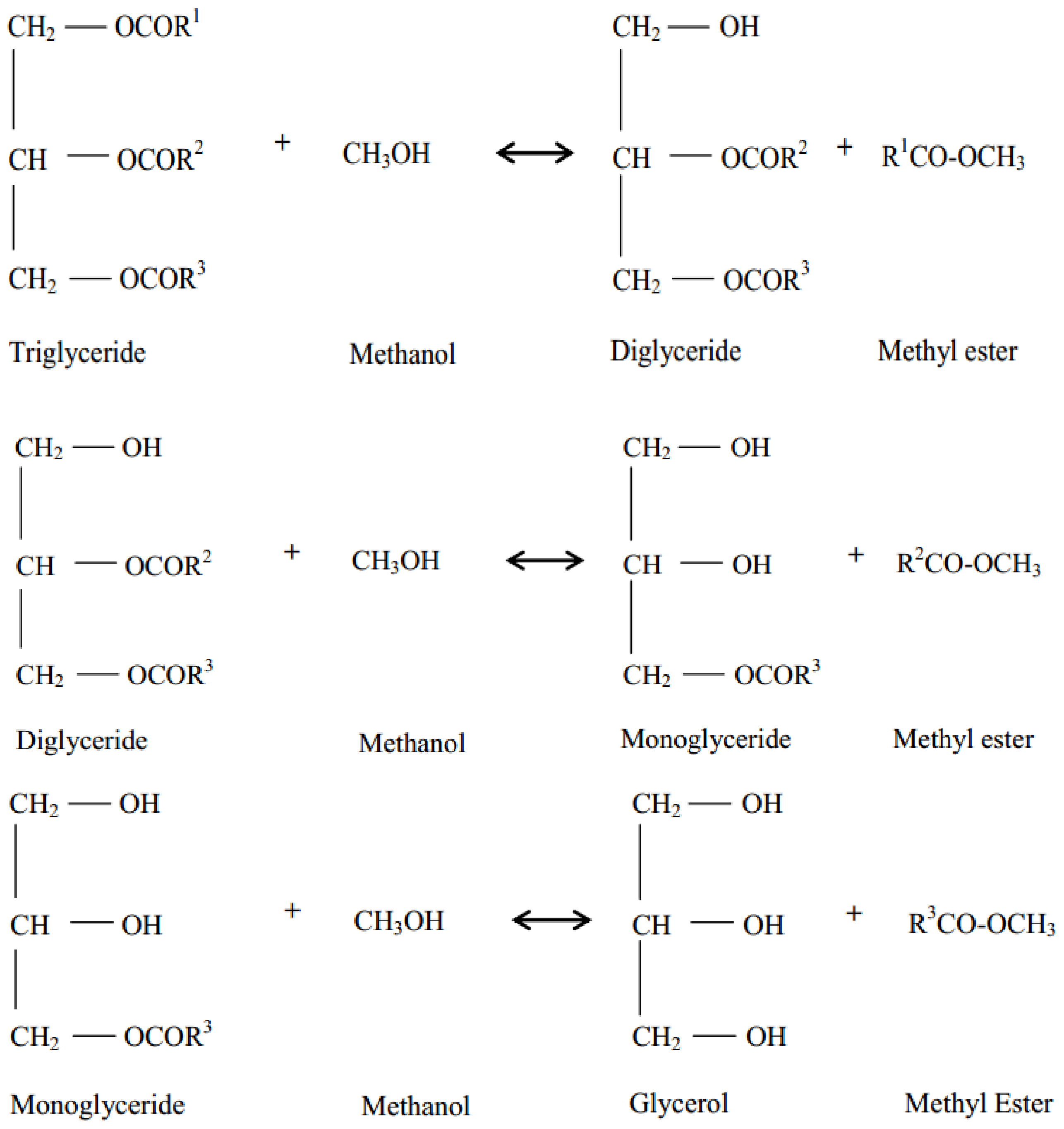

***Figure 2. 5: General mechanism of transesterification reaction process***

There are different transesterification processes that can be applied to synthesize biodiesel: (a) alkali or base-catalyzed transesterification, (b) acid-catalyzed transesterification, (c) enzyme-catalyzed transesterification, and (d) supercritical alcohol transesterification.

#### *2.4.4.1 Alkali or base catalyzed transesterification*

- **Homogeneous catalyst**

The transesterification reaction is catalyzed by alkaline metal hydroxides or alkoxides, as well as sodium or potassium carbonates. The alkaline catalysts give good performance when raw materials with high quality (FFA < 1 wt.% and moisture < 0.5 wt.%) are used [35]. The reaction is carried out at a temperature of 60–65 °C under atmospheric pressure with an excess amount of alcohol, usually methanol. The molar ratio of alcohol to oil is often 6:1 or more. It often takes several hours to complete the reaction when alkaline hydroxides such as NaOH or KOH are used. Alkaline alkoxides, e.g., sodium alkoxide, are the most reactive catalysts because the yield of FAME that can be attained is higher than 98% in a short reaction time of 30 min. Alkaline hydroxides are cheaper than the alkaline alkoxides, but less active.

The yield of FAME can be improved by simply increasing the amount of the alkaline hydroxides by one or two mol% to oil, and thus they are a good alternative to the alkaline alkoxides [36]. Researchers produced BDF from raw material dairy waste scum and the FAME yield reached 96.7% under the optimal conditions: KOH 1.2 wt.%; molar ratio of methanol to oil 6:1; reaction temperature 75 °C; reaction time 30 min at 350 rpm [37]. One of the biggest drawbacks for the base-catalyst is that it cannot be applied directly when the oils or fats contain large amounts of FFA, i.e., >1 wt.%. Since the FFA is neutralized by the base catalyst to produce soap and water, the activity of the catalyst is decreased. Additionally, the formation of soap inhibits the separation of glycerol from the reaction mixture and the purification of FAME with water [38]. Removal of these saponified catalysts is technically difficult and it adds extra cost to the production of biodiesel. Furthermore, since homogeneous base catalysts mainly dissolve in the glycerol and alcohol phase after the reaction is completed, they cannot be recycled for the following batches, and the crude BDF must be purified by a washing process with water or a distillation at high temperature under reduced pressure. In consequence, with vegetable oils or fats containing low FFA and water, the base-catalyst transesterification is much faster than the acid-catalyst transesterification and is most commonly used commercially on the industrial scale [39].

Biodiesel is currently synthesized using homogeneous alkaline catalysts because the transesterification reaction by an acid catalyst is much slower than the base-catalyzed reaction.

There are several comprehensive studies of basecatalyzed transesterification.[18, 19] The most common basic catalysts are potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium methoxide ($NaOCH_3$), and sodium ethoxide ($NaOCH_2CH_3$) [40].

- **Heterogeneous catalyst**

Homogeneous base-catalyst transesterification are high energy consumption, costly separation of the catalyst from the reaction mixture and the purification of crude BDF. Therefore, to reduce the cost of the purification process, heterogeneous solid catalysts such as metal oxides, zeolites, hydrotalcites, and alumina, have been used recently, because these catalysts can be easily separated from the reaction mixture, and can be reused. Most of these catalysts are alkali or alkaline oxides supported on materials with a large surface area. Similar to homogeneous catalyst, solid base-catalysts are more active than solid acid-catalysts [25, 26]. Homogeneous and heterogeneous catalysts are compared in appendix A4.

- **Activated Oxides of Calcium and Magnesium**

Oxides of alkaline earth metals such as Be, Mg, Ca, Sr and Ba have been used for synthesis of BDF in several studies. CaO and MgO are abundant in nature and widely used among alkaline earth metals [26-28]. The main advantage of solid catalyst is after each run, the catalyst was recovered by centrifuge and washed with methanol, and used for the next run. The results of many researches showed that the yield of FAME was more than 90% up to the seventh repetition [29]. Researchers carried out the transesterification of Jatropha curcas oil with methanol catalyzed by calcium oxide, and the yield of FAME was higher than 93% under the conditions namely the catalyst amount of 1.5 wt.%; temperature of 70 °C; molar ratio of 9:1; and reaction time 3.5 h [30].

The activity of the solid catalyst is dependent on the active sites on the surface of CaO or MgO. Since the surface of these metal oxides is easily poisoned by absorption of carbon dioxide and water in the air to form carbonates and hydroxides, respectively, the activity of these catalysts decreases with time.

However, the catalytic activity of these metal oxides can be recovered by calcination of the catalysts to remove carbon dioxide and water at high temperature. There are different calcination temperatures used to activate CaO depending on the oil and fat that the feed material contain [41].

Different calcination temperature and variables for maximum yield are listed on appendix B4. Additionally Tri-Potassium Phosphate, Metal Oxides Supported on Silica And Mixed Oxides of $TiO_2$–MgOv can be listed as solid catalyst.

### *2.4.4..2 acid catalyzed transesterification*

- **Homogeneous catalyst**

The transesterification reaction can also be catalyzed by Brønsted acids, preferably sulfonic and sulfuric acids, but the reactions rates are low and require relatively high temperatures to get high product yields [23] According to an acid-catalyzed mechanism for esterification. With starting raw materials containing a high amount of FFA such as waste cooking, Jatropha curcas, rubber, tobacco oils, etc., an acid-catalyst, usually a strong acid such as sulfuric, hydrochloric or phosphoric acid, is more favorable than base-catalyst because the reaction does not form soap. However, the acid-catalyst is very sensitive to the water content of the raw materials. It was reported that a small amount of water, i.e., 0.1 wt.% in the reaction mixture affected the FAME yield of the transesterification of vegetable oil with methanol. If the concentration of water is 5 wt.%, the reaction is completely inhibited.

Researchers conducted simultaneous esterification and transesterification reactions with acid catalysts where the yield of FAME attained was more than 90% with water content of less than 0.5 wt.% under the reaction conditions of temperature 60 °C; molar ratio of methanol to oil 6:1; sulfuric acid 3.0 wt.%, and reaction time 96 h [25]. Disadvantages of the acid-catalyst are that they require higher temperature and longer reaction time, in addition to causing undesired corrosion of the equipment. Moreover, to increase the conversion of triglyceride, a large excess amount of methanol, e.g., molar ratio of methanol to oil of higher than 12:1, should be used. In practice, therefore, to reduce the reaction time, the process with an acid-catalyst is adapted as a pretreatment step only when it is necessary to convert FFA to esters, and is followed by a base-catalyst addition for the transesterification step to transform triglyceride to esters. In general, acid-catalyst transesterification is usually performed at the following conditions: a high molar ratio of methanol to oil of 12:1; high temperatures of 80–100 °C; and a strong acid namely sulfuric acid [9].

- **Heterogeneous catalysis**

Despite lower activity, solid acid catalysts have been used in many industrial processes because they contain a variety of acid sites on their surfaces with different strengths of Brönsted or Lewis acidity, compared to the homogenous acid-catalysts. Solid acid-catalysts such as Nafion-NR50, sulfated zirconia and tungstated zirconia were chosen to catalyze biodiesel-forming transesterification due to the presence of sufficient acid site strength [32].

Sulfonic acid ion-exchange resins have been reported to show excellent catalytic activity in esterification reaction as a pretreatment step for oils containing a high amount of FFA [42,14]. In a pioneering study, Santacesaria et al. studied the kinetics of esterification of a mixture of triglyceride and oleic acid (with initial acidity in the range of 47.1–58.3 wt.%) with methanol using an acid ion-exchange polymeric resin (2 wt.%) as the heterogeneous catalyst. The sulfonic acid resin displays an active catalyst for esterification with the conversion of oleic acid to methyl oleate reaching more than 80% within 2 h reaction time at 85 °C [15].

Researchers performed the transesterification of refined and crude vegetable oils with a sulfonic acid-modified mesostructured catalyst resulting in a yield of FAME purity of over 95 wt.%, for oil conversion close to 100%, under the best reaction conditions: temperature 180 °C, methanol/oil molar ratio 10, and catalyst loading 6 wt.% with regard to the amount of oil. They found that these sulfonated mesostructured materials are promising catalysts for the preparation of biodiesel; however, some aspects related to the adsorption properties of the silica surface and the enhancement of the catalyst's reusability need to be addressed [25]. Recently, promising catalysts based on biomass pyrolysis by-products (sugars, biochar, flyash, etc.) have been developed for production of biodiesel [15].

#### *2.4.4.3 Enzyme-Catalyzed Transesterification*

Although enzyme-catalyzed transesterification processes are not yet commercially developed, new results have been reported in recent articles and patents.

The common aspects of these studies involve optimization of the reaction conditions (solvent, temperature, pH, type of microorganism which generates the enzyme, etc.) in order to establish suitable characteristics for an industrial application [43]. However, the reaction yields as well as the reaction times are still unfavorable compared to those of the base-catalyzed systems.

Lipase enzymes can also catalyze methanolysis of triglycerides. The use of lipases as enzyme-catalysts for biodiesel production is also increasingly interesting [44]. The main purpose is to overcome the issues involving recovery and treatment of the by-products that requires complex processing apparatus. The main drawback of the enzyme-catalyzed process is the high cost of the lipases. In order to reduce the cost, enzyme immobilization has been studied for ease of recovery and reuse. Additionally, inactivation of the enzyme that leads to decrease of yields is mostly restricted by the low solubility of the enzyme in methanol [45]. Although lipase catalyzed transesterification offers an attractive alternative, the industrial application of this technology has been slow due to feasibility aspects and some technical challenges [26]. Researches have been done For instance, the optimized reaction conditions for the transesterification of tallow with temperatureof 45 °C; stirring speed of 200 rpm; enzyme concentrations of 12.5–25%, based on triglyceride; molar ratio of methanol to oil of 3:1, and reaction time 4–8 h (for primary alcohols) and 16 h (for secondary alcohols). Lipozyme, i.e., IM 60 was most effective for the transesterification of tallow with a conversion of 95% when primary alcohols were used. In contrast, lipase from C. antarctica and P. cepacia (PS-30) was the most efficient with a conversion of 90% when secondary alcohols were used [46].

Large amounts of research have focused recently on the use of enzymes as a catalyst for the transesterification. Researchers have found that very good yields could be obtained from crude and used oils using lipases. The use of lipases makes the reaction less sensitive to high free fatty-acid content, which is a problem with the standard biodiesel process. One problem with the lipase reaction is that methanol cannot be used because it inactivates the lipase catalyst after one batch. However, if methyl acetate is used instead of methanol, the lipase is not in-activated and can be used for several batches, making the lipase system much more cost effective.

### *2.4. 4. 4 Supercritical Transesterification*

As a catalyst free method for transesterification uses, a supercritical methanol method has been investigated at high pressure (around 80 atm) and high temperatures (300–400 °C) in a continuous reactor. Under the supercritical condition, the reaction mixture becomes a single phase, and the reaction takes place rapidly and spontaneously [47].

Compared to processes using catalysts, the supercritical method has three main advantages as follows: The first, this process is friendly for the environment, because no catalyst is needed in the reaction, therefore, the separation process of the catalyst and soap from alkyl esters is unnecessary. The second, the supercritical reaction has a shorter reaction time, i.e., 2–4 min, than conventional methods using catalysts, and the conversion rate is very high [48]. The third, neither FFA nor the water content influences the reaction in the supercritical method. The FFA is converted to FAME instead of soap. Therefore, this process can be applied to a wide variety of feedstocks. However, the disadvantages of the supercritical methods stem mainly from the high pressure and temperature requirement, and the high molar ratio of methanol to oil (usually 42:1) that makes the cost of the production process expensive [3].

To conduct the transesterification in the supercritical condition under a lower temperature, Demirbas carried out the reaction of sunflower oil with methanol in the presence of CaO catalyst in supercritical methanol for biodiesel production. The results revealed that the transesterification was essentially completed within 6 min with an amount of CaO catalyst of 3 wt.%, molar ratio methanol to oil 41:1 at 525 K instead of a temperature of more than 600 K in the case without catalyst.

Most preferred, accepted and widely applicable method for biodiesel production is transesterification because it is less costly, simple method.

## 2. 5 Factor Affecting the Yield of Biodiesel Production

The main factors affecting the production of biodiesel are discussed as follows.

### 2. 5.1. Effect of Methanol to Oil Ratio

The most effective variable affecting the methyl ester production yield during the transesterification reaction is the molar ratio of alcohol to oil. Since transesterification is an equilibrium reaction, a large excess of alcohol is required for the reaction to move forward and avoid the reversible reaction [42].

The amount of alcohol added to vegetable oil is one of the important factors that affect conversion efficiency as well as production cost of biodiesel. The conversion efficiency is defined as the yield of the process represented in terms of percentage. Generally the amount of alcohol required for transesterification reaction is analyzed in terms of volumetric ratio. Stoichiometriclly, the alcohol/ oil molar ratio is 3:1. Higher amount of alcohol is required to drive the reaction to completion at faster rate. It is observed that lower amount of alcohol requires longer reaction periods. The conversion efficiency of transesterification reaction with increasing amount of alcohol obtained [49].

### 2. 5. 2 Effect of Catalyst type and Amount

Catalyst concentration this parameter is highly affected by the kind of catalyst used, different catalysts will require different concentrations. Even if they belong to the same group (as in the case of potassium hydroxide and sodium hydroxide), different concentrations will be necessary to attain the same yields. Therefore, the optimum value for every catalyst will have to be determined by titration. If the amount of catalyst is higher than the optimum, there will be a decrease in the yield of methyl esters due to the formation of soap in presence of high amount of catalysts, which apart from lowering the yield increases the viscosity of the reactants [48].

As earlier stated great efforts have being made by several researchers and industries to explore and exploit use of heterogeneous catalysts in the production of biodiesel. Some of the reasons for the recent growth and development of heterogeneous catalysts include among others:

biodiesel yield of 98wt% and simplicity in catalyst separation process, high-purity by-products, less cost of separation and low energy consumption [50].

The nature of catalyst used plays a great role during transformation of vegetable oil to biodiesel. As a result, catalyst is among the key factors determining the rate and yield of biodiesel during biodiesel production process [51].

- **Recovery and Reuse of Catalyst**

Recovery of catalyst from the reaction mixture is an important operational parameter. From a financial economic point of view, the use of heterogeneous catalyst in biodiesel production could reduce its price becoming competitive with diesel. The used catalyst was recovered and reused for further transesterification reactions. The obtained results showed the recovered catalyst was still efficient even after seven successive uses. This suggests that the use of manganese carbonate could be a fruitful approach for biodiesel production.

### 2. 5.3 Effect of Reaction Temperature

Temperature values for the transesterification reaction vary depending on the literature source. It is well known that higher temperatures speed up the reaction and shorten the reaction time. Apart from that, higher temperatures usually mean obtaining higher ester yields [48]. However; It should also be noted that if the reaction temperature is higher than the boiling point of the alcohol, it will evaporate, resulting in a lower yield [48]. It is also an accepted fact that usually the optimum temperatures for the transesterification range between 50 and 60ºC, depending on the kind of oil to be processed In the case of rapeseed oil, the optimum temperature value for its methanolysis has been found to be 65ºC [48].using high temperature lead to evaporation, it is highly recommended to use methanol at (60 ºC) close to the boiling point.

### 2. 5.4 Effect of Reaction Time

The reaction time clearly influences the outcome of the reaction, since the conversion rate increases with the reaction time [52]. If the reaction time is not long enough the ester yield will be low, therefore, part of the oil will be unreacted. For the rapeseed oil, when heat is used in the reaction, the optimum reaction time is two hours [48].

### 2. 5 .5 Effect of Agitation speed

Agitation speed plays an important role in the formation of end product (mono alkyl ester or biodiesel), because agitation of oil and catalyst mixture enhances the reaction. For example the mixing intensities chosen were 200 rpm, 400 rpm, 600 rpm and 800 rpm for 60 min while other parameters were kept constant. At 400 rpm higher conversion of end product were obtained. Because, lower stirring speed shows lower product formation. On the other hand higher stirring speed favors formation of soap. This is due to the reverse behavior of transesterification reaction [66]

There are different parameters that surely effect the yield of biodiesel the most common types are listed above and other parameters such as selection of the right catalyst and Effect of Reactant Volumetric Flow Rate Should be included.

## 2. 6 Biodiesel Storage

Storage Stability can refer to two issues for fuels: long-term storage stability or aging and stability at elevated temperatures and/or pressures as the fuel is recirculated through an engine’s fuel system. For petroleum diesel, long-term storage stability is commonly referred to as oxidative stability. Thermal stability is the common term for the stability of fuels at elevated fuel system temperatures.

In biodiesel, fuel aging and oxidation can lead to high acid numbers, high viscosity, and the formation of gums and sediments that clog filters. If the oxidation stability, acid number, or viscosity measurements exceed the limits in ASTM D6751, the B100 is degraded to the point where it is out of specification and should not be used. Biodiesel with high oxidation stability (longer induction time) will generally take longer than biodiesel with low oxidation stability to reach an out-of-specification condition.

Monitoring the induction time and acid number of B100 over time can provide an indication of oxidation. B100 should be tested at receipt to ensure it is within specification. If the biodiesel will be stored prior to blending, the induction time and acid number should be monitored at regular intervals to ensure the biodiesel is not oxidizing.

The higher the level of unsaturation, the more likely that the B100 will oxidize. Saturated fatty acid esters are fairly stable, and each time the level of unsaturation increases (for example, from monounsaturated to polyunsaturated), the stability of the fuel decreases exponentially. The points of unsaturation on the biodiesel molecules can react with oxygen, forming peroxides that break down into acids, sediments, and gums.

- Heat and sunlight will accelerate this process.
- Certain metals such as iron, rust, copper, brass, bronze, lead, tin, and zinc will accelerate the degradation process and form even higher levels of sediment. B100 should not be stored in systems that contain these metals.
- Some types of feedstock processing and biodiesel processing can remove natural antioxidants, potentially lessening inherent stability. Plant oils and fats are produced with natural antioxidants—nature's way of protecting the oil from degradation. Bleaching, deodorizing, or distilling oils and fats, either before or as part of the biodiesel process, can remove these natural antioxidants.
- Antioxidants, whether natural or incorporated as additives, can significantly increase the storage life or stability of B100.
- Keeping oxygen from the biodiesel reduces or eliminates fuel oxidation and increases storage life. Commercially, this is done by using a nitrogen blanket on storage tanks or storing biodiesel in sealed drums or totes with minimal headspace.

B100 should not be stored longer than four months unless it has been treated with synthetic antioxidants and has an oxidation stability of 6 hours or longer. Non-oxidizing storage conditions in containers with little head space or under a nitrogen blanket will also be helpful. In fact, when B100 is being stored longer than about two months, it should be tested for oxidation stability every two weeks. One of the best ways to stabilize biodiesel is to blend it with petroleum diesel Biodiesel over time will soften and degrade certain types of elastomers and natural rubber compounds.

Materials like bronze, brass, copper, lead, tin and zinc may oxidize the diesel or Biodiesel fuels and create sediments.

## 2.7 Literature summary

There are various methods available for producing biodiesel, the alkali-catalyzed transesterification of vegetable oils and animal fats is currently the most commonly adopted method. Transesterification is basically a sequential reaction. However, when the raw materials (oils or fats) contain a high percentage of free fatty acids or water, the alkali catalyst will react with the free fatty acids to form soaps and the water can hydrolyze the triglycerides into diglycerides and form more free fatty acids. These are undesirable reactions which reduce the yield of the biodiesel product. Therefore, after refining the raw materials, the acidic feed stocks should be pre-treated to inhibit the saponification reaction. The transesterification reaction requires an alcohol as a reactant and a catalyst. The most commonly used alcohol is methanol while sodium hydroxide and potassium hydroxide are the most commonly used homogeneous catalysts were as Calcium oxide and Magnesium Oxide are heterogeneous Catalyst.

There are four primary factors affecting the yield of biodiesel, i.e. alcohol quantity, reaction time, reaction temperature, and catalyst concentration. Production of biodiesel from *Argemone Mexicana* by Manganese carbonate was achieved similarly Calcium Oxide were taken on this research, parameters were taken from previous research (Manganese Carbonate).To ensure a complete transesterification reaction, the molar ratio of alcohol to triglycerides should be increased in the range of (3:1 -8:1) with the use of an alkali catalyst in range of (0.2 – 3.0%). For oils with a high percentage of free fatty acids, a higher molar ratio is needed. Because the conversion rate of fatty acid esters increases with reaction time. The reaction time were taken in between (20-90 min) higher reaction temperature can decrease the viscosity of oils, lead the alcohol to evaporate and it was taken in the range of (25-75$^o$C). Maximum biodiesel (90%) yield was achieved at 5:1 methanol to oil molar ratio, 1 Wt% catalyst concentration, 45 min time of reaction and 60$^o$C temperature.

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

# CHAPTER THREE

## 3. Materials and Methods

### 3.2.5 Crude Oil Purification

**Oil degumming**

The crude oil first heated to 70 $^oC$ under stirring by mechanical stirrer at 1000 rpm in a jacketed glass vessel connected to a circulation thermostat. 3% of distilled water (which was heated to approximate to 90 $^oC$) and 2% phosphoric acid (85%) were added to the vessel. The mixture was stirred for 1 hour and allowed to settle for 20 minutes. The black formed precipitate was separated by centrifuging for 0.5 hour at 3500 rpm [54].

**Washing**

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

**Figure 3. 1 crude oil washing**

## 3.1 Chemicals/Reagents and Materials Used

During this study, some of the chemicals used were methanol, ethanol, diethyl ether, calcium carbonate, sodium hydroxide, phenolphthalein, distilled water and Argemone seeds. These

chemicals were analytical grade and taken from school of chemical and bioengineering laboratories and purchased from chemical supplier companies in Addis Ababa, Ethiopia.
Argemone seed, The main equipment used during the study reactor, flask, beaker, measuring cylinder, pipette, burette, separatory funnel, centrifuge, Buche-funnel, vibro viscometer, vacuum pump, water bath, thermometer, hot plate with magnetic stirrer, digital balance and glassware among others.

- **Seed collection**

The required amount of Mexican poppy (Argemone mexicana ) seeds (Fig. 3.1 A and B) were collected from dried poppy plant grown on farmers agricultural fields which was located in Amhara Regional State. 15 kg of A. mexicana were collected from Lalibela (ayna bugina) werda.

**Figure 3. 2 A) A.mexicana on farm B) collected seed of A.mexicana**

## 3.2 Experimental Methods

The methodology of the research was began by preparing calcineted CaO catalyst and methanol to produce biodiesel from A. mexicana seeds at laboratory scale with batch production of biodiesel, through transesterification method. Since the ultimate objectives of the present study were to identify the effects of different process parameters for Biodiesel production and to find the optimum conditions to maximize the yield of Biodiesel , reaction time, alcohol to oil molar ratio and catalyst to oil molar ratio (wt/wt) were the reaction parameters considered.

The values of reaction parameters used in this research were selected based on the gaps indicated on the previous works done by different researchers [53].

The physicochemical parameters were considered for crude A. mexicana oil and FAME, The present study include; density (specific gravity), kinematic viscosity, acid value, iodine value, flash point and cetane number were conducted. Finally, the results were compared against to the standard specifications of ASTM/EN. The Design-Expert 7.0.0 Trial software program was used for the purpose of optimization.

### 3.2.1 A. mexicana Seed Preparation

The collected seeds were separated from the chaffs and other impurities, and the selected (clean, wet seeds) weighted before drying to remove excess moisture. After the moisture contents were noted by weight balance method the moisture was removed by drying the seed in 105 $^{o}$c for 6 hours in the laboratory oven.

### Size Reduction (crushing)

A. mexicana seeds were crushed using grinder (Fig. 3.2 A). This operation ruptures the cell wall and releases the solute (Fig. 3.2 B) for direct contact with the solvent during the contact equilibrium process.

**Figure 3. 3 A) Coffee crusher B) crushed seed**

### 3.2.2 Determination of moisture content of A. mexicana

Sample was taken to determine the moisture content of the seed according to AOAC standard (AOAC 1980). A 100 g of each crushed sample were inserted in crucible, the crucible was weighed with and without the amount of crushed seed. The crucible with seed was dried in an oven at 105 °C for 7 h. The sample was removed each 2h from the oven and placed in the desiccator for 30 minutes to cool and re-weighed till constant weight is obtained. .The test was replicated 3 times and the average moisture content of the seed was then calculated using the following equation 3.1.

$$Moisture\ Content\ = 100 \times \left[\frac{w_1 - w_2}{w_2}\right]\% \qquad (3.1)$$

Where: - $W_1$ original weight of the sample before drying

$W_2$ weight of the sample after drying

### 3.2.3 Oil Extraction

The extraction was performed in Soxhlet extractors by using hexane as a solvent.

The dried seeds were then weighed and powdered. The fine seed, was then subjected to Soxhlet extraction using n-hexane as a solvent. The duration of each batch was 10 hrs for complete extraction. The solvent required for extraction of per kg seeds was in the ratio of 5:1 (5 L solvent for 1 kg seeds). The water bath was adjusted above the boiling point of the solvent which 70 $^{o}$C (figure 3.3 a). The oil was recovered from the solvent by rotary evaporator (figure 3.3 b). The extracted oil was then measured to calculate the percentage oil in the seeds [53].

a) b)

**Figure 3. 4 A) oil extaction B) rotray evaporator**

### 3.2.4 Determination of the Percentage of the Seed Oil Extracted

40 g of the sample was placed in the thimble and about 200 ml of hexane was poured into round bottom flask. The apparatus was heated at 68 $^{0}$C and allowed for 10 hr of continuous extraction using soxhlet apparatus. The experiment was repeated in triplicate. At the end, the solvent was distilled off using rotary evaporator.

The percentage of oil extracted was determined using Equation 3.2

$$oil\ yield\ \% = \left[\frac{Mass\ of\ crude\ oil\ extracted}{Mass\ of\ total\ seed\ used} \times 100\right] \tag{3.2}$$

**Figure 3. 5 Crude A. mexicana oil**

## 3.3 Catalyst Calcination

The surfaces of Calcium Oxide can be covered with carbon dioxide and water as it is handled in air. In order to have maximum basic sites on the surface of CaO catalyst, pretreatment at high temperatures is required maffle furnace is used as show in the figure 3.6. Commercial CaO was calcinated within 700 $^0$C temperature has the best catalytic activity on the reaction conditions of 6:1 methanol to oil ratio, 1 % catalyst and 2 hours reaction time for high yield of biodiesel. Using excess alcohol is suggested for the reaction to be completed in short time.

**Figure 3. 6 maffle furnace**

## 3.4 Biodiesel Production Procedure

The transesterification process was performed in this work as shown in the (figure 3.6 a) below. A 100 ml glass reactor equipped with mechanical stirrer in the water bath and condenser was used in all the experiments. The reaction was connected in the water bath within the adjusted temperature. A mechanical stirrer fitted with stainless steel propeller provided the mixing requirement.

Initially, about 25 ml of purified A. mexicana seed oil was poured into a 100 ml glass reactor and a steady state temperature of 60 $^{O}$C at atmospheric pressure was reached before mixing with the amount of methanol and heterogeneous catalyst. The reaction was timed as soon as mechanical stirrer was turned on.

The transesterification reaction was carried out by fixing agitation speed constant and temperature for the whole experiment and changing the main parameters, which are molar ratio of oil to methanol at 1:3, 1:6 and 1:9 mass ratio of catalyst to oil 1%, 1.5% and 2% and time of 1 hr, 1.5 hr and 2 hr.

Finally, the resulting mixture was poured in to separatory funnel and allowed to stand overnight to separate into two layers as shown in the (figure 3.7 b), a separate phase of glycerol with catalyst and biodiesel based liquid phases. Then the bottom layer was decanted since its glycerol and then biodiesel was obtained and remained in the separatory funnel.

The product was washed repeatedly with hot water until a clear layer of biodiesel was obtained and unreacted methanol and trace moisture was removed from the product by rotary evaporator. These procedures are used for each experiments executed at different parameters using the experimental design matrix and further characterization was held.

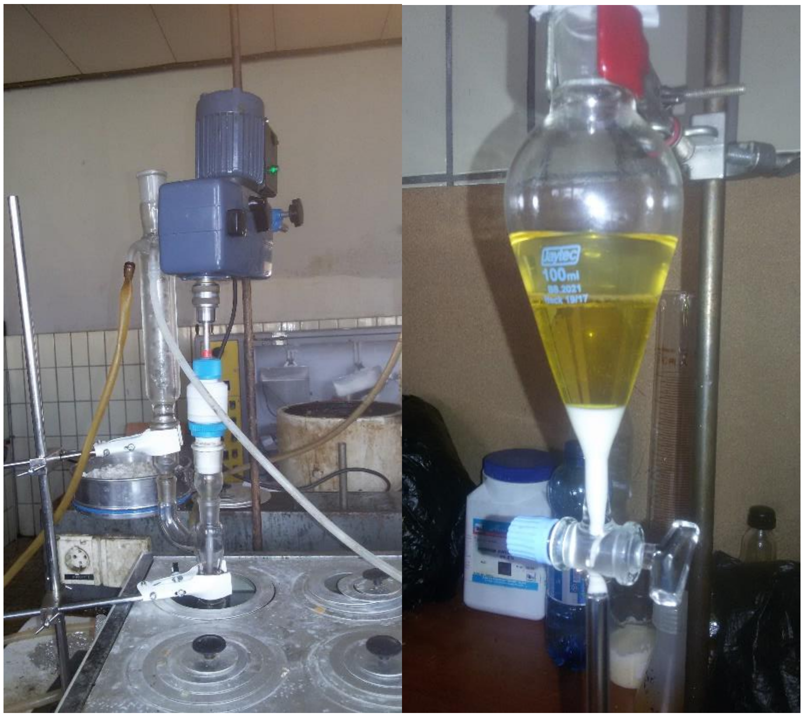

**Figure 3. 7 A) FAME production B) FAME phase separation**

### 3.4.1 Feed Material Requirement for Biodiesel Production

25 ml of purified A. mexicana oil was used for each run. Hence, the amount of methanol and catalyst was calculated as follows using the process parameters.

The volume of methanol required was calculated by using the listed equations, when the molar ratio of oil to methanol changes.

$$\frac{n\ oil}{n\ methanol} = (Y) \qquad (3.3)$$

Where: - Y is the ratio of methanol to oil (amount) used in the runs

n is mass oil.

Substitute mass for mole;

$$\frac{\frac{\rho oil \times Voil}{Moil}}{\frac{\rho methanol \times VMethanol}{M\ methanol}} = Y$$

The amount of catalyst required was calculated by using the equation 3.4 and 3.5

$$moil = \rho\, oil \times Voil \qquad (3.4)$$

$$\frac{mass\ of\ catalyst}{mass\ of\ oil} = X \qquad (3.5)$$

Where: - X is the amount of catalyst need for each runs (%)

The amount of methanol and catalyst used for the experiment were attached on appendix D.

## 3.5 Physicochemical Analysis Method

Physicochemical properties of the samples (FAME and AMO) were analyzed for its oil density (specific gravity), kinematic viscosity, acid value, saponification content, iodine value, cetane number and flash point using the test methods outlined below. All determinations were done three times and the average values were recorded.

***Table 3. 1: Physicochemical analysis parameters***

| **Characteristics** | **AMO** | **FAME** |
|---|---|---|
| Specific gravity | X | X |
| Density | X | X |
| Kinematic Viscosity | X | X |
| Acid Value | X | X |
| Saponification Value | X | X |
| Iodine Value | X | X |
| Higher Heating Value | X | X |
| Flash Point | X | X |
| Cetane Number | - | X |

**X** :-conducted works

### 3.5.1 Determination of density and specific gravity

The specific gravity and density were measured by density meter samples which were injected to the density mater equipment to display the result.

### 3.5.2 Determination of Kinematic Viscosity (KV)

Vibro viscometer was used to determine the viscosity of oil, and the sample was kept in the water thermostat bath until the oil reaches 40 $^{o}$C. After maintaining the equilibrium temperature, the Vibro viscometer tip was inserted to the sample and the reading was taken from the controller as dynamic viscosity. The kinematic viscosity which is equal to the ratio of dynamic viscosity to density of the oil can be given by Equation 3.6.

$$\mu = \frac{V}{\rho} \tag{3.6}$$

Where;-

μ=kinematic viscosity, mm$^2$/s

ν=dynamic viscosity, mPa.sec and ρ=density, kg/m$^3$

**Figure 3. 8 Vibro viscometer**

### 3.5.3 Determination of acid value

Standard alcoholic potassium hydroxide solution (0.1 N) was prepared by dissolving KOH (pellet) with 95 %ethanol. The solution was filtered and stored in brown bottle for five days. A phenolphthalein 10 g per liter of 95% v/v ethanol was used as an indicator. Furthermore, a mixture of 1 to 1 ratio (v/v) 95% ethanol and diethyl ether was prepared by mixing 500 ml diethyl ether and 500 ml of ethanol. 25 ml of diethyl ether was mixed with 25 ml of hot ethanol and 1 ml of phenolphthalein solution (1 %). Next, the mixture was carefully neutralized with 0.1N KOH.

About 5g of the melted oil was dissolved in the mixed neutral solvent and titrated with aqueous 0.1N ethanolic KOH shaking uniformly until a pink colour appears which persisted about 15 seconds is requried. The volume of 0.1 N ethanolic KOH (V) for the titration was noted [55, 47].

The total acidity (acid number) in mg of KOH/g of oil was calculated using equation 3.7 (a). The free fatty acid, FFA, of the oil was calculated from the acid value using Equation 3.7 (b).

$$Acid\ Number = \frac{V \times N \times 56.1}{M} \qquad 3.7\ (a)$$

Where:-

V - Volume expressed in mili liter of 0.1N solution of ethanolic KOH

M - Mass in gram of test portion

N - Concentration of ethanolic KOH

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

$$\%\ FFA = AV/\ 2 \qquad 3.7\ (b)$$

### 3.5.4 Determination of saponification value

Saponification value is a measure of the total free and combined acids especially in fat , wax or resin expressed as the number of milligrams of potassium hydroxide required for the complete saponification of one gram of substance.To find the value Potassium hydroxide solution of 0.5M, in 95 %( v/v ethanol) was prepared. 35 g of KOH pellet was dissolved in 20 ml water, and the solution was mixed with 1000 ml of 95% ethanol. The solution was allowed to stand for 12 hours at room temperature and a clear supernatant solution decanted off. The filtered solution was then kept in the dark for storage. Hydrochloric acid of 0.5M was standardized and a 2% phenolphthalein as indicator was prepared. 2 g of the oil sample was introduced into a 250 ml conical flask connected to a reflux condenser and 25 ml of alcoholic KOH solution was added into it. The flask was heated at 78 $^{o}$C (boiling temperature of ethanol) for 1hr, swirling intermittently using magnetic stirrer until complete saponification. The flask was removed from the heat mantel, and then 5 drops of phenolphthalein indicator was added, and the hot soap solution obtained was slowly titrated against the 0.5N HCl. The end point was reached when pinkish coloration changed to colorless.

Blank determination was also conducted along with the sample, using the same reagents minus sample (and volume the saponification value (SV) (expressed as the number of milligram of KOH required to saponify 1g fat) saponification value was calculated using Equation 3.3 [48].

$$Saponification\ Number = \frac{(Vb - Va)\ \times N \times 56.1}{W} \qquad (3.8)$$

Where:-

W - Weight of oil taken in gram
N - Normality of HCl solution
Va - Volume of HCl solution used in the test in milliliter
Vb- Volume of HCl solution used in black in milliliter

### 3.5.5 Determination of Iodine Value (IV)

The iodine value of the FAME was determined using the empirical formula suggested by other researcher's for determination of higher heating value by using equation 3.9 to 3.11. After rearrangement the iodine value was calculated from equation 3.12. Equations 3.9 were developed for the calculation of the Higher Heating Value (HHV) of vegetable oils and FAME from their viscosity (ν). Relationships derived from physical properties of vegetable oil and biodiesel fuels [46]. The equations between viscosity and higher heating values are

For vegetable oils.

$$\text{HHV} = 0.0317\ \nu + 38.053 \qquad (3.9)$$

For FAME;

$$\text{HHV} = 0.4625\ \nu + 39.450$$

$$\text{HHV} = 49.43 - [0.041(\text{SN}) + 0.015(\text{IV})] \qquad (3.11)$$

$$IV = \frac{HHV - 49.43 + 0.041\ (SN)}{1!0.015} \qquad (3.12)$$

Where :- SN – sponofication numer

### 3.5.6 Determination of Cetane Number (CN)

The cetane number of the FAME was determined using the empirical formula suggested at equation 3.8, using the result of saponification number (SN) and the iodine value (IV) of the FAME [41].

$$CN= 46.3 + (54.58/SN) - 0.225(IV) \qquad (3.13)$$

### 3.5.7 Determination of Flash Point (FP)

The flash point of the FAME was determined using open cup method. The cup was filled with the FAME up to the mark (about 75 ml) and the cup was heated by a Bunsen burner.

A small open flame was maintained from an external supply of natural gas. Periodically, the flame was passed over the surface of the oil. When the flash temperature was reached the surface of the oil catch flame, the temperature at the moment was noted and reported as flash point temperature.

### 3.5.8 Determination of high heating values

Calorific value (energy content or heat of combustion) of a fuel was determined using bomb calorimeter.

## 3.6. Experimental Design

A three-level-three-factor and 6 center points were used on Central Composite Design experiment was applied for carrying out the optimization studies to maximize the yield of FAME in the transesterification process. A total of 20 experiments were conducted separately for getting the experimental response of FAME yield. The reaction time (R) (hours), methanol to oil ratio (w/w) (M) and the catalyst concentration (c) (%) were the independent variables selected for investigation. The coded and uncoded levels of the independent variables used for the transesterification of FAME are given in Table 3.2.

*Table 3. 2: Independent variables used for CCD in transesterification process*

| **Variables** | Level | | |
|---|---|---|---|
| | -1 | 0 | 1 |
| The reaction time (hours) (R) | 1 | 1.5 | 2 |
| Methanol/oil molar ratio (w/w) (M) | 1:3 | 1:6 | 1:9 |
| Catalyst loading wt.(%) (C) | 1 | 1.5 | 2 |

The design-expert program was used in the regression analysis and analysis of variance (ANOVA). There are about five known model equation that can model the responses of the variables in Design expert software. These are: mean, Linear, FI, Quadratic and Cubic model equation. The model selection process is based on the greater value of F-value, significance of the model.

# CHAPTER FOUR

## 4. Result and Discussion

## 4.1 Seed Preparation, Oil extraction, Purification and Characterization

### 4.1.1 Moisture content of Seed

After the seed samples were cleaned and selected, the moisture content test of the A. mexicana seed was conducted three times and the results were summarized in Table 4.1 based on equation 3.1 (materials and methods session).

***Table 4. 1: Moisture content of A. mexicana seed***

| Sample Run | Samples weight (g) | | | Moisture content (%w/w) |
|---|---|---|---|---|
| | $W_1$ | $W_2$ | $W_1 - W_2$ | Per sample |
| 1 | 100 | 91 | 9.27 | 9.27 |
| 2 | 100 | 90.9 | 9.1 | 9.1 |
| 3 | 100 | 91.3 | 8.7 | 8.7 |
| Average | | | | 8.99 |

Where: - $W_{1:}$ initial weight of the sample, $W_{2:}$ after oven weight

As the result shown in Table 4.1 the average value of moisture content of A.mexicana seed was 8.99%. If the moisture content isn't reduced, it will decrease the yield of biodiesel by forming side reaction. Therefore, in this study the moisture content of the oil was removed by putting the seed into the oven at 105 $^oC$ for 6 hours as recommended by other researchers.

### 4.1.2 Oil Extraction

The desired amount A. mexicana oil was extracted from the collected seeds using soxhlet apparatus. The extraction step was prepared for 40 g of the sample and the experiment was repeated in triplicate. The oil content (oil yield) of the crushed seeds was calculated by equation 3.2.

***Table 4. 2: Oil yield of A. Mexican seed***

| Run | Sample (g) | V ($cm^3$) | M=s*v | Yield (%) | Average |
|---|---|---|---|---|---|
| 1 | 40 | 19.26 | 17.8 | 44.5 | 40.4 |
| 2 | 40 | 26.08 | 24.1 | 37.5 | |
| 3 | 40 | 16.99 | 15.7 | 39.25 | |

The average oil content of the seed was calculated and obtained an average of 40.4 %. This value was found to be similar with the pervious finding [53]. This indicated that the Argemone seed has high oil content which can be good potential for biodiesel production with non-edible plant that could not compete with human food consumption.

### 4.1.3 Physicochemical Properties of A. mexicana Seed Oil

The physicochemical properties of the oil were studied to determine its potential for use as a biodiesel feedstock. The physicochemical parameters (Table 4.3) suggest the suitability of the oil for conversion into biodiesel. The content of Free Fatty Acid (FFA) of the oil was slightly high; as a result earlier reports suggested that higher FFA content lowers the biodiesel yield which may be due to formation of soap which makes the separation of biodiesel difficult [9]. However, in the present study, the yield was reportedly increased by employing a heterogeneous catalyst. Similarly, [64] reported the use of a heterogeneous catalyst in the preparation of biodiesel production.

***Table 4. 3: Physicochemical properties of A. mexicana oil***

| Physiochemical properties | Unit | Value |
|---|---|---|
| Acid Value | mg KOH/g | 20.42 |
| FFA | % | 10.21 |
| Specific gravity(15 $^oC$) | - | 0.924 |
| Density (15- 40 $^oC$) | g/ $m^3$ | 0.925 -0.907 |
| HHV | MJ/Kg | 37.912 |
| Iodine Value | I2g/100g | 177.4 |
| Oil yield | % | 40 |
| Saponification value | mgKOH/g | 192.7 |
| Viscosity (40 $^oC$) | $mm^2 s^{-1}$ | 25.7 |
| Flash point | $^oC$ | 240 |

The physical parameters such as flash point, specific gravity, density and viscosity were measured for diesel. In addition, the chemical parameters such as iodine value, acid value, and saponification value were estimated and presented.

### 4.1.3.1 Specific gravity and density

A. mexicana oil was injected to the density meter at 40 $^{0}$C and the standard was adjusted at 15 $^{0}$C and the readings were displayed in the screen below (Fig. 4.1).

Method: Crude Oil (API)
Sample:
1:07:12 PM
Administrator

API Density 15 °C: 0.92457 g/cm³
Density: 0.9079 g/cm³
API Spec. Gravity 15 °C: 0.92548 -
Density Temperature: 39.97 °C
° API Gravity 15 °C: 21.39 -
Density Condition: filling warning
Finished

***Figure 4. 1: Specific Gravity and density measurement***

The density and viscosity and specific gravity are important when considering the spray characteristic of the fuel within the engine. Higher density and viscosity of the liquid fuels affects the flow properties of the fuel, such as spray atomization, subsequent vaporization and air fuel mixing in the compression chamber. As shown in Table 4.3 the value of specific gravity and density of purified A. mexicana oil were 0.924 and 0.907 g/cm$^{3}$ respectively and these were due to the purification processes (degumming). The specific gravity and density of purified A. mexicana oil were in agreement with the EN standard specification.

### 4.1.3.2 Kinematic viscosity

Since viscosity is a key fuel property because it persuades the atomization of a fuel upon injection into the diesel engine ignition chamber and ultimately, the formation of engine deposits, the present study has measured the viscosity of the oil by vibro viscometer to know the resistance to flow with vibration. The device detects the dynamic viscosity. The kinematic viscosity were calculated by using equation 3.6.

The kinematic viscosities of A. mexicana must be reduced for biodiesel application since the kinematic viscosity of biodiesel was very low compared to vegetable oils. High viscosity of the purified A. mexicana were not suitable if it used directly as engine fuel, often results in operational problems such as carbon deposits, oil ring sticking, and thickening and gelling of lubricating oil as a result of contamination by the vegetable oils. While low viscosity causes leakage in the fuel system, high viscosity causes poor fuel atomization and incomplete combustion Different methods such as preheating, blending, ultrasonically assisted methanol transesterification and supercritical methanol transesterification were being used to reduce the viscosity and make them suitable for engine applications [56].Therefore, methanol transesterification was used, and accordingly the result of the detected kinematics viscosity of the purified A. mexicana was 25.7 $mm^2$/sec at 40 $^0$C. Since biodiesel kinematic viscosity value was beyond the limit of the scope of both the ASTM D 6751 and EN 14214 biodiesel specification ranges. This indicated the oil needs more neutralization to reduce the value into ASTM D6751 and EN 14214 ranges.

The kinematic viscosity of purified A. mexicana sample was lower than the result reported by other researcher's which was 29.6 mm2/sec [48,57]. This variation occurred due to the chemical composition of A. mexicana which was grown in different agro climatic conditions [53, 57].

#### *4.1.3.3 Saponification value*

Saponification value is used to determine the total acid content, both free and combined, of A. mexicana. The combined acids are primarily esters formed by reaction with the neutral components present in the original A. mexicana. The saponification value was therefore a measure of A. mexicana quality. It was determined by measuring the alkali required to saponify the combined acids and neutralize the free acids.

As result was presented in Table 4.3, the saponification number of purified A. mexicana was lower than that of the result reported by other researcher which was 202.5 mg KOH/gm [53, 57].
This was caused by the variation of fatty acid composition depending on the agro climatic condition [58, 59].

#### *4.1.3.4 Acid value*

The acid value is a measure of the amount of fatty acids, which have been liberated by hydrolysis from the triglycerides due to the action of moisture, temperature and/or lypolytic enzyme lipase. In this study, the acid value was found to be 20.42 mgKOH/g (Table 4.3) which is higher than the recommended value but lower than other researchers report 76.2 mgKOH/g [53, 57]. The FFA content was 10.21% which was higher than that of A. mexicana from Malaysia 2.23% [65]. The obtained FFA is far above the 1% limit for satisfactory transesterification reaction using alkaline catalyst.

The acid value of oil determines indirectly the total acidity of the oil due to the presence of free fatty acids (carboxylic acids). In the presence of base catalyst, oil with high free fatty acid reacts with the base catalysts forming soap, a product other than biodiesel. The side reaction affects the performance of base catalyst and hence the transesterification reaction.

The acid value of crude A. mexicana, shown in Table 4.3, was found to be 20.42 mgKOH/g of oil.

#### *4.1.3.5 Iodine value*

The iodine value is a measure of the average amount of unsaturation of fats and/or oils and is expressed in terms of the number of milligrams of iodine absorbed per gram of sample. Iodine value is used to measure the chemical stability property of substance against oxidation and the higher the iodine value the higher the number of double bond and hence lesser stability. Unsaturation could have an impact emissions, as free radical scavenging may be impacted by the number of olefinic and linoleic bonds present in the oil and also this may be due to the limitation of unsaturated fatty acids, is necessary due to the fact that heating higher unsaturated fatty acids results in polymerization of glycerides. This can lead to the formation of deposits or to deterioration of the lubricating the physicochemical properties of the oil [59, 60].

As results shown in the Table 4.3, the iodine value of the purified A. mexicana oil was 177.4 $I_2$/100g. This was due to purification processes and fatty acid compositions .Higher iodine value occurs due to higher proportion of unsaturated fatty acid compositions attribute of that geography, as stated by the other researcher’s that the altitudinal variation determines the proportion of unsaturation which increases with altitude [61].

### *4.1.3.6 Flash point*

The value of flash point was found to be 240 $^{0}$C which were similar with other researcher’s value at 235 $^{o}$C [53].

## 4.2 Feed Material Requirement

The amount of methanol to oil ratio and catalyst used in the experimental runs was calculated by using equation 3.3, 3.4 and 3.5 (materials and methods session).

## 4. 3 Statistical Analysis

The Design Expert 7.0.0 program was used in the regression analysis and analysis of variance (ANOVA).

The Statistical software program was used to generate surface plots, using the fitted equation obtained from the regression analysis, holding one of the independent variables constant

Experimental as well as predicted values of percentage conversion of the oil to biodiesel at the design points are shown in Table 4.4.

All 20 of the designed experiments were conducted. The actual yield of biodiesel produced at different process parameters was calculated. The yield of the transesterification processes were calculated as sum of weight of biodiesel produced to weight of oil used, multiplied by 100.

The formula is given as:

$$\text{Yield of biodiesel} = \frac{\text{weight of biodiesel}}{\text{weight of oil used}} * 100 \qquad (4.1)$$

The results are given in Table 4.4 biodiesel obtained ranged from 57.34 to 90.54 %

*Table 4. 4: CCD arrangement and response biodiesel %*

| Run | Actual Factors | | | % biodiesel | |
|---|---|---|---|---|---|
| | M | C | T | Actual Value | Predicted Value |
| 1 | 6 | 1.5 | 1.5 | 63.5 | 62.92 |
| 2 | 6 | 1.5 | 1.5 | 61.7 | 62.92 |
| 3 | 6 | 1.5 | 1.5 | 63.1 | 62.92 |
| 4 | 6 | 1.5 | 1.5 | 63 | 62.92 |
| 5 | 11.05 | 1.5 | 1.5 | 88.4 | 89.9065 |
| 6 | 6 | 1.5 | 1.5 | 61.5 | 62.92 |
| 7 | 3 | 1 | 1 | 65 | 65.88 |
| 8 | 6 | 1.5 | 1.5 | 62.3 | 62.92 |
| 9 | 9 | 1 | 2 | 73 | 73.72 |
| 10 | 6 | 1.5 | 2.34 | 70 | 69.7067 |
| 11 | 0.95 | 1.5 | 1.5 | 62.5 | 61.9551 |
| 12 | 6 | 0.66 | 1.5 | 67 | 66.6122 |
| 13 | 9 | 2 | 2 | 81 | 80.26 |
| 14 | 6 | 1.5 | 0.66 | 73 | 73.1039 |
| 15 | 9 | 1 | 1 | 91.2 | 90.54 |
| 16 | 3 | 2 | 2 | 70.9 | 71.68 |
| 17 | 9 | 2 | 1 | 74 | 75.76 |
| 18 | 3 | 1 | 2 | 56.3 | 57.34 |
| 19 | 3 | 2 | 1 | 57 | 58.9 |
| 20 | 6 | 2.34 | 1.5 | 66 | 66.2423 |

Central composite design gives predict values and variables that leads to achieve High yield of biodiesel on actual term. From the above table the best variables for high yield of biodiesel can be selected easily. The model equation that correlates the response (yield of the oil to biodiesel) to the transesterification process variables in terms of actual value after excluding the insignificant terms was given below. The predicted (coded factor) model for percentage of biodiesel content (yield) is shown in equation 4. 2 below:

**Final Equation in Terms of Coded Factors:**

$$\begin{aligned}\text{yield }\% = {} & +62.54 - 0.81 \times T + 8.32 \times M - 0.31 \times C - 2.05 \times T \times M + 5.98 \times T \times C \\ & - 1.97 \times M \times C + 3.04 \times T^2 + 4.44 \times M^2 + 1.28 \times C^2 \end{aligned} \tag{4.2}$$

Where , M = molar ratio of methanol to oil

C = weight of catalyst amount

T = reaction time

The statistical analysis of the ANOVA is given in Tables 4.5. The multiple regression coefficients were obtained by employing a least square technique to predict quadratic polynomial model for the fatty acid methyl ester content (Table 4.6). Hence, the best fitting model was determined. The model was selected based on the highest order polynomial where the additional terms were significant and the model was significant by the DOE software.

***Table 4. 5: Analysis of variance (ANOVA) for response surface quadratic model for FEMA***

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

| Source | Sum of Squares | Df | Mean Square | F Value | P- value Prob > F | |
|---|---|---|---|---|---|---|
| Model | 1693.13 | 9 | 188.13 | 206.79 | < 0.0001 | Significant |
| T | 8.93 | 1 | 8.93 | 9.82 | 0.0106 | |
| M | 944.25 | 1 | 944.25 | 1037.92 | < 0.0001 | |
| C | 1.34 | 1 | 1.34 | 1.48 | 0.2524 | |
| TM | 33.62 | 1 | 33.62 | 36.96 | 0.0001 | |
| TC | 285.61 | 1 | 285.61 | 313.94 | < 0.0001 | |
| MC | 31.20 | 1 | 31.20 | 34.30 | 0.0002 | |
| $T^2$ | 133.58 | 1 | 133.58 | 146.83 | < 0.0001 | |
| $M^2$ | 284.23 | 1 | 284.23 | 312.42 | < 0.0001 | |
| $C^2$ | 23.49 | 1 | 23.49 | 25.82 | 0.0005 | |
| Residual | 9.10 | 10 | 0.91 | | | |
| Lack of fit | 5.81 | 5 | 1.16 | 1.77 | 0.2737 | Not significant |
| Pure Error | 3.29 | 5 | 0.66 | | | |
| Cor Total | 1702.23 | 19 | | | | |

The Model F-value of 206.79 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case T, M, TM, TC, MC, $T^2$, $M^2$, $C^2$ are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

The "Lack of Fit F-value" of 1.77 implies the Lack of Fit is not significant relative to the pure error. There is a 27.37% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

***Table 4. 6: Model summary***

| Source | Std. Dev. | R –Squared | Adjusted R – Squared | Predicted R- Squared | PRESS | |
|---|---|---|---|---|---|---|
| Linear | 6.84 | 0.5608 | 0.4784 | 0.2800 | 1225.68 | |
| 2FI | 5.33 | 0.7666 | 0.6589 | 0.4756 | 892.68 | |
| Quadratic | 0.95 | 0.9947 | 0.9898 | 0.9706 | 50.13 | Suggested |
| Cubic | 0.87 | 0.9973 | 0.9916 | 0.8363 | 278.59 | Aliased |

The quality of the model developed was evaluated based on the correlation coefficient value, $R^2$. The $\mathbf{R^2}$ value was **0.9947**. This indicated that 99.47% of the total variation in the biodiesel yield was attributed to the experimental variables studied. The closer the $\mathbf{R^2}$ value to unity, the better the model will be as it will give predicted values which are closer to the actual values for the response.

Additionally, from the ANOVA analysis the lower value of coefficient of variation (C.V. =1.73) indicates the better precession and reliability of the experiments carried out. The C.V. as a ratio of the standard error of estimate to the mean value of the observed response (as % biodiesel yield) is the measure of reproducibility of the model and as general rule a model can be considered reasonably reproducible, if the model C.V. value is not greater than 10% [62].

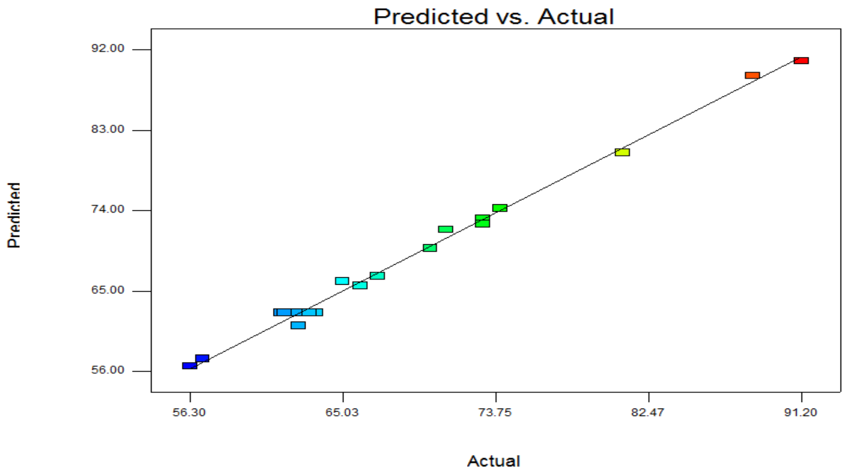

***Figure 4. 2: Yield Plot for the observed and predicted of biodiesel yield***

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

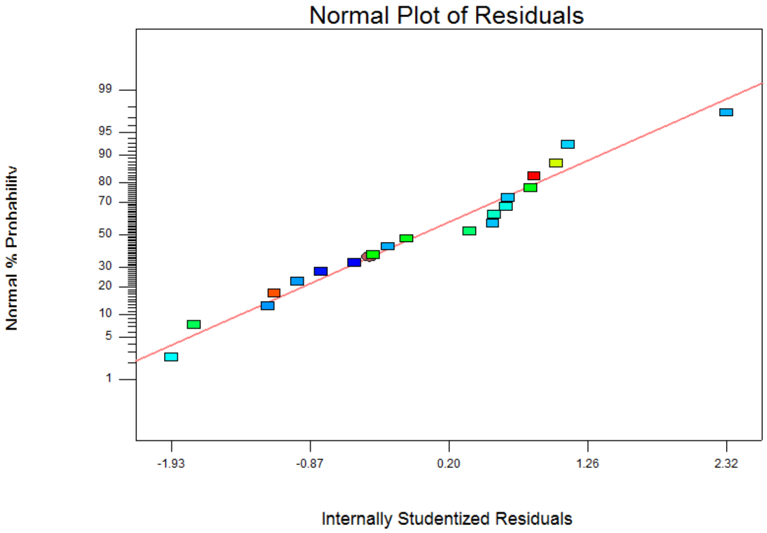

*Figure 4. 3: Normal plots of residuals*

To identify the statistical properties of the model, the CCD normal probability plot of the residuals shows the normality of the model. Figure 4.3 shows the diagnostic graph of the model. The data points should be approximately linear. A non-linear pattern indicates abnormality in the error term which may be corrected by transformation. From figure 4.3 there is no any sign of any abnormality in the model.

## 4. 4 Effect of Process Parameters

Based on the analysis of variance, the transesterification reaction was significantly affected by various interactions between the process variables. This result demonstrated the advantage of using design of experiments in capturing the interaction between variables that affects the transesterification reaction. The effect could be due to the independent variable alone or due to their interaction. The individual and interaction effects of the variables are well discussed below

### 4.4.1 Effect of individual parameter on biodiesel yield

#### *4. 4.1.1 Effect of methanol-to-oil molar ratio*

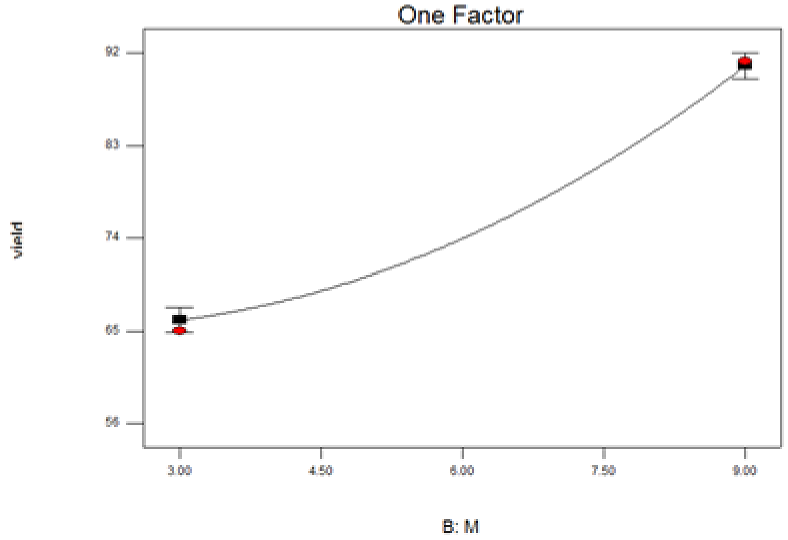

***Figure 4. 4: Effect of methanol-to-oil molar ratio on biodiesel yield***

The methanol-to-oil ratio is one of the important factors that affect the conversion of triglyceride to biodiesel. Stoichiometrically, three moles of methanol are required for each mole of triglyceride, but in practice, a higher molar ratio is required in order to drive the reaction towards completion and produce more biodiesel as products. The results obtained in this study are in agreement with this. As shown in Figure 4.4, the methanol-to-oil ratio showed positive influence to the yield of methyl ester, the yield started to increase as the ratio is increased. The increase is due to the positive sign in the experimental model and higher ratio of methanol used allow for complete conversion of the oil to biodiesel.

#### *4. 4.1.2 Effect of catalyst concentration*

From Figure 4.5, it was observed that the catalyst concentration influenced the biodiesel yield in a positive manner up to a certain concentration. Beyond this concentration, the biodiesel yield decreased with increase in calcium oxide concentration.

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

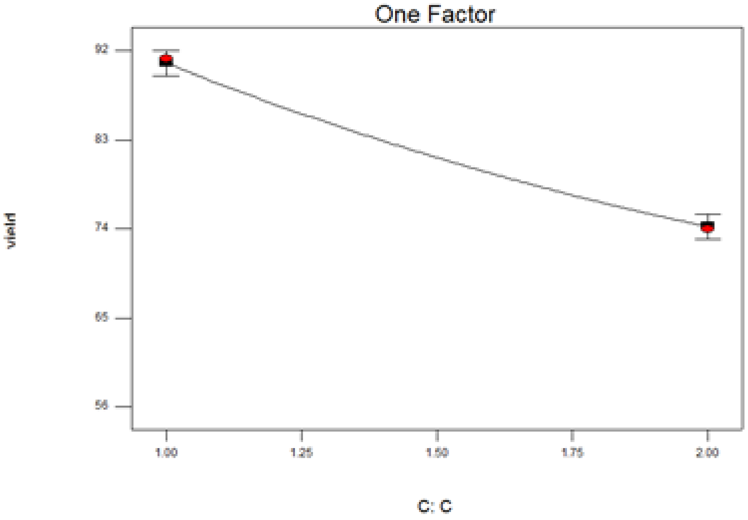

*Figure 4. 5: Effect of catalyst concentration ratio on biodiesel yield*

#### *4.4.1.3* **Effect of time**

The Time decrease clearly influences the reaction rate and biodiesel yield in positive manner. The time decrease at 1 hour gives high yield of biodiesel. Through time increase in time lead to low yield of biodiesel.

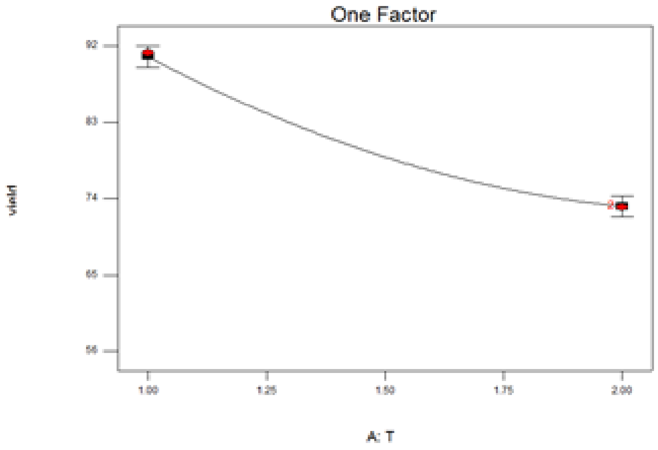

*Figure 4. 6: Effect of time on biodiesel yield*

### 4. 4.2 Interaction Effect on the Yield

Contour plots and 3D Figures were drawn to show the relationships between dependent and independent variables of the developed model. Each contour curve presented the effect of two variables on the methyl ester yield, holding the third variable at constant level. The third variable is held at zero level. However, the interaction factor also must be considered as the individual effect plot does not give information regarding the significant interaction involved.

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

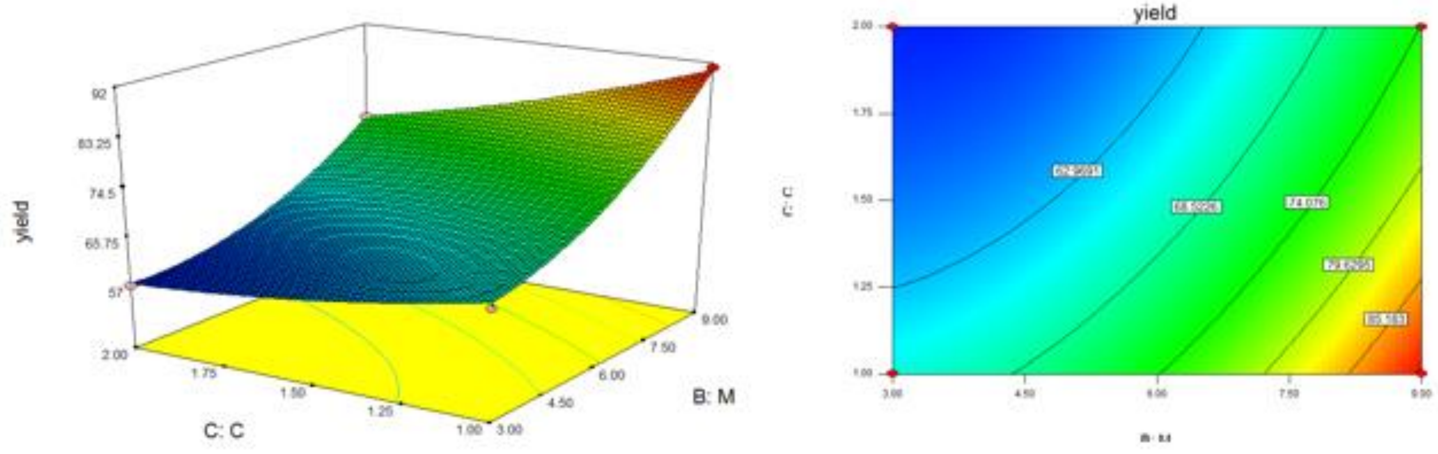

*Figure 4. 7: Methanol to oil ratio vs catalyst amount when time is 1 hr*

The effect between catalyst concentration and methanol to oil molar ratio on the biodiesel yield percentage is shown in form of 3D and contour plots in Figure 4.7.The reaction temperature and time were fixed at 60 $^{o}$C, and 1 hr respectively for high yield.

As shown in the Figure above the molar ratio of methanol to oil is increased from 3:1 to 9:1 the yield of methyl ester rose considerably from 57.34 to 90.54 %. The maximum biodiesel yield 90.54 % was achieved at 1:9 molar ratio, higher molar ratio of ester formation and could ensure complete reaction within 1 % catalyst loading.

Large Amount of time is required for the subsequent separation stage because separation of the ester layer from glycerol was difficult due to the fact that methanol with one polar hydroxyl group could emulsify the produce. Hence the best methanol to oil molar ratio was selected as 1:9 with catalyst concentration of 1 %. This result indicates that both biodiesel factors have significant effect on the % biodiesel yield. The ANOVA analysis also showed the interactions effect of reaction time and methanol to oil molar ratio have “Prob.>F” value of 0.0002, which indicates the significance of the factors on the percentage of biodiesel yield.

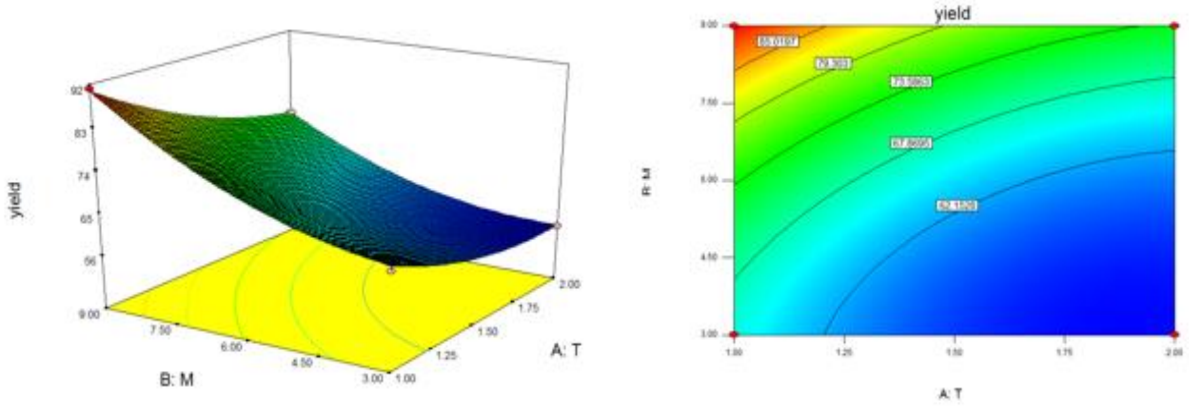

*Figure 4. 8: Methanol to oil ratio vs reaction time when catalyst amount is 1%*

As shown in the Figure 4.8 the effect of methanol to oil molar ratio and reaction time of 3D and contour plots there is an interaction effect between the amounts of methanol to oil ratio and reaction time. The reaction temperature and catalyst loading were fixed at 60 $^0$c and 1 wt.% . As shown in the Figure above, at high time and low methanol to oil molar ratio, the yield was small. Conversely, at the time decrease and methanol to oil molar ratio increases the yield increases. However, as the time increases, the yield slightly decreases and the yield increases with increase in methanol to oil ratio.

The ANOVA analysis also showed the interaction effects of the amounts of methanol to oil ratio and reaction time have “Prob.>F” value of 0.0001, which indicates the significance of the factors on the percentage of biodiesel yield.

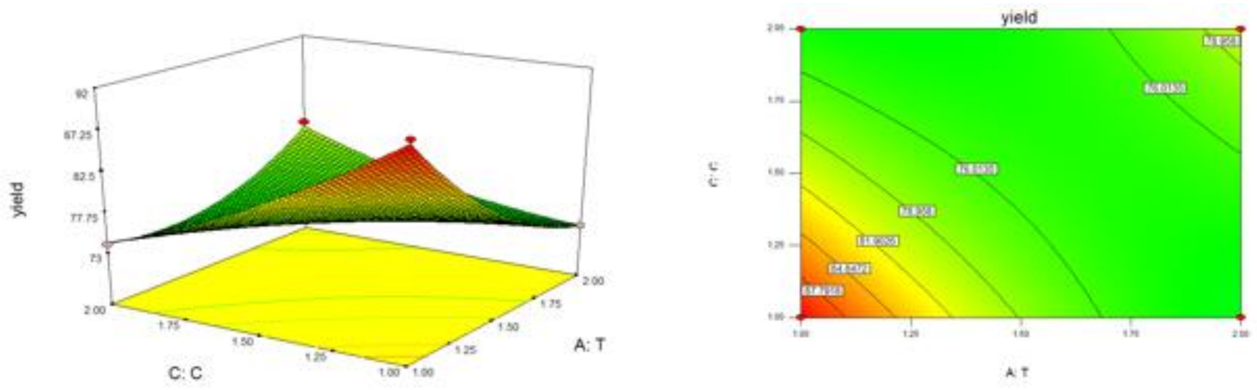

*Figure 4. 9: Catalyst concentration vs time when methanol to oil ratio is 1:9*

The effect between reaction time and catalyst concentration on the biodiesel yield percentage is shown in form of 3D and contour plots in Figure 4.9. The reaction temperature and methanol/oil molar ratio were fixed at 60 $^{o}$C, and 1:9 respectively. When the catalyst amount and time decrease to 1% and 1hr, the FAME yield increases. At low reaction time and catalyst concentration the biodiesel yield was high.

The reaction profile of Figure 4.9 indicates that high yield obtained at minimum catalyst concentration and time. Further increment of catalyst amount and time lead to low yield. However, at maximum reaction time and catalyst loading the yield was significantly increased due to exposure of the active site of the catalyst. The ANOVA analysis also showed the interaction effects of reaction time and catalyst concentration have "Prob.>F" value of 0.0001, which indicates the significance of the factors on the percentage of biodiesel yield.

## 4.5 Physicochemical Properties of Biodiesel

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

***Table 4. 7: Physicochemical properties of A. mexicana   biodiesel***

| Physiochemical properties | Unit | Value |
|---|---|---|
| SG ($15^0$c) | $g/cm^3$ | 0.88 |
| Density ($40^0$c) | $g/cm^3$ | 0.89 |
| Acid Value | mgKOH/g | 0.89 |
| FFA | % | 0.445 |
| HHV | MJ/Kg | 42.37 |
| Iodine Value | $I_2$g/100g | 12.9 |
| Saponification value | mgKOH/g | 146.1 |
| Viscosity ($40^0$c) | $mm^2\ s^{-1}$ | 9.05 |
| Flash point | $^0$C | 180 |
| Cetane number | - | - |

### 4.5.1 Specific Gravity

Both the SG and density was measured by digital density meter. SG of the biodiesel was found to be 886 $Kg/m^3$, the density of the biodiesel produced were found to be 869 $kg/cm^3$. The results are compared within the range specified by EN14124 (860–900 $kg/m^3$) and with the ASTM D6751 for FAME 870–890 $kg/m^3$ is acceptable. The change in the density shows that the density of the biodiesel decreased with increasing molar ratio. This was due to a decrease in residual triglycerides. The density of the biodiesel decreased with the influence of the catalyst amount and time.

### 4.5.2 Viscosity

Viscosity is the most important of FAME 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. As the result were presented in Table 4.7, The kinematic viscosity value 9.05 $mm^2/sec$ at 40 °C.

Generally, the kinematic viscosity of FAME was higher compared to that of fossil diesel (3.6 $mm^2$/sec) the implication was that FAME has lubricating effect in engines which will be an added advantage to the users, since it will reduce wear and tear in the engine [62, 63].

### 4.5.3 Acid Value

The Acid value of the biodiesel produced was found to be 0.89 mgKOH/g. The result indicates that acid value of the diesel decreased significantly after transesterification reaction. Furthermore, higher acid value resulted in low yield of biodiesel. Acid value affects storage ability of biodiesel. Contact with air and water is the major factors affecting storage stability. Oxidation is usually accompanied by an increase in the acid value and viscosity of the fuel. In the presence of water the ester can hydrolyze to long chain FFA, which also causes the acid value to increase.

Acid value or neutralization number is a measure of mineral acids and free fatty acids contained in a fuel sample. It is expressed in milligrams of KOH required to neutralize 1 g of fatty acid methyl esters and it sets to a maximum value of 0.5 and 0.8 mg KOH/g in the EN-14214 and ASTM D664 specifications respectively.

### 4.5.4 Higher Hating Value

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

The Heat of combustion refers to the measure of energy content in the fuel. Heating value of fuels is an important measure of its releasing energy for producing work. As results presented in Table 4.7 the highest calorific value was 42.37 MJ/kg which is in agreement with standard specification limit EN 14214 (>35 MJ/kg).

### 4.5.5 Iodine Value

The iodine index is measured as iodine adsorbed (g) per 100 g of sample, and is related to the level of unsaturation (double bonds) present in the oil, i.e. the higher the unsaturates content the higher the iodine index. Iodine value is used to measure the chemical stability property of substance against oxidation and the higher the iodine value the higher the number of double bond and hence lesser stability. It can be observed from Table 4.7, that the iodine value is 12.9 g $I_2$/100 g. the result was in the acceptable range as the upper limit for EN14214 standard is 120 g $I_2$/100 g. The ASTM requirement is a maximum of 115.

In general, the result of iodine value of FAME yield revealed a higher value compared with that of fossil diesel (9.5 g$I_2$/100 g). This shows that the fossil diesel is more stable compared to the FAME. However, the double bonds in biodiesel helps attract oxygen to the compound, and aid proper burning of biodiesel over fossil diesel and affect the FAME to polymerize easily.

### 4.5.6 Cetane Number

Cetane number is a dimensionless indicator of the ignition quality of a FAME, if the cetane number is high, combustion can occur before the fuel and air are properly mixed, resulting in incomplete combustion and smoke, and if is low, engine roughness, misfiring, higher air temperatures, slower engine warm-up, and also incomplete combustion occur.

As the result shown in Table 4.7 the cetane number were found to be 46.77 based on methods listed on chapter 3(Materials and methods) and the result were similar with standard specification limit of ASTM, diesel engines will operate on fuels with cetane number > 47(ASTM D613).

### 4.5.7 Flash Point

Flash point is the lowest temperature by which a fuel vapors will ignite in air. A non-flammable FAME should have flash point high enough to within the standard limit for safe storage purpose. High content of methanol will lower the flash point and viscosity of the FAME and thus lead to dangerous storage instabilities. The higher the flash point the safer the fuel and vice versa. As

result shown in Table 4.7 the flash point were found to be 180 $^{o}$C. Based on methods listed on chapter 3(Materials and methods).
The result was in agreement within the lower limit of standard with 120 $^{o}$C (EN14214) and 130 $^{o}$C (ASTM D6751) and Similar with previous researches.

The flash point of FAME was higher than that of fossil diesel (70 $^{o}$C) and therefore it could be said that FAME is safer to handle than fossil diesel. The flash point determined in oil was very high as compared to its methyl ester and diesel. The blending of A. mexicana seed oil with petroleum diesel is known to bring down the flash point.

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

***Table 4. 8: Biodiesel summary***

| Properties | A .Mexicana FAME Values | ASTM D6751 | EN14214 |
|---|---|---|---|
| Density (kg/m3) | 89 | 870–890 | 860–900 |
| Kinematic Viscosity at 40oc (mm$^{2}$/sec) | 9.05 | 3.6 | |
| Flash point ($^{o}$C) | 180 | 130 Minimum | 120 Minimum |
| Heating value MjKg-1 | 42.37 | | >35 |
| Cetane number | 46.77 | > 47 | |
| Acid Values(mg KOH/g) | 0.89 | 0.8 | 0.5 |
| Iodine values (I2g100g-1) | 12.9 | Maximum of 115. | 120 |

Most of the fuel properties of the A. mexicana methyl ester tested compare well with ASTM D6751 EN14214 standards as shown in Table 4.8.

Among the general parameters, kinematic viscosity and density are key fuel properties for diesel engines. According to ASTM standard, for biodiesel to be used in diesel engines the kinematic viscosity must be between 1.9 and 6.0 $mm^2s^{-1}$ and according to EN-14214 standard, the density must fall between 860 and 900 $Kgm^{-3}$. The comparison showed that the A. mexicana biodiesel density fulfill the standard but the viscosity differs, to reduce the viscosity blending with diesel is the best alternative.

The physicochemical studies and the comparisons revealed that transesterification improved the important fuel properties. As expected, the methyl ester of A. mexicana has relatively closer fuel properties.

## 4.6 Numerical Optimization

The optimum conditions for three factors, i.e Reaction time (A), Methanol/oil ratio(B) and Catalyst concentration (C) were determined using the numerical optimization feature of the Design expert software. The software searched for a combination of factors that simultaneously satisfied the requirements placed on the response and each of the factors. Table 4.10 shows the optimum working conditions (ultimate goals, high and low limits) of the response (% biodiesel yield)) and factors (Reaction time (A), Methanol/oil ratio (B) and Catalyst concentration (C)), employed during the optimization analysis. In view of the targeted criterion was maximized for % biodiesel yield while the values of Reaction time (A), Methanol/oil ratio (B), and Catalyst concentration (C) were set in the ranges studied.

The optimum conditions obtained were then evaluated by the composite desirability, which has a value from 0 to 1, to determine the degree of satisfactory of the optimum conditions for the ultimate goal of response.

Table 4.11 presents the optimum conditions in uncoded units (Reaction time (A), Methanol/oil ratio(B) and Catalyst concentration (C) which give the highest composite desirability (1.0) from the Design expert software. The predicted (93.8588 %) and experimental (93 %) values of % biodiesel yield) under the optimum conditions are also presented.

The very small deviation, i.e., 0.009%, between the predicted and experimental values of % biodiesel yield) indicates that the model (Eq. 4.2) is suitable and sufficient to predict the biodiesel yield process using A.Mexicana oil, methanol and calcined CaO catalyze transesterification in the range of variables studied. The physicochemical property of the optimized yield was conducted and the result was within in the ASTM standards.

***Table 4. 9: Working conditions of response and factors for optimization***

| Variables | Ultimate Goal | Experimental region | |
|---|---|---|---|
| | | Lower limit | Upper limit |
| Reaction time (hours) | In the range | 1 | 2 |
| Methanol to oil molar ratio | In the range | 3 | 9 |
| Catalyst concentration wt.% | In the range | 1 | 2 |
| % biodiesel yield | Maximize | 56.3 | 91.2 |

***Table 4. 10: Optimum conditions and model validation***

| Variables | Optimum result |
|---|---|
| Reaction time | 1.78 |
| Methanol to oil molar ratio | 9:1 |
| Reaction temperature | 60 |
| Catalyst concentration | 2.21 |
| % FAME yield | 93.8588 |
| Desirability | 1 |
| Experimental % biodiesel yield | 93 |
| % deviation | 0.009 |

# CHAPTER FIVE

## 5. Conclusion and Recommendation

## 5.1 Conclusion

A.mexicana is one of the promising drought tolerant annual wild herb and adaptable to various kind of soil condition. It grows well on roadside, wasteland so that their production does not exert any pressure on agriculture lands. It does not require much care and its cultivation is not much expensive. Converting this invasive plant to FAME has a big achievement and advantage for the biodiversity. Therefore, in this work the main findings were summarized as follows;

- A total of 40 % of oil was extracted from fresh seeds of A. mexicana , through the Soxhlet apparatus as mentioned in material and method.
- This oil was then converted into methyl ester by the process of transesterification. A. mexicana methyl ester showed the better fuel properties compared to the oil.
- The statistical and experimental design was done by using design expert 7.0.0 software. The outputs of the experiments conducted have been analyzed by employing physicochemical and instrumental parameter determination.
- Based on the experimental results, it was found that all the process variables exhibited significant individual and interaction effect on the yield of FAME. The effects of the methanol-to-oil molar ratio, catalyst concentration, and reaction time were investigated to determine the best strategy for producing biodiesel from A. mexicana .
- The ester yield, generally, increased with high amount molar ratio with less amount of catalyst concentration and reaction time. Methanol to oil molar ratio and catalyst amount has played an important role in improving the FAME yield.
- The best result was obtained at a heterogoenous (CaO) acatalyst concentration of 1.0%, molar ratio 9:1 and reaction time of 1 hr, respectively, while the reaction temperature was set at 60 $^{0}$c. The ester yield obtained from transesterification process ranged from 56.3 to 91.2%.
- The fuel properties tested are within the ASTM and EN standards and were found to be very close to those of petroleum diesel.

- The results showed that transesterification improved the important fuel properties tested. The calorific value, Flash Point, Acid Value and Density of the A.Mexicana biodiesel are in the range of the ASTM and EN standards.
- The density and the viscosity were indicators of the biodiesel quality against the process variables. The viscosity of A. mexicana is higher than that of diesel but similar with other researches.
- The calculated cetane number is low as compared with the standard.
- The iodine value is higher than the standard, Higher iodine value indicates a higher quantity of double bonds in the sample and greater potential to polymerize in engine and hence lesser stability. Generally, the FAME of A. mexicana has relatively closer fuel properties to petroleum diesel than the oil.
- 93 % of biodiesel yield was obtained from optimum conditions found from design expert software and this result indicates the potential of the plant for producing biodiesel.

## 5.2 Recommendation

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

Additionally further research should be conducted on storage problem to increase the shelf life of biodiesel.

It is also recommended to use the seed cake of A. mexicana to biogas production and designing a mini stove by using A. mexicana oil, FAME or gas.

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

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# APPENDICS

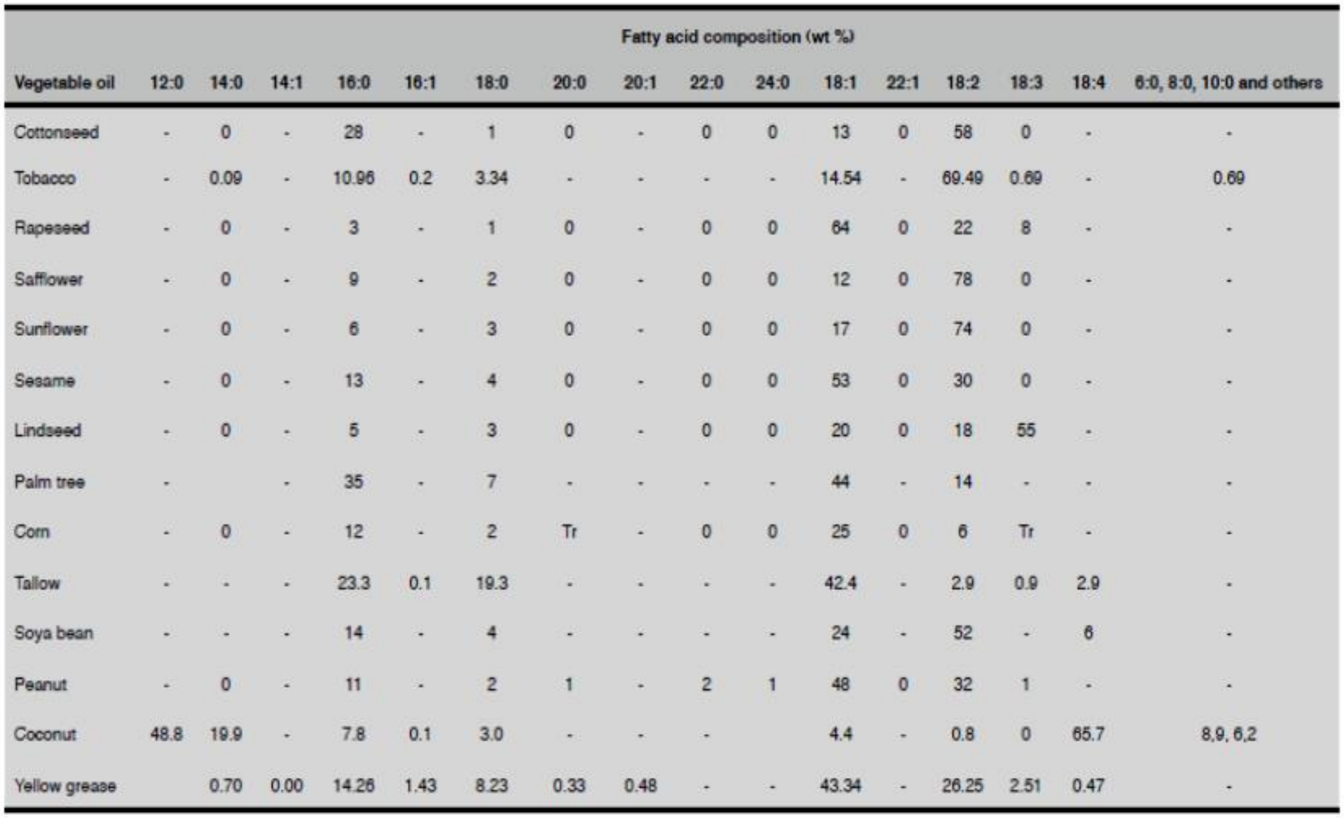
# Appendix A: Composition of A. mexicana oil

## Table A1: Fatty Acid composition of A. mexicana

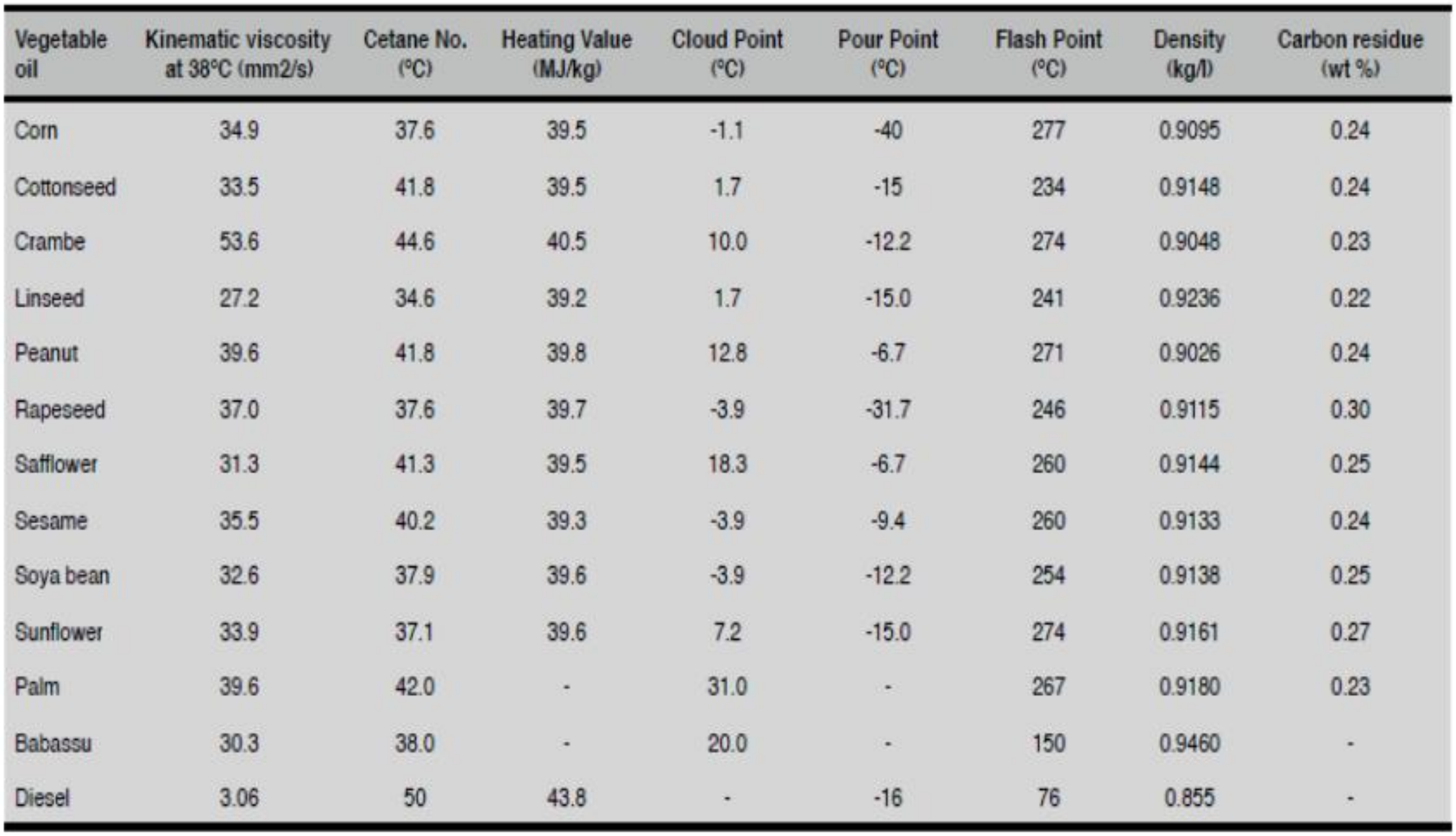
| Fatty Acid | Formula | Systematic Name | Structure | Wt% |
|---|---|---|---|---|
| Myristic | $C_{14}H_{28}O_2$ | Tetradecanoic | 14:0 | 0.1 |
| palmitic | $C_{16}H_{32}O_2$ | Hexadecanoic | 16:0 | 14.7 |
| Palmitoleic | $C_{16}H_{30}O_2$ | Cis-9-hexadecanoic | 16:1 | 1.3 |
| Stearic | $C_{18}H_{36}O_2$ | Octadecanoic | 18:0 | 6.75 |
| Oleic | $C_{18}H_{34}O_2$ | Cis-9-Octadecanoic | 18:1 | 40.0 |
| Linoleic | $C_{18}H_{32}O_2$ | Cis-9,Cis-12-Octadecatrienoic | 18:2 | 36.6 |
| Linolenic | $C_{18}H_{30}O_2$ | Cis-6,Cis-9, Cis-12-Octadecatrienoic | 18:3 | 0.3 |
| Arachidic | $C_{20}H_{40}O_2$ | Eicosanoic | 20:0 | 0.3 |
| Behenic | $C_{22}H_{44}O_2$ | Decosanoic | 22:0 | 0.2 |

**Source:** **Rajeshwer Y. Rao et al,2012 [ ]**

**Table A2:** properties of different oils



|  | Fatty acid composition (wt %) |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Vegetable oil** | **12:0** | **14:0** | **14:1** | **16:0** | **16:1** | **18:0** | **20:0** | **20:1** | **22:0** | **24:0** | **18:1** | **22:1** | **18:2** | **18:3** | **18:4** | **6:0, 8:0, 10:0 and others** |
| Cottonseed | - | 0 | - | 28 | - | 1 | 0 | - | 0 | 0 | 13 | 0 | 58 | 0 | - | - |
| Tobacco | - | 0.09 | - | 10.96 | 0.2 | 3.34 | - | - | - | - | 14.54 | - | 69.49 | 0.69 | - | 0.69 |
| Rapeseed | - | 0 | - | 3 | - | 1 | 0 | - | 0 | 0 | 64 | 0 | 22 | 8 | - | - |
| Safflower | - | 0 | - | 9 | - | 2 | 0 | - | 0 | 0 | 12 | 0 | 78 | 0 | - | - |
| Sunflower | - | 0 | - | 6 | - | 3 | 0 | - | 0 | 0 | 17 | 0 | 74 | 0 | - | - |
| Sesame | - | 0 | - | 13 | - | 4 | 0 | - | 0 | 0 | 53 | 0 | 30 | 0 | - | - |
| Lindseed | - | 0 | - | 5 | - | 3 | 0 | - | 0 | 0 | 20 | 0 | 18 | 55 | - | - |
| Palm tree | - |  | - | 35 | - | 7 | - | - | - | - | 44 | - | 14 | - | - | - |
| Corn | - | 0 | - | 12 | - | 2 | Tr | - | 0 | 0 | 25 | 0 | 6 | Tr | - | - |
| Tallow | - | - | - | 23.3 | 0.1 | 19.3 | - | - | - | - | 42.4 | - | 2.9 | 0.9 | 2.9 | - |
| Soya bean | - | - | - | 14 | - | 4 | - | - | - | - | 24 | - | 52 | - | 6 | - |
| Peanut | - | 0 | - | 11 | - | 2 | 1 | - | 2 | 1 | 48 | 0 | 32 | 1 | - | - |
| Coconut | 48.8 | 19.9 | - | 7.8 | 0.1 | 3.0 | - | - | - |  | 4.4 | - | 0.8 | 0 | 65.7 | 8.9, 6.2 |
| Yellow grease |  | 0.70 | 0.00 | 14.26 | 1.43 | 8.23 | 0.33 | 0.48 | - | - | 43.34 | - | 26.25 | 2.51 | 0.47 | - |



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

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

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

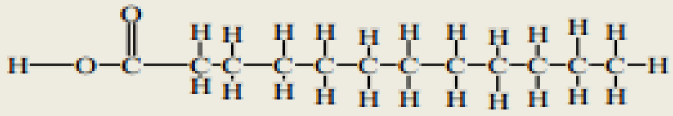
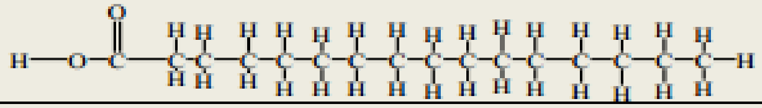
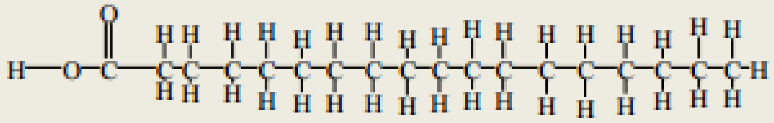
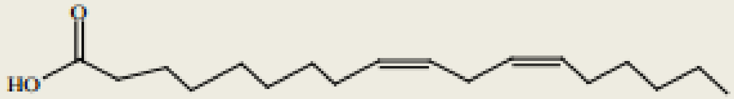
| SATURATED | | | |
|---|---|---|---|
| Fatty acid | STRUCTURAL FORMULA | Symbol | Molecular formula |
| Lauric acid |  | C12:0 | $C_{12}H_{24}O_2$ |
| Palmitic acid |  | C16:0 | $C_{16}H_{32}O_2$ |
| Stearic acid |  | C18:0 | $C_{18}H_{36}O_2$ |
| UN SATURATED | | | |
| Oleic acid |  | C18:1 | $C_{18}H_{34}O_2$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

**Table A** 4: The comparison between homogeneous catalysts and heterogeneous catalyzed

| **Factors** | **Homogeneous catalysts** | **Heterogeneous catalysts** |
|---|---|---|
| Reaction Rate | Fast and high conversion | Moderate conversion<br>Not sensitive |
| After treatment | Catalyst cannot be recovered, must be neutralized leading to waste production | Catalyst can be recovered |
| Processing methodology | Limited use of continuous methodology | Continuous fix bed operation possible |
| Presence of water/free fatty acids | Sensitive | Not Sensitive |
| Catalyst reuse | Not possible | Possible |
| Cost Comparatively | Costly | Potentially cheaper |

# Appendix B: Standard Specifications of Biodiesel

**Table B1**: Standard Specifications of Biodiesel: USA and European

| **Property** | **Unit** | **USA ASTM D6751** | **EU EN 14214** | **Recommendation Test method** |
|---|---|---|---|---|
| Density, 15 $^{O}$C | Kg/m$^{3}$ | - | 860 - 900 | ASTM D445 |
| Kinematic Viscosity 40$^{O}$C | mm$^{2}$/s | 1.9-6.0 | 3.5 -5.0 | |
| Flash point | $^{O}$C | $\geq 120$ | $\geq 130$ | ASTM D 93 |
| Cloud Point | $^{O}$C | - | - | |
| Total Sulphur 100% | W% | $\leq 0.05$ | $\leq 0.01$ | ASTM D5433 |
| Sulphated Ash | W% | $\leq 0.02$ | $\leq 0.02$ | ASTM D 874 |
| Water Content | mg/Kg | - | $\leq 500$ | |
| Total Contamination | mg/kg | - | $\leq 24$ | |
| Water and sediment | % vol. | | $\leq 0.05$ | ASTM D 2709 |
| Corrosion (Cu) @ 50 $^{O}$C | | $\leq$ No. 3 | Class 1 | ASTM D 130 |
| Cetane number | Mg | $\geq 47$ | $\geq 51$ | ASTM D 613 |
| Acid number | KOH/g | $\leq 0.8$ | $\leq 0.5$ | ASTM D 664 |
| Oxidation | | | $\geq 6$ | |
| Ester content | %W% | | $\geq 96.5$ | |
| Triglycerides | %w% | | $\leq 0.20$ | |
| Diglycerides | %w% | | $\leq 0.80$ | |
| Monoglycerides | %w% | | | |
| Methanol Content | %W% | | $\leq 0.2$ | |
| Free glycerol | %W% | $\leq 0.02$ | $\leq 0.02$ | ASTM D 6584 |
| Total glycerol | %w% | $\leq 0.24$ | $\leq 0.25$ | ASTM D 6584 |
| Iodine value | gI$_{2}$/100g | | | |
| phosphorus | mg/Kg | $\leq 10$ | $\leq 10$ | ASTM D4951 |

**Source: adopted from (biodiesel industries austrlia,2003)**

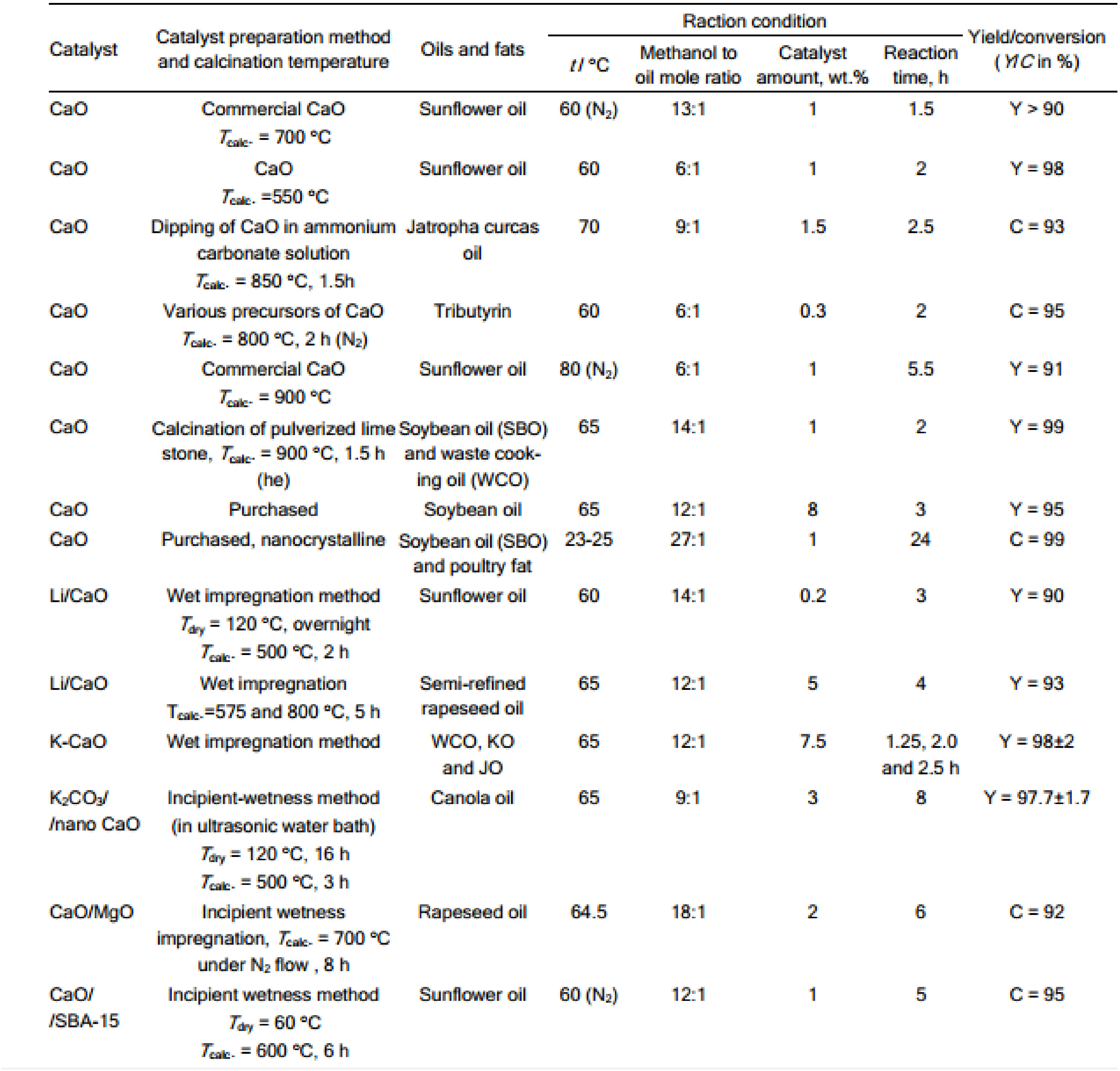
**Table B2:** Physico-Chemical Properties of Biodiesel from Different oil raw material

| Feed stock | Kinematic Viscosity (at 40 OC) | Density (g/cm3) | Saponification Number | Iodine Value | Acid value (mg KOH/g) | Heating value (MJ/Kg) | Cetane Number |
|---|---|---|---|---|---|---|---|
| Soybean | 4.08 | 0.885 | 201 | 138.7 | 0.15 | 52 | 40 |
| rapeseed | 4.3 – 5.83 | 0.88 – 0.888 | | | 0.25-0.45 | 45 | 49 – 50 |
| Sunflower | 4.9 | 0.88 | 200 | 142.7 | 0.24 | 45.3 | 49 |
| Palm | 4.42 | 0.86 – 0.9 | 207 | 60.07 | 0.08 | 34 | 62 |
| peanut | 4.42 | 0.883 | 200 | 67.45 | | 40.1 | 54 |
| Corn | 3.39 | 0.88 – 0.89 | 202 | 120.3 | | 45 | 58 – 59 |
| camelina | 6.12 – 7 | 0.882 – 0.88 | | 152 – 157 | 0.08-0.52 | | |
| canola | 3.53 | 0.88 – 0.9 | 182 | 103.8 | | 45 | 56 |
| cotton | 4.07 | 0.875 | 204 | 104.7 | 0.16 | 45 | 54 |
| pumpkin | 4.41 | 0.8837 | 202 | 115 | 0.48 | 38 | |
| Tallow | | 0.856 | 244.5 | 126 | 0.65 | | 59 |
| Nile tilapia | | | | 88.1 | 1.4 | | 51 |
| Jatropha curcas | 4.78 | 0.8636 | 202 | 108.4 | 0.496 | 40-42 | 61 – 63 |
| poultry | | 0.867 | 251.23 | 130 | 0.25 | | 61 |
| Used cooking oil | 4 | | | | | | |
| Pongamina Pinnata | 4.8 | 0.883 | | | 0.62 | 42 | 60-63 |
| palanga | 3.99 | 0.869 | | | | 41 | |

**Table B 3:** AMO and FAME literature characteristics

| **Property** | **Range AMO** | **Range FAME** |
|---|---|---|
| Percentage yield (%) | 28 – 40 | 92 |
| density (g/cm3) $40^0$c | 0.91 | 0.86 - 0..87 |
| Specific gravity (g/cm$^3$)$35^0$c | 0.914 | - |
| calorific value(MJ/Kg) | 36 | 40.8 |
| Flash point | 235 | <120 -171 |
| Cetane Value | - | 44.8 |
| Saponification number(mg/g) | 202-202.5 | 167-201 |
| Viscosity at 40 Oc(cSt) | 28.2 -29.6 | 10.2 -11.1 |
| Iodine number (mgI2/g) | 127 | 127 |
| acid number (mgKOH/g) | 76.2 | 0.41 -0.95 |

**Table B 4:** Summary of CaO-based catalysts, preparation methods and reaction conditions on the fatty acid methyl ester (FAME) yield conversion



| Catalyst | Catalyst preparation method and calcination temperature | Oils and fats | Raction condition | | | | Yield/conversion (*Y*/*C* in %) |
|---|---|---|---|---|---|---|---|
| | | | *t* / °C | Methanol to oil mole ratio | Catalyst amount, wt.% | Reaction time, h | |
| CaO | Commercial CaO<br>$T_{calc.}$ = 700 °C | Sunflower oil | 60 ($N_2$) | 13:1 | 1 | 1.5 | Y > 90 |
| CaO | CaO<br>$T_{calc.}$ =550 °C | Sunflower oil | 60 | 6:1 | 1 | 2 | Y = 98 |
| CaO | Dipping of CaO in ammonium carbonate solution<br>$T_{calc.}$ = 850 °C, 1.5h | Jatropha curcas oil | 70 | 9:1 | 1.5 | 2.5 | C = 93 |
| CaO | Various precursors of CaO<br>$T_{calc.}$ = 800 °C, 2 h ($N_2$) | Tributyrin | 60 | 6:1 | 0.3 | 2 | C = 95 |
| CaO | Commercial CaO<br>$T_{calc.}$ = 900 °C | Sunflower oil | 80 ($N_2$) | 6:1 | 1 | 5.5 | Y = 91 |
| CaO | Calcination of pulverized lime stone, $T_{calc.}$ = 900 °C, 1.5 h (he) | Soybean oil (SBO) and waste cooking oil (WCO) | 65 | 14:1 | 1 | 2 | Y = 99 |
| CaO | Purchased | Soybean oil | 65 | 12:1 | 8 | 3 | Y = 95 |
| CaO | Purchased, nanocrystalline | Soybean oil (SBO) and poultry fat | 23-25 | 27:1 | 1 | 24 | C = 99 |
| Li/CaO | Wet impregnation method<br>$T_{dry}$ = 120 °C, overnight<br>$T_{calc.}$ = 500 °C, 2 h | Sunflower oil | 60 | 14:1 | 0.2 | 3 | Y = 90 |
| Li/CaO | Wet impregnation<br>$T_{calc.}$=575 and 800 °C, 5 h | Semi-refined rapeseed oil | 65 | 12:1 | 5 | 4 | Y = 93 |
| K-CaO | Wet impregnation method | WCO, KO and JO | 65 | 12:1 | 7.5 | 1.25, 2.0 and 2.5 h | Y = 98±2 |
| $K_2CO_3$/ /nano CaO | Incipient-wetness method (in ultrasonic water bath)<br>$T_{dry}$ = 120 °C, 16 h<br>$T_{calc.}$ = 500 °C, 3 h | Canola oil | 65 | 9:1 | 3 | 8 | Y = 97.7±1.7 |
| CaO/MgO | Incipient wetness impregnation, $T_{calc.}$ = 700 °C under $N_2$ flow , 8 h | Rapeseed oil | 64.5 | 18:1 | 2 | 6 | C = 92 |
| CaO/ /SBA-15 | Incipient wetness method<br>$T_{dry}$ = 60 °C<br>$T_{calc.}$ = 600 °C, 6 h | Sunflower oil | 60 ($N_2$) | 12:1 | 1 | 5 | C = 95 |

# Appendix C: Experimental Result

**Table C1:** Viscosity of AMO

| Dynamic Viscosity (mpa.sec 40 $^{0}$c) | | | Average dynamic Viscosity (mpa.s) | Density g/cm3 | Kinematic Viscosity ($mm^2/s$) |
|---|---|---|---|---|---|
| 21.5 | 23.2 | 24.8 | 23.13 | 0.92 | 25.74 |

**Table C2:** Acid Value of AMO

| Run | $N_{koH}$ | $V_{KOH}$ | Mass of oil | AV | FFA |
|---|---|---|---|---|---|
| 1 | 0.1 | 18.2 | 5 | 20.42 | 10.21 |
| 2 | 0.1 | 17.9 | 5 | 20.08 | 10.04 |
| 3 | 0.1 | 18.5 | 5 | 20.754 | 10.39 |
| | | | Average | 20.41 | 10.33 |

**Table C 3:** Saponification number AMO

| | **Saponification number (mg KOH/g)** | | | |
|---|---|---|---|---|
| | **R1** | **R2** | **R3** | **Average** |
| AMO | 196 | 195.5 | 193.5 | 195 |

**Table C4:** Viscosity of FAME

| Dynamic Viscosity (mpa.sec 40 $^0$c) | | | Average dynamic Viscosity (mpa.s) | Density g/cm3 | Kinematic Viscosity (mm$^2$/s) |
|---|---|---|---|---|---|
| 7.5 | 7.56 | 8.3 | 7.78 | 0.86 | 9.05 |

**Table C5:** Acid Value of FAME

| **Run** | $N_{koH}$ | $V_{KOH}$ (ml) | Mass of oil (g) | AV |
|---|---|---|---|---|
| **1** | 0.1 | 1 | 5 | 1.12 |
| **2** | 0.1 | 0.9 | 5 | 0.78 |
| **3** | 0.1 | 0.9 | 5 | 0.78 |
| | | | Average | 0.89 |

**Table C 6:** Saponification number FAME

| | **Saponification number (mg KOH/g)** | | | |
|---|---|---|---|---|
| | **R1** | **R2** | **R3** | **Average** |
| FAME | 191.5 | 192 | 193 | 192.1 |

# Appendix D: Calculations for FAME Production (%Yield)

Transesterification reaction is a reversible reaction:

3 alcohol (MeOH ) + 1 Oil (Triglyceride) = 3 FAME + Glycerol

Amount of oil volume for each run = 25 ml in each experiment

- Oil molecular weight = 277.8 g / mol.
- Oil density = 0.92 g/ml
- Methanol density= 0.79 g/ml
- Methanol molecular weight= 32.04 g/mol.

The theoretical amount of biodiesel which can be obtained assuming 100% conversions, are calculated and becomes:

Oil weight = Oil Volume x Oil density = 25 ml x 0.92 g / ml = 23 g (D.1)

Oil mole = Oil weight / Oil molecular weight (D.2)

= 23 g / 277.8 g / mol. = 0.0827 mol.

According to stoichiometry of the reaction, one mole of oil produces three mole of FAME.

Theoretical yield of FAME = 3 x 0.101 mol. = 0.248 mol of FAME. Hence, the amount of methanol and catalyst were calculated as follows using the process parameters.

$$\frac{n\ oil}{n\ methanol} = Y \qquad (D3)$$

Where: - Y is the ratio of methanol to oil used which is 1:3, 1:6, 1:9

Substitute mass for mole;

$$\frac{\frac{\rho oil * Voil}{Moil}}{\frac{\rho methanol * VMethanol}{M\ methanol}} = Y \qquad (D4)$$

$$\frac{\frac{0.92 g/ml * 25 ml}{277.8\ g/mol}}{\frac{0.79\ g/ml *\ V\ methanol}{32.04\ g/mol}} = \frac{1}{6}$$

Therefore

$V\ MeOH$ = 20.14 ml

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

$$moil = \rho\ oil * Voil \qquad (D5)$$

$$moil = 0.92g/ml * 25ml$$

$$= 23\ gm$$

$$\frac{mass\ of\ catalyst}{mass\ of\ oil} = X \qquad (D6)$$

Where: - X is the amount of catalyst used 1%, 1.5%, 2%

$$mass\ of\ catalyst = 1\% * mass\ of\ oil$$

$$= 0.23\ gn$$

The amount of methanol and catalyst used for the Whole experiment is attach on appendix D1

**Table D1:** The amount of catalyst and methanol

| Oil to methanol ratio | | Catalyst amount | |
|---|---|---|---|
| Ratio | Amount used (ml) | | Amount used (%) |
| 1:3 | 10.07 | 1% | 0.23 |
| 1:6 | 20.14 | 1.5% | 0.34 |
| 1:9 | 30.21 | 2% | 0.46 |