Addis Ababa University

Addis Ababa Institute of Technology (AAIT)

School of Graduate Studies

Department of Chemical Engineering

(Process Engineering)

Biodiesel Production from Jatropha Oil Using Ethanol with Alkali Catalyst

by

Adamu Esubalew

Advisor

Professor Walter Sokol

July 2011

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A Thesis is Submitted to Addis Ababa Institute of Technology

School of Graduate Studies in Partial Fulfillment for

Degree of Master of Science in Chemical Engineering

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Professor Walter Sokol

Department of Chemical Engineering

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ACKNOWLEDGMENT

First of all I would like to thank God for giving me health and patience to accomplish this thesis work successfully. A special thank goes to my advisor Professor Walter Sokol for his invaluable feedback and his continuous guidance and encouragement.

I would like to acknowledge the Department of Chemical Engineering for giving me the chance to undertake this study and furnishing all necessary facilities. My gratitude goes to Chemical Engineering Lab Staffs for their uninterrupted support.

I am also very grateful to Mr. Muche Bayleyegn, Eng. Tefera Desta, Mr. Ayehunie Abebe, Eng. Gebeyehu Ayalew and Mr. Destaw Muche for whose invaluable cooperation during my study.

I would like to thank again to Selam Technical and Vocational College for whose invaluable support.

My special gratitude goes to my mother and family members for their encouragement and financial support.

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ACRONYMS AND NOTATIONS

A: Temperature

AB: Temperature and Catalyst

ABC: Temperature, Catalyst and Alcohol

AC: Temperature and Alcohol

ANOVA: Analysis of Variance

AOCS: American Oil Chemists' Society

ASTM: American Standards Tests and Materials

AV: Acid Value

B: Catalyst

B100: Biodiesel 100% pure

B20: Biodiesel 20% blend

BC: Catalyst and Alcohol

BLTV: Blank Level Titration Volume

C: Alcohol

C_m: Concentration of Mass

EN: European Normalization (European Standards)

FFA: Free Fatty Acid

M_m: Molecular Mass

Ms: Mass of Sample

N: Normality

SV: Saponification Value

TF: Titration Factor

TV: Titration Volume

V/V: Volume per Volume

V/W: Volume per Weight

W/W: Weight per Weight

Y: Actual Yield

Y_r: Yield from Regression Equation

ABSTRACT

The jatropha oil was extracted using solvent extraction and mechanical pressing. The extracted oil was refined through degumming and neutralization followed by washing and drying. The acid value, amount of free fatty acid, saponification value and flash point of the extracted jatropha oil were determined. The biodiesel was produced from jatropha oil using anhydrous ethanol (99.4% w/w) anhydrous NaOH catalyst (97% w/w). The experimental design was done in two parts. The first one was done for one factor of four levels to establish the parameters influence independently on biodiesel yield. To determine the temperature effect, experiments were done at temperatures of 35^{o}C, 55^{o}C, 65^{o}C and 75^{o}C. Similarly, to investigate the effect of amount of catalyst, experiments were done at 0.25% (w/w), 0.5% (w/w), 1% (w/w) and 2% (w/w) of NaOH catalyst. In addition, to determine the influence of molar ratio of alcohol to oil, molar ratios of 6:1, 8:1, 10:1 and 12:1 were used. In the second of the experimental design, the full factorial, was done for the three factors at two levels and two replicas at a temperature of 55^{o}C and 65^{o}C, molar ratio of alcohol to oil 6:1 and 8:1, and the amount of catalyst required was 0.5% (w/w) and 1% (w/w), which were used to investigate the effects of the three parameters and their interaction simultaneously on biodiesel yield. It was found that the standardized effect of molar ratio of alcohol to oil had the highest effect whereas the least effect was observed at the interaction of temperature and alcohol. The standardized effect of the interaction of all the three parameters together was greater than the temperature effect alone. The average maximum biodiesel yield was 83.6% (w/w) at 55^{o}C, 8:1 molar ratio of alcohol to oil and 1% (w/w) NaOH catalyst amount. On the other hand, the average minimum biodiesel yield was 64.9% (w/w) at 65^{o}C, 6:1 molar ratio and 0.5% (w/w) catalyst amount. The viscosity, density, flash point, acid value, saponification value, moisture content and ash content of the produced biodiesel were determined. These properties were matched with ASTM specifications except viscosity which was slightly higher than ASTM limit.

1. INTRODUCTION

1.1. Background

Presently energy needs are met through non-renewable resources such as, petrochemicals, natural gas and coal. These resources will be depleted as a result of continued increase in the demand and the cost of petroleum based fuels and the present pattern of consumption [1]. Petroleum fuels also deteriorate the atmosphere and cause global warming in diesel engine emissions due to the presence of sulphur results in sulphur oxides and sulfates. When these sulfur chemicals are released into the atmosphere, they form sulfur dioxide which combines with water to form sulfuric acid. This acid is carried by winds to neighboring regions, dropping onto the land in the form of acid rains. Substitution of a small fraction of the total diesel fuel consumption by alternative fuels will have a significant impact on economy and the environment [2]. Hence efforts are being made to explore for alternative sources of energy such as biofuels that are technically feasible, economically competitive, and environmentally acceptable and readily available [3].

Among biofuels biodiesel is the one alternative energy source which is free from sulphur since it is derived from vegetable oils and its use substantially reduces the emissions of sulfur dioxide as well [4]. It does not cause acid rains and its blends also help in reducing the effects of acid rains. The usage of biodiesel is friendliness with the environment. Even on blending with mineral diesel, biodiesel significantly reduces emissions. Its combustion does not increase net atmospheric levels of greenhouse gases [5].

Biodiesel is a methyl or ethyl ester of fatty acid made from renewable biological resources such as vegetable oils, both edible and no edible, recycled waste vegetable oil and animal fats. The use of vegetable oils as alternative fuels has been started since 1900 when the inventor of the diesel engine Rudolph Diesel first tested peanut oil in his compression ignition engine [6]. There are different types of feed stocks that are used to produce biodiesel. Among plant feed stocks, jatropha seeds contain non-edible oil with properties that are well suited for the production of biodiesel. The oil content of the seeds varies from 30 to 50% depending on the variety, place and the method of oil extraction [7]. The oil is almost all stored in the seed kernel.

1.2. Statement of the Problem

At present, due to industrial development and high population growth, the demand of fossil fuel is increasing rapidly. To substitute the fossil fuel demand by renewable fuel, biodiesel production from vegetable oils is one alternative for energy demand. The use of edible oils to produce biodiesel in Africa and other developing continents is not feasible due to a huge gap between demand and supply of such oils in the developing world [6]. Therefore, there is a need to explore alternative non-edible oils which are used in production of biodiesel. Jatropha has been recognized as new energy crop for the countries to grow their own renewable energy source with many promising benefits [6, 8]. Jatropha seed oil is non-edible. At present jatropha plants are available in semi arid regions of Ethiopia. Therefore, jatropha oil will be suitable to produce biodiesel.

Short chain alcohols such as methanol, ethanol and butanol are used for biodiesel production. Although the use of different alcohols presents some differences with regard to the reaction kinetics, the final yield of esters remains more or less inalterable [8]. Therefore, selection of the alcohol is based on cost, availability and performance consideration. Worldwide, most of biodiesel productions from jatropha oil have been done using methanol alcohol. However, methanol is toxic and expensive relative to ethanol and not available in Ethiopia. In addition, methanol is nonrenewable since it is produced from fossil fuel gases. Ethanol is being produced from agricultural renewable resources, thereby attaining total independence from petroleum based alcohols. Ethanol is an extraction solvent and is preferable to methanol because of its much higher dissolving power for oils [8]. Therefore, producing ethyl esters rather than methyl esters is of considerable interest.

Hence, local availability, less toxicity and less cost over methanol were the main reasons that ethanol was used as an appropriate alcohol for the transesterification of jatropha oil.

Potassium hydroxide catalyst is expensive, lower in concentration and not available as compared to sodium hydroxide. That means sodium hydroxide is available in higher concentration and cheaper relative to potassium hydroxide. Thus, due to this reasons sodium hydroxide was used to produce biodiesel.

1.3. Objectives

1.3.1. General objective

The objective of the research was parameters investigation for production of biodiesel from jatropha oil using ethanol.

1.3.2. Specific objectives

The specific objectives were the following:

- To investigate the effects of reaction temperature and amount of alkali catalyst on biodiesel yield.
- To identify the influence of alcohol to oil molar ratio on biodiesel production.
- To determine physical and chemical properties of the biodiesel produced.

1.4. Significance of the Study

Jatropha oil and ethanol alcohol are locally available. The study may help to produce biodiesel at optimum condition from these raw materials which is used as a fuel for different purpose engines to substitute fossil fuel consumption. Furthermore, biodiesel has no sulfur and nitrogen oxide emissions during combustion since raw materials are agricultural products, which are free of sulfur and nitrogen molecules. This helps to reduce engine corrosion and environment burden. In addition, the study may help as a reference material for jatropha plant owners who need to produce biodiesel in pilot plant using ethanol alcohol and sodium hydroxide catalyst. This may help to stimulate rural communities to cultivate more jatropha plants to increase their income.

2. LITERATURE REVIEW

2.1. Biodiesel

The American Society for Testing and Materials (ASTM) defines biodiesel fuel as monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat. The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters and glycerol [3, 4, 9].

Biodiesel, as an alternative fuel, has many merits. It is derived from a renewable, domestic resource, thereby relieving reliance on petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum based diesel, biodiesel has a more favorable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect. Biodiesel has a relatively high flash point, which makes it less volatile and safer to transport or handle than petroleum diesel. It provides lubricating properties that can reduce engine wear and extend engine life. Due to these reasons, the use of biodiesel has grown dramatically during the last few years [6, 8, 9].

Feedstock costs account for a large percent of the direct biodiesel production costs. One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids such as inedible oils, animal fats and waste food oil and by products of the refining vegetables oils. The availability and sustainability of sufficient supplies of less expensive feedstock is a crucial determinant delivering a competitive biodiesel to the commercials filling stations. Fortunately, inedible vegetable oils, mostly produced by seed bearing trees can provide an alternative. With no competing food uses, this characteristic turns attention to jatropha curcas, which grows in tropical and subtropical climates across the developing world. The fact that jatropha oil cannot be used for nutritional purposes without detoxification makes its use as energy or fuel source very attractive as biodiesel [3-5].

2.2. Jatropha Curcas Plant

Jatropha curcas is one of many species of the genus jatropha, a member of the large and diverse euphorbiaceous family. It was first described by Swedish botanist Carl Linnaeus in 1753[9]. Jatropha tree and applications are shown in Figure 2.1 and Table 2.1, respectively.

Figure 2.1: Jatropha plant.

Table 2.1: Uses of jatropha plant.

Jatropha plant parts	Uses
Jatropha stock	Soil erosion control, livestock fence and land demarcation
Leaves and fruits	Biogas production, medicinal uses and anti-inflammatory
Seed oil	Biodiesel production, soap making and as insecticide
Seed husk and cake	Organic fertilizer, combustible fuel and biogas production

2.2.1. Jatropha oil applications

Crude jatropha oil is relatively viscous. It is characteristically low in free fatty acids which improve its storability. The presence of unsaturated fatty acids, high iodine value, allows it to remain fluid at lower temperatures. Oil characteristics are influenced by environment and genetic interaction, seed size, weight and oil content. Jatropha oil has many applications. Some of the uses are described below [9].

2.2.1.1. Pure jatropha oil as direct fuel for engines

Jatropha oil may be used directly in some diesel engines, without converting it into biodiesel. The oil must be of a quality satisfactory for long term performance of engines run on jatropha oil. Although fresh jatropha oil is low in free fatty acids, it shall be stored in closed, dry, cool conditions to prevent formation of free fatty acids.

2.2.1.2. Jatropha oil as cooking fuel

Jatropha oil can be used as cooking fuel. There are clear advantages to using jatropha oil instead of traditional biomass for cooking. The advantages include the health benefits from reduced smoke inhalation, and environmental benefits from avoiding the loss of forest cover.

2.2.1.3. Jatropha oil as soap making

Jatropha oil is used for soap making in developing countries. Jatropha soap is made by adding a solution of sodium hydroxide to jatropha oil in the presence of water. This simple technology has turned soap making into a viable small scale rural enterprise appropriate to many rural areas of developing countries. Jatropha soap is valued as a medicinal soap for treating skin illness.

2.2.1.4. Jatropha oil as a biodiesel feedstock

The production of jatropha biodiesel is a chemical process whereby the oil molecules called triglycerides react with methanol or ethanol molecules in the presence of catalyst to form methyl or ethyl ester. Glycerol is formed as a side product.

2.3. Jatropha Oil Extraction Methods

Two main methods of extracting the oil are used. These are solvent extraction with n-hexane and the mechanical extraction using either a manual press or an engine driven expeller. Solvent extraction with n-hexane can produce about 41% yield by weight of oil per kg of the jatropha seed [10]. Oils are currently obtained mechanically when samples are big enough, but in most cases their extraction efficiency is low. Chemical extraction with hexane has been

reported with an extraction efficiency of 95-99% when working with a soxhlet apparatus for 24 hours [11]. The extraction temperature for jatropha oil is from 55-65^{o}C for an engine driven expeller mechanical pressing whereas near to the boiling point, 68^{o}C, of hexane for solvent extraction [10, 11].

2.3.1. Oil extraction processes

Two methods of oil extraction processes are known. These are solvent extraction and mechanical extraction. Solvent and mechanical method oil extraction processes are given in Figure 2.2 and 2.3, respectively [12].

2.3.1.1. Oil extraction using solvent

To extract oil using solvent, jatropha seeds cover is removed and seed kernels are crushed at the required size. The crushed kernel and hexane at ratio of1:5(w/v), respectively are fed to soxhlet apparatus to extract oil. The extraction temperature is near the boiling point of hexane. The solid cake and mixture of oil and hexane are separated using vacuum filter. Oil and hexane are separated using distillation at a temperature of slightly higher than the boiling temperature of hexane, which is recovered again for further extraction with fresh hexane.

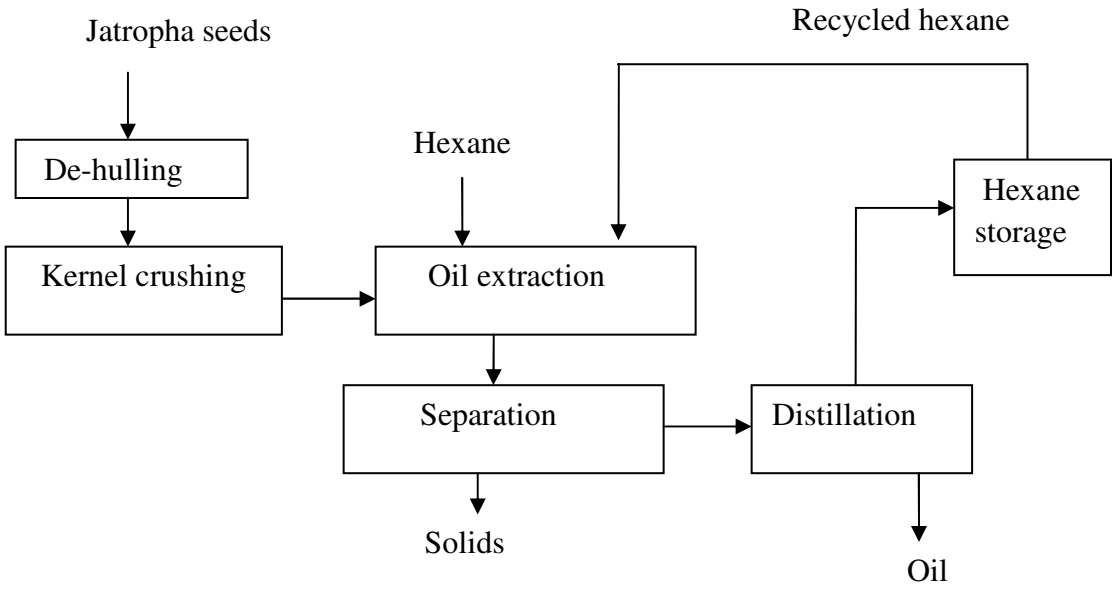


Figure 2.2: Oil extraction using hexane solvent.

2.3.1.2. Mechanical pressing oil extraction

For oil extraction using mechanical pressing, jatropha seeds cover is removed. The seeds kernel is fed to mechanical presser which exerts high pressure to extract oil. The pressure varies depend on type and capacity of mechanical presser. When pressure is exerted at the required amount, kernel cake is removed in one side; oil and some impurities are collected in another side. Oil and impurities are separated using gravity settling or centrifuge.

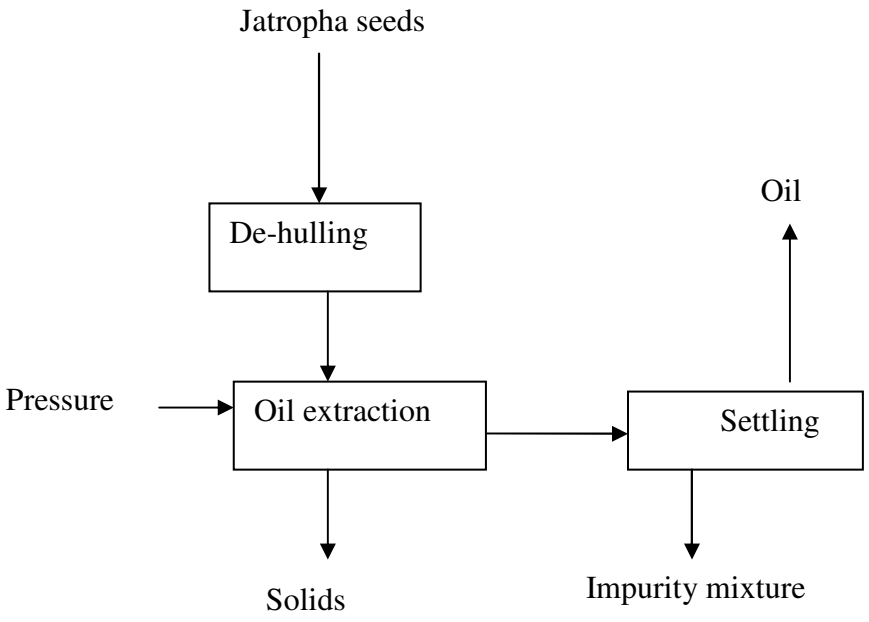


Figure 2.3: Mechanical press oil extraction.

2.3.2. Properties of jatropha oil

Jatropha oil properties are established to ascertain suitability for biodiesel production and to determine a suitable production process. Oil properties are determined by American Oil Chemists' Society (AOCS) method. The oil properties and its fatty acid composition determined by standard method are shown in Tables 2.2 and 2.3, respectively [13, 22].

Table 2.2: Properties of jatropha oil.

Jatropha oil properties	Density at 15^0C (kg/m^3)	Kinematic viscosity at 40^oC (mm^2/s)	Acid value (mgKOH/g)	Saponification value (mgKOH/g)	Iodine value ($gI_2/100g$)
Values	918.6	34.48	4.24	169.9	111.6

Table 2.3: Fatty acid composition of jatropha oil.

Jatropha oil fatty acid types	Jatropha oil fatty acid composition (%)
Palmitic (16:0)	18.22
Stearic (18:0)	5.14
Linoleic acid (18:1)	48.18
Oleic (18:2)	28.46
Average molecular weight	874g/mol

As shown in the Table 2.3, the oil chains are designated by two numbers separated by a colon. The first number designates the number of carbon atoms in the chain and the second number designates the number of double bonds. The number of carbon atoms includes the carbon that is double bonded to the oxygen atom at one end of the fatty acid [14-17]. The structure of fatty acid of triglyceride is shown in Figure 2.4.

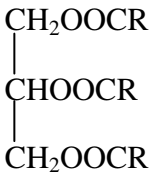


Figure 2.4 : Triglyceride structure.

Palmitic: R = - $(CH_2)_{14}$ – CH_3, 16 carbons and 0 double bonds (16:0)

Stearic: R = - $(CH_2)_{16}$ – CH_3, 18 carbons and 0 double bonds (18:0)

Linoleic: R = - $(CH_2)_7$ CH=CH-CH_2-CH=CH $(CH_2)_4CH_3$, 18 carbons and 2 double bonds (18:2)

Oleic: R = - $(CH_2)_7$ CH=CH $(CH_2)_7CH_3$, 18 carbons and 1 double bond (18:1)

2.3.3. Jatropha oil property analysis

The oil acid value and saponification value tests can be determined by titration methods. The details of these methods are given below [14, 17, 18].

2.3.3.1. Acid value

Acid value is obtained through titration. The titration volume is used to determine the acid value of the oil. Acid value tells us the amount of free fatty acid content in the oil. This helps to know how much extra catalyst will be required to convert the oil to quality fuel. The amount of free fatty acid in mg/g of oil is approximately one half of the acid value [19].

$$\text{Acid value(AV)}, \text{mgKOH/g} = \frac{\text{N} \times \text{M}_\text{m} \times \text{TV}}{\text{M}_\text{s}} \quad (2.1)$$

where:

M_m is the molecular mass of KOH, 56g/mol

M_s is the mass of sample, g

N is the normality of KOH, mol/L

TV is the titration volume, ml

$$\text{Free fatty acid(FFA)}, \text{mg/g} \approx \frac{1}{2}\text{Acid Value(AV)} \quad (2.2)$$

2.3.3.2. Saponification value

Saponification value is expressed by potassium hydroxide or sodium hydroxide in mg required to saponify 1g of oil. Like acid value, saponification value is also determined by titration method. It depends on the kind of fatty acid contained in the oil.

$$RCOOH + KOH \rightarrow R\,COOK + H_2O \quad (2.3)$$

$$KOH + HCl \rightarrow KCl + H_2O \quad (2.4)$$

$$\text{Saponification value, mgKOH/g} = \frac{(BLTV - TV) \times TF \times C_m}{M_s} \quad (2.5)$$

where:

BLTV is the blank level titration volume, ml

C_m is the molar concentration ×molecular mass of KOH, mg/ml

M_s is the mass of sample, g

TF is the titration factor, TF=1.006

TV is the titration volume, ml

2.4. Biodiesel Production Process Options

Biodiesel can be produced in two process options. These are batch process system or continuous process system [19].

2.4.1. Batch process system

The simplest method for producing methyl or ethyl esters is to use a batch, stirred tank reactor. The reactor may be sealed or equipped with a reflux condenser. The operating temperature is usually near to the boiling point of alcohol. Thorough mixing is necessary at the beginning of the reaction to bring the oil, catalyst and alcohol into intimate contact. Towards the end of the reaction, less mixing can help increase the extent of reaction by allowing the inhibitory product, glycerol to phase separation.

The oil is first charged to the system, followed by the catalyst and alcohol solution. The system is agitated during the reaction time. In some processes, the reaction mixture is allowed to settle in the reactor to give an initial separation of the esters and glycerol. In other processes the reaction

mixture is pumped into a settling vessel, or is separated using a centrifuge. The alcohol is removed from both the glycerol and ester stream using an evaporator. The esters are neutralized, washed gently using warm water to remove residual alcohol and soaps.

2.4.2. Continuous process system

Feeds are entered and products are withdrawn continuously. The continuous stirred tank reactors in series can be varied in volume to allow for a longer residence time in the first continuous stirred tank reactor to achieve a greater extent of reaction. After the initial product glycerol is decanted, the reaction in the second continuous stirred tank reactor is followed. An essential element in the design of a continuous stirred tank reactor is sufficient mixing input to ensure that the composition throughout the reactor is essentially constant. This has the effect of increasing the dispersion of the glycerol product in the ester phase. The result is that the time required for phase separation is extended. There are several processes that use intense mixing, either from pumps or motionless mixers, to initiate the esterification reaction. The result is a continuous system that requires rather short residence times for near completion of the reaction.

2.5. Biodiesel Production Processes

Biodiesel is the monoalkyl esters of long chain fatty acids derived from vegetable oil or animal fats, for use in compression ignition engine [15, 16, 19]. It composed of fatty acid methyl or ethyl esters that can be prepared from triglycerides in vegetable oils by transesterification with methanol alcohol or ethanol alcohol in the presence of catalyst. It can be blended at any level with petroleum diesel to create a biodiesel blend or can be used in its pure form. Biodiesel is a liquid which varies in color between golden and dark brown depending on the production feedstock.

The base catalyzed production of biodiesel generally has the following process steps [15].

2.5.1. Mixing of alcohol and catalyst

The catalyst is typically sodium hydroxide or potassium hydroxide. It is dissolved in the alcohol to produce alkoxide solution using a standard agitator or mixer.

2.5.2. Chemical reaction

The alcohol and catalyst mix is then charged into a closed reaction vessel where the oil or fat is added. The reaction system is totally closed to the atmosphere to prevent the loss of alcohol. The temperature of reaction mixture is kept just near the boiling point of the alcohol to speed up the reaction. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters. The reaction of oil and alcohol stoichiometry equation is written and explained detail in Section 2.6.3.

2.5.3. Separation

Once the reaction is complete, two major products exist. These are glycerol and biodiesel. Each has a substantial amount of the excess alcohol that was used in the reaction. The reacted mixture is sometimes neutralized at this step if needed. The glycerol phase is much denser than biodiesel phase. The two products can be separated by gravity using settling vessel. The glycerol is drawn off at the bottom of the settling vessel and biodiesel is drawn off at the top. In some cases, a centrifuge is used to separate the two materials faster.

2.5.4. Alcohol removal

Excess alcohol is removed in two ways. Once the glycerol and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. It is the common one to remove excess alcohol. On the other hand, the alcohol is removed and the mixture neutralized before the glycerol and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is re-used.

2.5.5. Biodiesel washing

Once separated from the glycerol, the biodiesel is sometimes purified by washing gently with warm water to remove residual catalyst, alcohol or soaps. The washed biodiesel needs drying in order to remove trace water. In some processes washing step is unnecessary depending on the quality required. As shown in Figure 2.5 biodiesel is produced with alcohol in the presence of catalyst [16, 18 19].

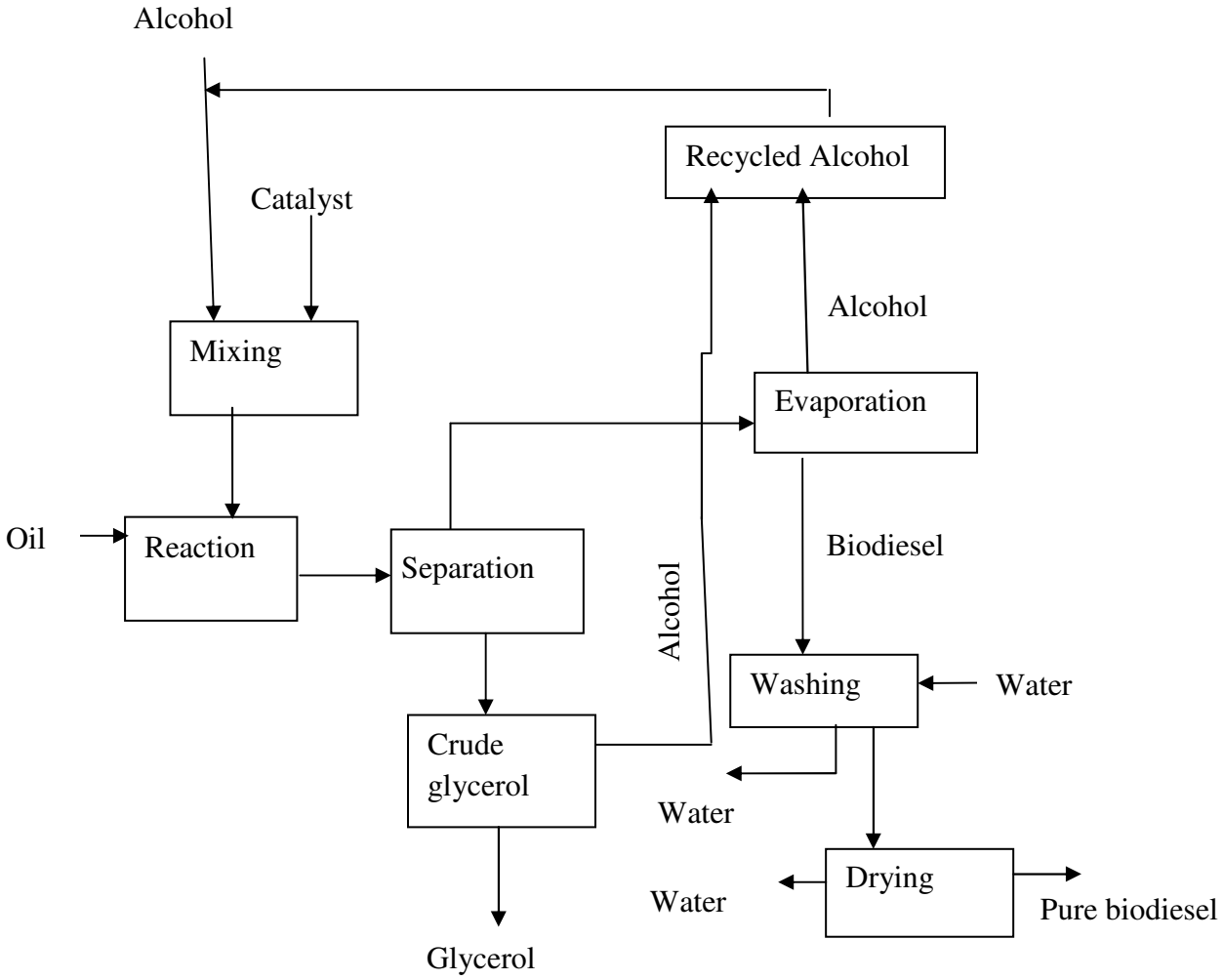


Figure 2.5: Biodiesel production.

2.6. Transesterification Reaction

The plant oils usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Because of these, the oil cannot be used as fuel directly. To overcome these problems the oil requires slight chemical modification through transesterification, pyrolysis, dilution and emulsification [15]. Among these, the transesterification is the key and foremost important step to produce the cleaner and environmentally safe biodiesel fuel from vegetable oils.

Transesterification is the reaction of triglycerides with alcohols to generate methyl or ethyl esters and glycerol as by-product. Transesterification of vegetable oil is commonly carried

out with methanol or ethanol, using alkali catalyst, acid catalyst, without catalyst by supercritical alcohol or enzyme catalyst [19- 21].

2.6.1. Supercritical transesterification

An alternative, catalyst free method for transesterification uses supercritical alcohol at high temperatures and pressures in a continuous process. In the supercritical state, the oil and methanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock. Free fatty acids are converted to esters instead of soap, so a wide variety of feedstocks can be used. Also the catalyst removal step is eliminated. High temperatures and pressures are required, but an energy cost of production is higher [20].

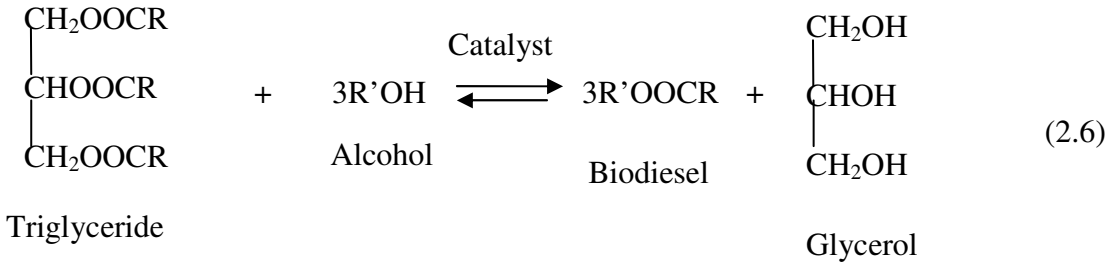
2.6.2. Lipase catalyzed transesterification

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 FFA 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 [21].

2.6.3. Transesterification reaction using alkali catalyst

Most of the commercial processes to produce biodiesel from plant oils use very effective homogeneous catalysts such as alkali or acid. Alkali catalysts such as sodium hydroxide or potassium hydroxide are more effective. Alkali catalyzed transesterification is much faster than the acid catalyzed reaction. However, the acid catalyzed transesterification reaction is more suitable if a vegetable oil has a high free fatty acid and water content. Most commercial transesterification reactions are conducted with alkaline catalysts [22]. This is due to partly the faster transesterification reaction and partly to the fact that alkaline catalysts are less corrosive to industrial equipment than acidic catalysts. However, these alkali compounds have some disadvantages such as the necessity of application of refined plant oils, problems related to the recovery of pure glycerol, and formation of soaps if oils contain high free fatty acids.

Transesterification is also called alcoholysis. A catalyst is used to improve the reaction rate and yield. The transesterification reaction of vegetable oil with alcohol is shown in equation (2.6).



(2.6)

where:

R is the alkyl group of triglyceride components (palmitic, stearic, oleic and linoleic)

Palmitic: R = - $(CH_2)_{14} – CH_3$, 16 carbons and 0 double bonds (16:0)

Stearic: R = - $(CH_2)_{16} – CH_3$, 18 carbons and 0 double bonds (18:0)

Linoleic: R = - $(CH_2)_7$ CH=CH-CH_2-CH=CH $(CH_2)_4CH_3$, 18 carbons and 2 double bonds (18:2)

Oleic: R = - $(CH_2)_7$ CH=CH $(CH_2)_7CH_3$, 18 carbons and 1 double bond (18:1)

R' is CH_3CH_2- for ethanol alcohol alkyl group.

The transesterification reaction consists of three reactions, which are equivalent, consecutive and reversible. The triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol. At every reaction step, one molecule of ester, biodiesel, is produced for each molecule of alcohol consumed.

From equation (2.6), the stoichiometry of the transesterification reaction needs 3 moles of alcohol per mole of triglyceride to yield 3 moles of fatty esters and 1 mole of glycerin [16, 22, 23]. Since transesterification reaction is reversible, the reaction requires an excess of alcohols to improve the efficiency of the transesterification process. To shift the transesterification reaction to the forward direction, it is necessary to use a large excess of alcohol or remove continuously one of the products from the reaction mixture.

2.7. Variables Affecting Alkali Catalyzed Transesterification Reaction

The transesterification reaction process is affected by various operating factors. These are reaction temperature, molar ratio of alcohol to oil, catalyst type and amount, reaction time, stirring rate, presence of moisture and free fatty acids [23].

2.7.1. Alkali catalyst amount

The limitation of alkali catalyzed process is its sensitivity to the purity of reactants; especially the alkali catalyzed system is very sensitive to both water and free fatty acids. The presence of water, under alkaline conditions, may cause ester saponification [23, 24].

Free fatty acids in the oil can react with an alkali catalyst to produce soaps and water. The resulting soaps can cause the formation of emulsions. These circumstances give rise to a consumption of the catalyst and cause difficulties in purification of the biodiesel.

When there is a large free fatty acid content, the addition of more bas catalyst, compensates this acidity and avoids catalyst deactivation. However, the addition of an excessive amount of catalyst gives rise to the formation of an emulsion, which increases the viscosity and leads to the formation of gels. These hinder the glycerol separation process and, reduce the apparent ester yield. In consequence, further increases in catalyst concentration did not increase the conversion and lead to extra costs because it was necessary to remove it from the reaction medium at the end.

If the oil has high free fatty acid content and more water, acid catalyzed transesterification is suitable. Therefore, a two step esterification process is required for these feedstocks.

Initially, the free fatty acid of these oils can be converted to partial fatty acid esters by an acid catalyzed pretreatment and the second step transesterification is completed by using alkali catalyst. In alkali catalyzed transesterification reaction, mostly sodium hydroxide or potassium hydroxide have been used in concentration from 0.4 to 2% w/w of oil. For refined oils with 1% either sodium hydroxide or potassium hydroxide catalyst amount is required in successful conversion.

2.7.2. Molar ratio of alcohol to oil

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. Stoichiometrically, 3 moles of alcohol and 1 mole of triglyceride are required for transesterification to yield 3 moles of fatty acid alkyl esters and 1 mole of glycerin. However, transesterification is an equilibrium controlled reaction in which excess of alcohol is required to drive the reaction in the forward direction. Further increase in molar ratio of alcohol to oil, the conversion efficiency is remains the same, but the energy required for the recovery of alcohol becomes higher. In addition, excessive amount of alcohol makes the recovery of the glycerol difficult since more excess alcohol hinders the decantation by gravity so that the apparent yield of esters decreases since part of the glycerol remains in the biodiesel phase.

In consequence, the alcohol to oil molar ratio is one of the most important variables affecting the esters yield. Although the stoichiometry ratio for transesterification requires 3 moles of alcohol and 1 mole of triglyceride, an excess of alcohol is used in the practice. The molar ratio is associated with the type of catalyst used. In alkali catalyzed transesterification reaction the alcohol to oil molar ratio of 6:1 to 12:1 are the most acceptable for maximum conversion to esters. When using acid catalyst instead of alkali catalyst, the desirable maximum conversion is obtained with sulfuric acid with alcohol to oil molar ratio of 30:1[9, 25, 26]. The molar ratio of alcohol to oil has no effect on acid value, saponification values and iodine values of esters.

2.7.3. Reaction time and temperature

The rate of reaction is strongly influenced by reaction temperature. Higher temperatures decrease the time required to reach maximum conversion. Transesterification can be conducted at various temperatures ranging from room temperature to the boiling point of the alcohol employed so that the reactor does not need to be pressurized. When the reaction temperature exceeds the boiling point of alcohol, the alcohol will vaporize and form a large number of bubbles which may inhibit the reaction. The completion of the basic catalyzed transesterification process depends on reaction time. The transesterification reaction is commonly conducted close to the boiling point of the alcohol at atmospheric pressure for

1hour to3hours [26]. Excess reaction time does not increase the conversion but favors the backward reaction, hydrolysis of esters, which results in a reduction of product yield.

2.7.4. Stirring rate

Since the reaction can only occur in the interfacial region between the liquids and also due to the fact that oils and alcohols are not totally miscible, transesterification reaction is a relatively slow process. As a result, vigorous mixing is required to increase the area of contact between the two immiscible phases.

The agitation intensity appears to be of a particular importance for the alcoholysis process. The mass transfer of triglycerides from the oil phase towards the alcohol-oil interface could be a critical step limiting the rate of alcoholysis reaction because the reaction mixture is heterogeneous. Poor mass transfer between two phases in the initial phase of the reaction results in a slow reaction rate, the reaction being mass transfer controlled. Fast stirring accelerates transesterification reaction. Therefore, variations in mixing intensity are expected to alter the kinetics of the transesterification reaction [23, 26].

2.7.5. Free fatty acid and moisture content

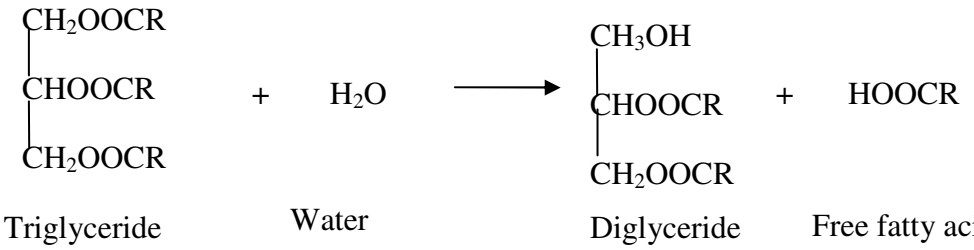
The free fatty acid and moisture content are the key parameters for determining the viability of vegetable oils to be used in transesterification process.

Presence of moisture content in the oil increases the amount of free fatty acids which causes the transesterification reaction to partially change to saponification, which produces soap and thus lowering the yield of esters. Saponification also renders the separation of ester and glycerol difficult since it increases the viscosity and form gels. To carry out alkali catalyzed transesterification reaction to completion, less than 3% free fatty acid content in oils is needed [27]. Higher the acidity of the oil, smaller is the conversion efficiency.

Free fatty acids react with the basic catalyst added for the reaction and give rise to soap, as a result of which, one part of the catalyst is neutralized and is therefore no longer available for transesterification. These high free fatty acid content oils are processed with an immiscible

basic glycerol phase so as to neutralize the free fatty acids and cause them to pass over into the glycerol phase [22, 23, 27].

When water is present, particularly at high temperatures, it can hydrolyze the triglycerides to diglyceride and form a free fatty acid. As shown below in equation (2.7) hydrolysis reaction of triglyceride is carried out.



(2.7)

Triglyceride Water Diglyceride Free fatty acid

where:

R is the alkyl group of triglyceride components (palmitic, stearic, oleic and linoleic)

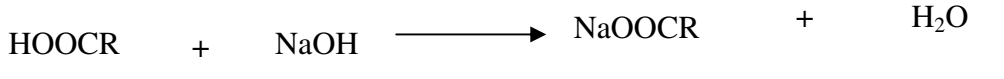
Palmitic: R = - $(CH_2)_{14} – CH_3$, 16 carbons and 0 double bonds (16:0)

Stearic: R = - $(CH_2)_{16} – CH_3$, 18 carbons and 0 double bonds (18:0)

Linoleic: R = - $(CH_2)_7$ CH=CH-CH_2-CH=CH $(CH_2)_4CH_3$, 18 carbons and 2 double bonds (18:2)

Oleic: R = - $(CH_2)_7$ CH=CH $(CH_2)_7CH_3$, 18 carbons and 1 double bond (18:1)

When an alkali catalyst is present, the free fatty acid reacts to form soap. This reaction is undesirable because it binds the catalyst into a form that does not contribute to accelerating the reaction. Excessive soap in the products can inhibit later processing of the biodiesel, including glycerol separation and water washing. As shown below in equation (2.8), the reaction of free fatty acid and alkali catalyst causes formation of soap.



(2.8)

Free fatty acid Sodium hydroxide Sodium soap Water

In order to reduce the above side reactions, the starting materials that are used for base catalyzed alcoholysis should meet certain specifications. The triglycerides should have lower acid value and all material should be substantially anhydrous. Addition of more sodium hydroxide catalyst compensates for higher acidity, but the resulting soap causes formation of gels that interferes in the reaction as well as with separation of glycerol.

2.8. Biodiesel Properties and Specification Standards

Biodiesel is a liquid which varies in color between golden and dark brown depending on the production feedstock. Specifications are used to define and set the quality standards for biodiesel. The standard is framed as a set of property specifications measured by specific ASTM test methods. The standard for biodiesel is ASTM 6751-02. ASTM D 6751 – 02 sets forth the specifications that must be met for a fatty acid ester product to carry the designation biodiesel fuel. Density, kinematics viscosity, flash point, acid value, ash content, iodine value, caloric value, cloud point, water content and cetane number are physicochemical properties of biodiesel [28, 29].

2.8.1. Biodiesel properties

2.8.1.1. Density

It is defined as mass per unit volume of a substance at a given temperature. The higher density of biofuel indicates presence of large mass in a given volume, which is heavy biofuel.

2.8.1.2. Viscosity

It is the resistance to flow of a fluid under gravity. The kinematic viscosity is equal to the dynamic viscosity per density. The kinematic viscosity is a basic design specification for the fuel injectors used in diesel engines. Too high a viscosity and the injectors do not perform properly.

2.8.1.3. Flash point

It is defined as the lowest temperature corrected to at atmospheric pressure at which application of an ignition source causes the vapors of a specimen to ignite under specified conditions of test.

2.8.1.4. Acid value

The acid number is a direct measure of free fatty acids in biodiesel. The free fatty acids can lead to corrosion and may be a symptom of water in the fuel.

2.8.1.5. Ash content

It is the residue remaining after a fuel sample has been burned. For biodiesel, this test is an important indicator of the quantity of residual materials in the fuel that came from the raw material and catalyst used in the transesterification process.

2.8.1.6. Iodine value

It indicates the level of saturation of the molecules. According to ASTM, the iodine number helps to indicate the oxidation stability of the biodiesel. Higher iodine number represents lower oxidation stability.

2.8.1.7. Caloric value

The caloric value of a fuel is the standard heat of reaction at constant pressure where the fuel burns completely with oxygen. The higher caloric value fuel gives higher heat output.

2.8.1.8. Cloud point

The cloud point of the fuel is the temperature at which wax crystals first begin to form. Below the cloud temperature, filters will start to become blocked and potentially starve the engine of the fuel. Cloud point of biodiesel is used as an indicator of cold temperature stability.

2.8.1.9. Water content

The amount of water content in the biodiesel determines the caloric value and the shelf life of the fuel. Biodiesel with higher water content has lower oxidation stability and the greater probability of oxidation products will be formed during long storage periods.

2.8.1.10. Cetane number

It is the measure of fuel's ignition and combustion quality characteristics. The higher cetane number biodiesel has lower ignition time delay, which means it, ignites immediately as required. Based on ASTM, fuels with lower cetane numbers will cause hard starting, rough operation, noise and increased smoke opacity in engines.

2.8.2. Biodiesel specification standards

The biodiesel specifications and standard methods are shown in Table 2.3.

Table 2.4: Biodiesel specifications and standard methods.

Properties	Specification quantity	Standard Methods
Density at 15 ^{o}C (kg/m^{3})	875-900	ASTM D6751-02
Kinematics viscosity at 40^{o}C (mm^{2}/s)	1.9-6.0	ASTM D6751-02
Flash point (^{o}C)	≥130	ASTM D6751-02
Acid value (mgKOH/g)	≤0.8	ASTM D6751-02
Saponification value (mgKOH/g)	-	ASTM D6751-02
Ash content (%w/w)	<0.02	ASTM D6751-02
Iodine value (I_2g/100g)	≤120	EN14214
Caloric value (MJ/kg)	-	ASTMD6751
Cloud point (^{o}C)	reported to customer	ASTMD6751
Water content, %w/w	<0.03	ASTM D6751-02
Cetane number	≥47	ASTM D6751

2.9. Biodiesel Applications

Biodiesel can be used in pure form, B100 or may be blended with petroleum diesel at any concentration in most injection pump diesel engines. Biodiesel can also be used as a heating fuel in domestic and commercial boilers, a mix of heating oil and biofuel which is standardized differently than diesel fuel used for transportation. A blend of 20 %biodiesel with 80 % petrodiesel, by volume, is termed B20. A blend of 2 % biodiesel with 98% petrodiesel is B2, and so on. Depending on engines construction materials the biodiesel blend can be restricted. For instance, new extreme high pressure common rail engines have strict factory limits of B5 or B20 depending on manufacturer. Biodiesel has different solvent properties than petrodiesel, and will degrade natural rubber gaskets in vehicles although these tend to wear out naturally and most likely will have already been replaced which is nonreactive to biodiesel [29].

3. MATERIALS AND METHODOLOGY

3.1. Materials

The materials that were required for biodiesel production were jatropha seeds oil, ethanol alcohol, sodium hydroxide catalyst, property test analysis chemicals as shown in Table 3.1. The jatropha seeds were brought from North Gondar Zone, Metema. Chemicals were bought from Neway Private Limited Company and Borufis Educational Materials Supply Private Limited Company in Addis Ababa.

Table 3.1: Chemicals used for biodiesel production.

Activities	Chemicals used
Acid value test	Potassium hydroxide, ethanol alcohol , phenophtaline and distilled water
Saponification value test	Potassium hydroxide, hydrochloric acid, ethanol alcohol, phenophtaline and distilled water
Oil degumming and neutralization	Phosphoric acid and sodium hydroxide
Biodiesel production	Ethanol alcohol and sodium hydroxide
Neutralization of excess catalyst	Tannic acid

3.2. Methodology

3.2.1. Experimental works

Experimental works were done in Chemical Engineering Department Laboratory. In addition, mechanical press oil extraction was done in BahirDar and Selam Technical and Vocational College in Addis Ababa.

3.2.1.1. Jatropha seeds sample preparation

To extract the oil the samples of seed were prepared. The jatropha seeds were de-hulled using three phase motor grinder in Chemical Engineering Size Reduction Laboratory. The seeds hull was separated from seeds kernel manually. The seed kernels are white in color.

The seeds kernel was crushed by motor mill with 1.0 mm to 2.0 mm sieve size in Chemical Engineering Size Reduction Laboratory. After crushing the sample was ready for oil extraction.

3.2.1.2. Jatropha oil extraction

The oil was extracted by solvent extraction and mechanical pressing extraction methods. Procedures of oil extraction using hexane solvent were based on [12].

3.2.1.2.1. Oil extraction using solvent

The seeds were de-hulled by a mill grinder and the seed covers were separated manually. Next, the kernels were crushed in a crushing mill with a particle size of 1.0 mm to 2.0 mm. Then, the crushed kernels and hexane solvent were placed in the extraction unit at a solvent to solid ratio of 3:1 (v/w). The solvent and crushed mixtures were mixed at 200 rpm speed and heated at constant temperature of 65^{o}C for 15 hours to extract the oil. After extraction the solids and the solvent-oil mixtures were separated by a settling followed by a vacuum filtration. The solvent and oil were separated in a rotary evaporator at a temperature of 70^{o}C. The solvent was recovered using condenser for reuse in extract oil. The oil was collected and stored for further purification.

3.2.1.2.2. Oil extraction using mechanical pressing

The seeds were de-hulled in a mill grinder and the seed covers were separated manually. Next, the kernels were crushed using a crushing mill with a particle size of 1.0 mm to 2.0 mm. Thereafter, the crushed kernels were tied by a cotton cloth and fed the top of a presser. At each batch 1kg of the crushed kernel was fed into the mechanical presser at atmospheric temperature. The presser was rotated manually until the screw tight strongly where the oil

extraction was taking placed. Since the crushed kernel was tied by the cotton cloth, there was no need for a cake filtration. The oil was collected at the bottom of the mechanical press.

More oil was extracted using mechanical pressing although its efficiency was lower due to high cost of hexane.

3.2.1.3. Jatropha oil refining

To refine the oil settling, degumming and neutralization methods were used.

a). Settling: The crude oil impurities were separated using a centrifuge at a speed of 800 rpm for 20 minutes.

b). Degumming: Phosphorus compounds were removed by degumming of crude oil using a phosphoric acid and a hot water. Distilled water 3% (v/v) of oil at 70^{o}C and 1.5% phosphoric acid (v/v) of oil were mixed with the oil which was heated at 70^{o}C. The mixtures were stirred at speed of 200 rpm for 1 hour at a temperature of 70^{o}C. The impurities were separated using a centrifuge at a speed of 800 rpm for 20 minutes.

c). Neutralization: After the oil free fatty acid (FFA) was determined, the free fatty acid was neutralized by 0.05N of NaOH. During neutralization the oil was heated at 70^{o}C. The mixture of oil and NaOH solution were stirred at 200 rpm at a temperature of 70^{o}C for 1 hour. The mixture was washed with a distilled water to remove a trace NaOH and produced soap. Finally, trace water was removed in an oven drying at a temperature of 105^{o}C for 6 hours.

3.2.1.4. Physicochemical properties of extracted oil

Acid value and saponification value tests were done based on experimental procedures of [17, 18, 29] to determine the oil property.

3.2.1.4.1. Acid value of oil

To determine the acid value, firstly, a titration solution of 0.1N of KOH in distilled water was prepared. Next, 2g of oil was added to the 250ml conical flask and heated at 70^{o}C for 3 minutes. Then, 20ml of anhydrous ethanol (99.4%w/w) and 5 drops of phenolphthalein were added into the titration beaker with sample oil.

After that, oil sample was mixed with 20ml of ethanol and 5 drops of phenolphthalein. Finally, titration solution, 0.1N of KOH was being added 1 drop at a time until the first color change was observed. Once the color change was observed, the titration volume (ml) was recorded and titration was stopped. The titration volume recorded (ml) was used to calculate the acid value.

3.2.1.4.2. Saponification value of oil

To determine saponification value of the oil, initially, 0.5mol/l potassium hydroxide in anhydrous ethanol (99.4%w/w) and 0.5mol/l hydrochloric acid solution in distilled water was prepared. Then, a 2 g sample was placed in a 250ml conical flask. Next, a 25ml of 0.5mol/l potassium hydroxide in ethanol solution was added. The flask was heated at a temperature of 70^{o}C and shaken when adjusting the heat so that backflow ethanol did not reach the top of cooling pipe. After that, the sample was heated for 30 minutes and it was cooled immediately. 5 drops of phenophtaline was added as indicator. Finally, the sample was titrated with 0.5mol/l hydrochloric acid solution before the test liquid solidified. The titration was stopped and the value was recorded when the color change was observed. A blank level test was also performed in parallel using all above procedures without the oil sample addition.

3.2.1.4.3. Density of oil

To measure the density of oil, 45ml of oil was filled into a measuring cylinder. Next, a hydrometer, specific gravity measuring instrument, was immersed in the cylinder which contained the oil. The reading on the instrument at the upper surface of oil was the specific gravity of the oil.

3.2.1.4.4. Kinematic viscosity of oil

A kinematic viscosity of the oil was measured indirectly using Vibro viscometer. Initially, a sample was heated at a temperature of 40^{o}C. A sample of 45ml oil was measured and fed to a sample holder of the viscometer. Next, a sensor of the viscometer was immersed on the oil sample. A dynamic viscosity of the oil was displayed on the viscometer screen automatically.

3.2.1.4.5. Flash point of oil

The flash point was measured using opened cup method. A sample of 45ml was added into the burning cup. Next, at the bottom of the sample cup the gas burner was ignited to heat the burning cup bottom when another igniter wire was used to take the flame from gas igniter to the surface of the sample to burn it. The sample was ignited and flame was observed where the temperature was reached at its flash point. To determine the flash point temperature of each sample, thermometer was immersed in the oil.

3.2.1.4.6. Moisture content of oil

To determine the moisture content of oil, 35g of sample was measured. Next, the sample was heated in an oven drying at a temperature of 105^{o}C for 2hours .After that, it was come out from an oven drying and the sample mass was measured. Then, the procedures were repeated until the mass measurement was obtained constant records.

3.2.1.4.7. Ash content of oil

The ash content of oil was determined using a furnace. A 15g of oil was added in a burning cup. Next, the sample was put in a furnace. A furnace was set at a temperature of 500^{o}C for 1 hour. After burning the residue sample was weighted and ash content was calculated.

3.2.1.5. Biodiesel production

3.2.1.5.1. Biodiesel production experimental design

To produce biodiesel the experimental design was done by two parts.

A). Part one: This part was done using four levels for each three factors independently, varying one factor while keeping other two factors constant. The reaction temperatures were 35^{o}C, 55^{o}C, 65^{o}C and 75^{o}C at 1% (w/w) of NaOH and 8:1 molar ratio of alcohol to oil. The catalyst amounts were 0.25% (w/w), 0.5% (w/w), 1% (w/w) and 2% (w/w) at a temperature of 55^{o}C and 8:1 molar ratio of alcohol to oil. The alcohol oil molar ratios were 6:1, 8:1, 10:1 and 12:1 at 55^{o}C and1% (w/w) of NaOH catalyst. The reaction time and mixing rate were constant at 2 hours and 300 rpm, respectively. This experimental design was used to determine the effect of each factor on yield. The design arrangement is given in Annex 3 (Table 0.1).

B). Part two: In this part two levels and two replicas were considered for full factorial experimental design. For "m" levels, "n" factors and "k" replicas, the experimental design that needs the number of experimental run is equal to $k\times m^n$ [30]. In this research "m" =2, "n" = 3 and "k" = 2. Therefore, for two levels, three factors and three replicas, the experimental design are equal to $k\times m^n=2\times 2^3=16$. The three factors at two levels were considered at constant reaction time of 2 hours, at atmospheric pressure and at constant mixing rate of 300 rpm. The temperatures were 55^{o}C and 65^{o}C; the amounts of catalyst were 0.5%w/w and 1 %w/w of oil and the molar ratios of alcohol to oil values were 6:1 and 8:1. The detail design arrangement is shown in Annex 3 (Table 0.2).

From Table 2.3, average molecular mass of jatropha oil (triglyceride) is 874g/mol. Therefore, 1mole of oil is 874g and a molecular mass of ethanol is 46g/mol and 3moles of ethanol is 138g. The density of oil was 0.910g/ml and that of anhydrous ethanol (99.4%w/w) 0.8g/ml.

Therefore, from stoichiometry equation (2.6), for 874g of oil 138g of ethanol alcohol was needed.

$$\text{Volume of substance} = \frac{\text{mass of substance}}{\text{density of substaance}} \qquad (3.1)$$

$$\text{Volume of oil} = \frac{\text{mass of oil}}{\text{density of oil}} = \frac{874\text{g}}{0.91\text{g/ml}} = 960\text{ml}$$

$$\text{Volume of ethanol} = \frac{\text{mass of ethanol}}{\text{density of ethanol}} = \frac{138\text{g}}{0.80\text{g/ml}} = 172.5\text{ml}$$

From the above calculations, for 960 ml of oil 172.5 ml ethanol was needed for transesterification reaction. Hence, 70 ml of oil needed 12.6 ml of ethanol for molar ratio of alcohol to oil of 3:1. For 100% excess ethanol (molar ratio of alcohol to oil is 6:1) and 167 % excess (molar ratio of alcohol to oil is 8:1), 70 ml of oil needed 25 ml and 34 ml of ethanol, respectively. The amounts of alkali catalyst 0.5% (w/w) of oil and 1% (w/w) of oil were taken. Thus, 70 ml (64g) of oil needed 0.32g and 0.64g of sodium hydroxide alkali catalyst, respectively.

3.2.1.5.2. Biodiesel production experimental procedures

Transesterification reactions were carried out in a 500ml glass reactor, provided with a thermostat, mechanical stirring and condensation system as shown in Figure 3.7. The experimental procedures for biodiesel production and separation were based on [16, 26, 31]. The required amounts of oil, ethanol and alkali catalyst were measured. An alkoxide solution was prepared from ethanol and alkali catalyst. The oil was heated up to the required temperature. An alkoxide solution and the oil were introduced into the reaction vessel and mixed vigorously during the reaction.

After the reaction, the biodiesel was separated from the glycerol using a centrifuge. After that, the excess alcohol was recovered by rotary evaporator. The pH of separated biodiesel was measured and the excess catalyst was neutralized by a tannic acid before the evaporation. The biodiesel was washed by warm water at 55^{o}C to remove the remaining alcohol, soap and trace alkali catalyst until its pH value was neutral. Then, the washed biodiesel was dried at a temperature of 105^{o}C using an oven dryer for 2 hours.

3.2.1.6. Analysis of the factors effect on biodiesel yield

The effects of temperature, amount of catalyst and molar ratio of alcohol to oil for one factor and four levels experimental design result were analyzed using Microsoft Office Excel. The effects of temperature, amount of catalyst, molar ratio of alcohol to oil and their interaction for two levels full factorial experimental design results were determined. Experimental design software was used to determine the factors and their interaction effects on biodiesel yield. The analysis methods of parameters standardized effects were based on procedure given in [30]. The design method to determine the effect of the factors alone and their interaction is shown in Table3.2**.**

Table 3.2: Design for analysis of the factors effect for two levels.

Experiment number	Design conditions							Operating conditions		
	A	B	C	AB	AC	BC	ABC	A (^{o}C)	B (g)	C (ml)
2	-1	+1	+1	-1	-1	+1	-1	55	0.64	34
4	+1	-1	-1	-1	-1	+1	+1	65	0.32	25
5	+1	+1	+1	+1	+1	+1	+1	65	0.64	34
8	-1	-1	-1	+1	+1	+1	-1	55	0.32	25
10	+1	+1	-1	+1	-1	-1	-1	65	0.64	25
11	+1	-1	+1	-1	+1	-1	-1	65	0.32	34
14	-1	+1	-1	-1	+1	-1	+1	55	0.64	25
15	-1	-1	+1	+1	-1	-1	+1	55	0.32	34

where:

+1 and -1 are the higher and lower levels, respectively

A, B and C are the temperature, catalyst and alcohol, respectively

AB is the interaction of reaction temperature and catalyst amount

ABC is the interaction of temperature, catalyst amount and alcohol

AC is the interaction of reaction temperature and ethanol alcohol

BC is the interaction of catalyst amount and ethanol alcohol

Σ is the Summation.

The effect of parameters and their interaction can be determined using sum square method and standardized method. Both methods are used to compare and identify which parameter or their interaction effects on biodiesel yield. However, due to simplicity for analysis standardized method was used.

$$\text{Effect of X} = \frac{\Sigma Y \text{ at} X^{+} - \Sigma Y \text{ at } X^{-}}{2^{k-1}} \quad (3.2)$$

where:

"X" is the parameter represents A, B, C, AB, AC, BC and ABC. The number of factors "k" is 3.

Regression equation model is used to formulate mathematical equations from experiment results. The regression model can be linear, quadratic or polynomial. The choice of regression model is based on the agreement of results from regression equation with the actual experiment results.

$$Y_r = b_0 + b_1A + b_2B + b_3C + b_{12}AB + b_{13}AC + b_{23}BC + b_{123}AB \quad (3.3)$$

$$b_0 = \frac{\Sigma Y_{total}}{N} \quad (3.4)$$

$$b_i = \frac{\text{Effect of X}}{2} \quad (3.5)$$

where:

i=1, 2, 3,12,13,23123; b_0,b_1,b_2,b_3,b_{12},b_{13},b_{23} and b_{123} are regression coefficients

Y_r is the biodiesel yield from linear regression model equation

3.2.1.7. Determination of biodiesel physicochemical properties

Acid value, saponification value, density, kinematic viscosity, flash point, moisture content and ash content were determined using the procedures those used for the oil.

4. RESULTS AND DISCUSSIONS

4.1. Extracted Oil

Oil was extracted using hexane solvent and mechanical press. Solvent extraction was difficult to extract the required quantity of oil since hexane cost was very expensive. The required quantity of oil was extracted using mechanical pressing. However, the extraction efficiency of mechanical pressing was lower. The oil was degummed and neutralized to remove impurities and free fatty acid for biodiesel production.

4.2. Physicochemical Properties of the Oil

Acid value and saponification value tests were performed based on experimental procedures given by [17, 18, 29].

4.2.1. Acid value of oil

For acid value test, the mixture was changed to pink when 1.4ml of titration volume was added. The titration results are shown in Table 4.1.

Table 4.1: Acid value test results.

Acid value test run	Titration volume, ml	Color change
Experiment 1	1.5	Gray to pink
Experiment 2	1.3	Gray to pink
Experiment 3	1.4	Gray to pink
Experiment 4	1.3	Gray to pink
Average value	1.375≈1.4	

The acid value was determined from equation (2.1)

$$\text{Acid value(AV), mgKOH/g} = \frac{\text{N} \times \text{M}_\text{m} \times \text{TV}}{\text{M}_\text{s}}$$

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

M_m=56g/mol

M_s=2g
N of KOH =0.1mol/l

TV=1.4ml

$$\text{Acid value(AV)} = \frac{0.1\text{mol/l} \times 56\text{g/mol} \times 1.4 \times 10^{-3}\text{l}}{2\text{g}} = 3.92\text{mgKOH/g}$$

Hence, the acid value was 3.92 mg KOH/g of sample oil.

The amount of free fatty acid in the sample was calculated from acid value using equation (2.2) value as follows.

$$\text{Free fatty acid, mg/g} = \frac{1}{2}(\text{acid value}) = \frac{1}{2}(3.92) = 1.96$$

Thus, the amount of free fatty acid in the oil was 1.96mg/g of oil.

4.2.2. Saponification value of oil

The blank level changed from pink to colorless for 16.7ml titration volume. The color in the saponification test changed from pink color to red. The titration results for saponification test are shown in Table 4.2.

Table 4.2: Saponification value test results.

Saponification value test run	Titration volume, ml	Color change
Experiment 1	3.0	Pink to red
Experiment 2	4.1	Pink to red
Experiment 3	3.5	Pink to red
Experiment 4	3.7	Pink to red
Average value	3.6	

A color in the saponification test changed from pink to red at average titration volume of 3.6 ml.

From equation (2.5), the saponification value was calculated as follows;

$$\text{Saponification value, mgKOH/g} = \frac{(\text{BLTV} - \text{TV}) \times \text{TF} \times \text{C}_\text{m}}{\text{M}_\text{s}}$$

where:

BLTV is the blank level titration volume=16.7ml

C_m is the mass concentration = 0.5mol/l×56g/mol=28gKOH/ml

M_s is the mass of sample =2g

TF is the reagent factor of HCl =1.006

TV is the titration volume=3.6ml

Substituting the above values in equation (2.5) gives the saponification value.

$$\text{Saponification value} = \frac{28 \times 1.006(16.7 - 3.6)}{2} = 184.5\text{mgKOH/g}$$

Therefore, the saponification value of the oil was 184.5mgKOH/g of oil.

4.2.3. Density of oil

The specific gravity of oil was 0.910. The specific gravity of oil was multiplied by density of water which gives the oil density.

$$\text{Density of oil} = \text{specific gravity of oil} \times \text{density of water} \qquad (4.1)$$

Substituting the values in equation (4.1) 1000kg/m^3 for water density and 0.91 for oil specific gravity gives oil density.

$$\text{Density of oil} = 0.91 \times 1000\text{kg/m}^3 = 910\text{kg/m}^3$$

Thus, the density of oil was 910kg/m^3.

4.2.4. Kinematic viscosity of oil

The dynamic viscosity of oil was 35.8m.Pa.s at a temperature of 40°C.

$$\text{Kinematic viscosity of oil} = \frac{\text{dynamic viscosity of oil}}{\text{density of oil}} \qquad (4.2)$$

Substituting the value of 910 kg/m^3 for density of oil, and the value of 35.8 m.Pa.s for dynamic viscosity of oil in equation (4.2) gives kinematic viscosity of oil.

Dynamic viscosity of oil=35.8mPa.s=35.8×10^{-3} kg/m.s

Density of oil=910 kg/m^3

$$\text{Kinematic viscosity of oil} = \frac{35.8 \times 10^{-3}\text{kg/m. s}}{910\text{kg/m}^3} = 39.4\ \text{mm}^2/\text{s}$$

The kinematic viscosity of the oil was 39.4 mm^2/s.

4.2.5. Flash point, moisture content and ash content of oil

4.2.5.1. Flash point

Form open cup method test, the flash point of the oil was 225°C. This temperature indicates that the oil is suitable for handling and storage since its high flash point resists spontaneous combustion.

4.2.5.2. Moisture content

$$\text{Moisture content\% (w/w)} = \left(\frac{\text{initial mass} - \text{final mass}}{\text{initial mass}}\right) \times 100\% \qquad (4.3)$$

Initial mass of oil=35g

Final mass of oil=34.971g

Substituting the above values in equation (4.3) gives the moisture content of oil.

$$\text{Moisture content\% (w/w)} = \left(\frac{35\text{g} - 34.971\text{g}}{35\text{g}}\right) \times 100\% = 0.083$$

Hence, the moisture content of oil was 0.083% (w/w). This lower value of oil moisture helps to prevent formation of soap during transesterification reaction which causes difficulty of glycerol separation and reduction of biodiesel yield.

4.2.5.3. Ash content

$$\text{Ash content \% (w/w)} = \frac{\text{final mass of sample after burnt}}{\text{initial mass of sample}} \times 100\% \quad (4.4)$$

Initial mass of sample=15 g

Final mass of sample=0.0032g

Substituting the above values in equation (4.4) gives the ash content of oil.

$$\text{Ash content \% (w/w)} = \frac{0.0032\text{g}}{15\text{g}} \times 100\% = 0.021$$

The ash content of oil was 0.021% (w/w). The lower ash content of oil indicates that the oil was refined; it was suitable for biodiesel production.

The physical and chemical properties of oil are summarized in Table 4.3.

Table 4.3: Physicochemical properties of the oil.

Physicochemical parameters	Values for oil
Density at 20^{o}C (kg/m^{3})	910
Kinematics viscosity at 40^{o}C (mm^{2}/s)	39.4
Acid value (mgKOH/g)	3.92
Free fatty acid (mg/g)	1.96
Saponification value (mgKOH/g)	184.5
Flash point (^{o}C)	225
Moisture content % (w/w)	0.083
Ash content % (w/w)	0.021

4.3. Biodiesel Production and Yield Analysis for One Factor Experimental Design

In this part the results were obtained by changing one factor at four levels while keeping the other two factors at constant value. The detail of experimental design is shown in Annex 3 (Table 0.1).

4.3.1. Effect of reaction temperature on biodiesel production

The effect of temperature at 35°C, 55°C, 65°C and 75°C on biodiesel yield for 1% (w/w) catalyst, 70 ml oil feed and 8:1 ratio of alcohol to oil is shown in Table 4.4 and Figure 4.1. The reaction time and mixing rate were 2 hours and 300 rpm, respectively.

Table 4.4: Effect of reaction temperature on biodiesel production.

Experiment number	1a	1b	1c	1d
Temperature(°C)	35	55	65	75
Biodiesel production volume (ml)	48	61	56	37

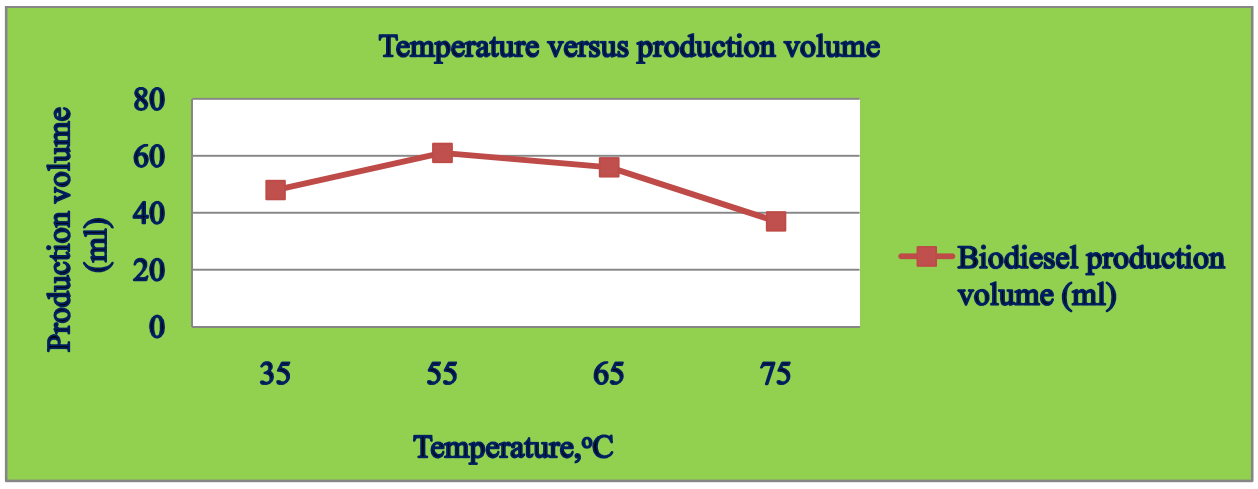


Figure 4.1: Effect of temperature on biodiesel production.

The biodiesel yield was directly related with reaction temperature up to 55°C and inversely related above 55°C. As the reaction temperature was increased from 35°C to 55°C, the biodiesel yield also increased. However, as the temperature further increased from 55°C to 75°C, the yield decreased.

The lowest yield obtained at 75°C was due to formation of a large quantity of the emulsion. Therefore, from four levels of temperature the maximum and minimum yield was obtained at a temperature of 55°C and 75°C, respectively.

4.3.2. Effect of catalyst amount on biodiesel production

The effect of catalyst at 0.25% (w/w), 0.5% (w/w), 1% (w/w) and 2% (w/w) NaOH on biodiesel production at 55°C temperature, 70 ml oil feed and 8:1 ratio of alcohol to oil is shown in Table 4.5 and Figure 4.2. The reaction time and mixing rate were 2 hours and 300 rpm, respectively.

Table 4.5: Effect of amount of catalyst on biodiesel production.

Experiment number	2a	2b	2c	2d
Amount of catalyst (%w/w)	0.25	0.5	1	2
Biodiesel production volume, ml	36	56	61	27

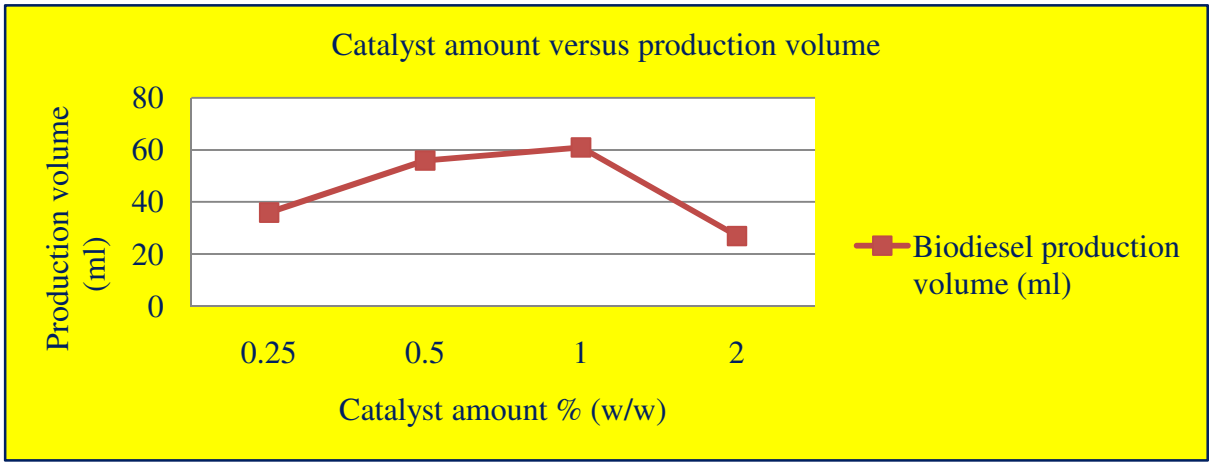


Figure 4.2: Effect of NaOH catalyst amount on biodiesel production.

The output product was directly related with the input catalyst from 0.25% (w/w) to 1% (w/w) and inversely related from 1%w/w to 2% (w/w). As the amount of catalyst was increased from 0.25% (w/w) to 1% (w/w), the yield also increased from 36ml to 61ml. But further addition of catalyst amount reduced the yield due to formation of the soap and the emulsion.

The maximum yield was achieved for a catalyst amount of 1% (w/w) where as the minimum yield was obtained at catalyst amount of 2% (w/w).

4.3.3. Effect of molar ratio of alcohol to oil on biodiesel production

The effect of molar ratio of alcohol to oil of 6:1, 8:1, 10:1 and 12:1 for 1% (w/w) catalyst, 70ml oil feed and at a temperature of 55^{o}C on biodiesel production is shown in Table 4.6 and Figure 4.3 . The reaction time and mixing rate were 2 hours and 300 rpm, respectively.

Table 4.6: Effect of alcohol on biodiesel production.

Experiment number	3a	3b	3c	3d
Molar ratio of alcohol to oil	6:1	8:1	10:1	12:1
Biodiesel yield, ml	51	61	60	57

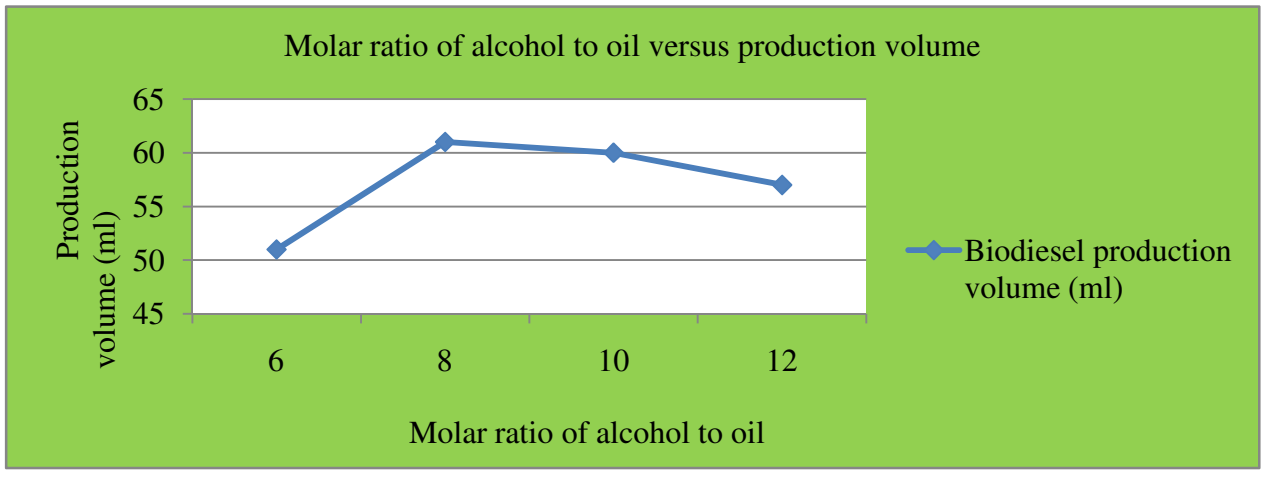


Figure 4.3: Effect of molar ratio of alcohol to oil on biodiesel production.

When the amount of input alcohol was increased from 6:1 to 8:1, the product increased from 51ml to 61ml. This means that the effect of amount of alcohol required was directly related to output yield. However, when the molar ratio of alcohol to oil was increased from 8:1 to 12:1, the yield decreased from 61ml to 57ml due to formation of the emulsion that crystallizes glycerol during separation processes. The maximum yield was obtained at a molar ratio of alcohol to oil 8:1 whereas the minimum yield was observed at a molar ratio of 6:1. Therefore, addition of excess alcohol greater than 8:1 did not increase the product yield.

4.4. Biodiesel Yield Analysis for Two Levels Full Factorial Experimental Design

The biodiesel yield is shown in Table 4.7 for two levels and two replicas full factorial design.

$$\text{Biodiesel yield \% (w/w)} = \frac{\text{mass of produced biodiesel}}{\text{mass of feed oil}} \times 100\% \qquad (4.5)$$

Table 4.7: Biodiesel yield for two levels and two replicas full factorial design.

Experiment numbers	Temperature (^{o}C)	Catalyst (g)	Alcohol (ml)	Oil feed (ml)	Biodiesel (ml)	Density of yield (g/ml)	Biodiesel yield (Y)% (w/w)
1	65	0.64	25	70	49	0.87	66.9
2	55	0.64	34	70	61	0.88	84.3
3	55	0.32	34	70	50	0.86	70.5
4	65	0.32	25	70	47	0.87	64.2
5	65	0.64	34	70	56	0.87	76.5
6	55	0.64	25	70	52	0.86	70.2
7	65	0.32	34	70	55	0.87	72.1
8	55	0.32	25	70	51	0.86	68.8
9	55	0.64	34	70	60	0.88	83.4
10	65	0.64	25	70	51	0.88	70.4
11	65	0.32	34	70	52	0.88	71.8
12	55	0.32	25	70	53	0.86	71.6
13	65	0.64	34	70	54	0.88	74.6
14	55	0.64	25	70	51	0.86	68.9
15	55	0.32	34	70	56	0.86	71.6
16	65	0.32	25	70	48	0.87	65.6

From Table 4.7, the maximum yield was 84.3 % (w/w), at experiment number 2, whereas the minimum yield was 64.2% (w/w), at experiment number 4. However, since the experiment was done with two replicas, another maximum and minimum yield was 83.4% (w/w) and 65.6% (w/w) at experiment numbers of 9 and 16, respectively. Experiment number 2 and 9; 4 and 16 are replicas. Therefore, the average maximum and minimum yield was 83.6% (w/w) and 64.9% (w/w), respectively.

The biodiesel and the glycerol are shown below in Figure 4.4 and 4.5, respectively.

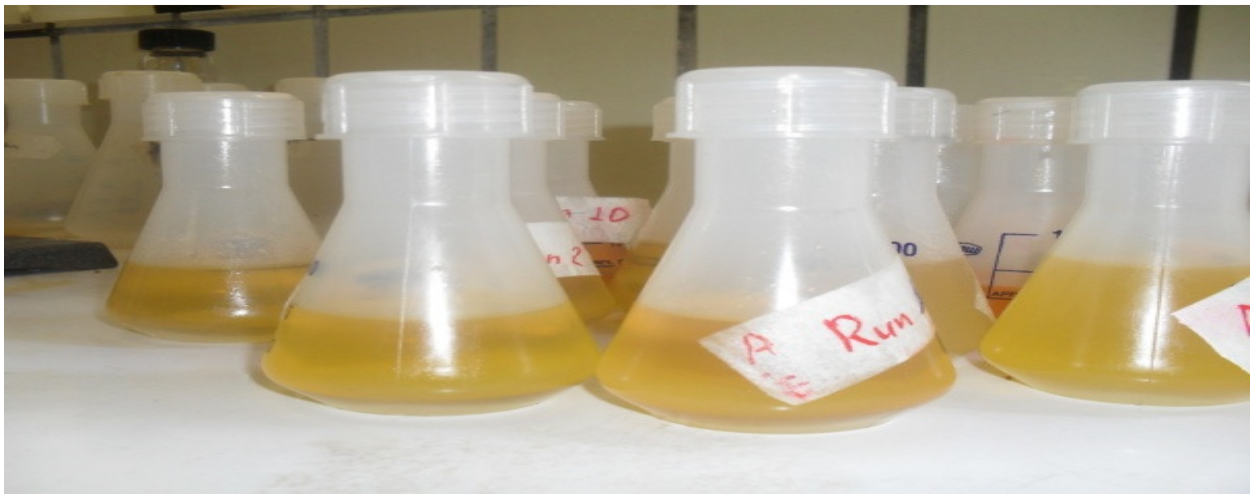


Figure 4.4: Biodiesel.

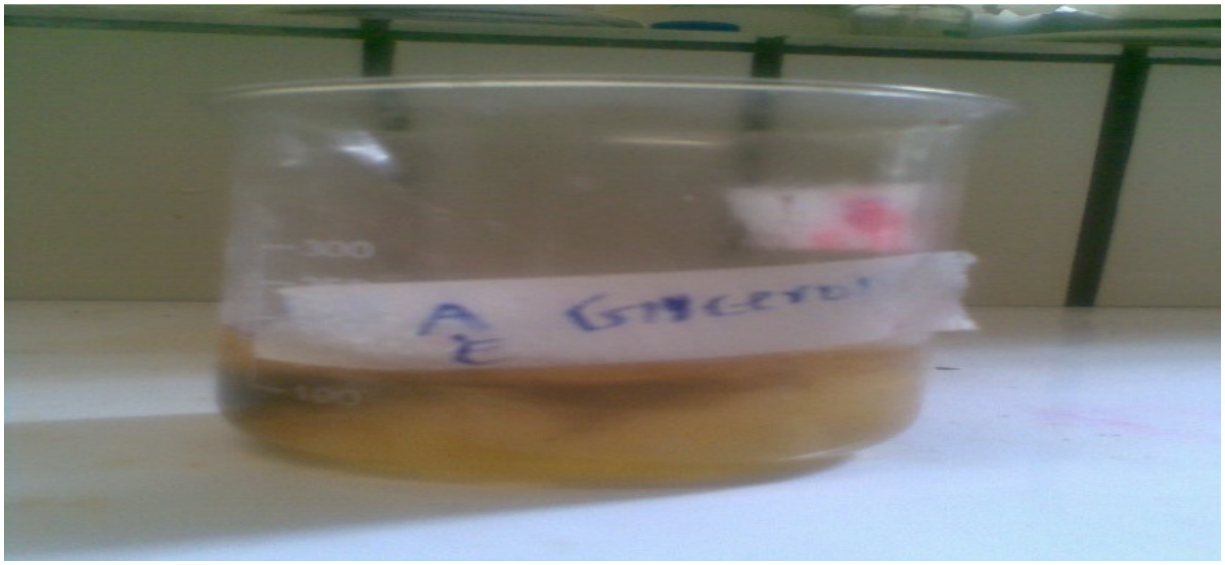


Figure 4.5: Glycerol.

The biodiesel yield variations for 16 experiment number results from Table 4.7 are shown below in Figure 4.6. The graph was used to observe the variation of biodiesel yield when the operating parameters were changed for each experiment.

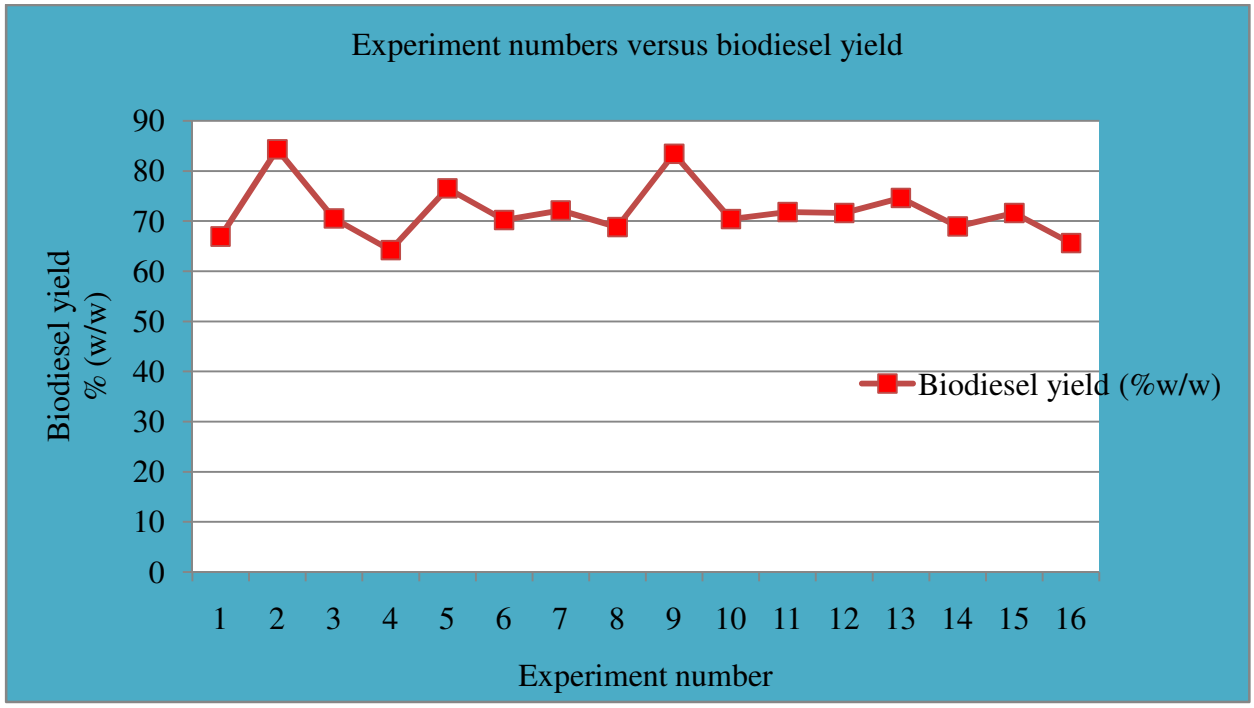


Figure 4.6: Biodiesel yield variation for experiment number.

The experiment numbers corresponding operating parameters are given in Table4.7 or Annex 3 (Table 0.2)

From Table 4.**7** and Figure 4.6, it can be observed that the maximum biodiesel yield was achieved at a temperature of 55^{o}C, 1% (w/w) catalyst and 8:1 molar ratio of alcohol to oil, experimental numbers of 2 and 9. The minimum yield was obtained at a temperature of 65^{o}C, 0.5% (w/w) catalyst and 6:1 molar ratio of alcohol to oil, experimental numbers of 4 and 16.

Note: Experiment number **2 and 9**, **4 and 16** are **replicas**. The corresponding operating parameters for each experiment number are given in Table 4.7.

4.4.1. Analysis of the parameters standardized effect on biodiesel yield

The analysis methods of parameters standardized effects were based on procedure given in [30]. The biodiesel yield and analysis method are shown in Table 4.8.

Table 4.8: Analysis of the three factors and two levels standardized effect.

Experiment number	Design conditions							Operating conditions			Average biodiesel yield
	A	B	C	AB	AC	BC	ABC	A (^{o}C)	B (g)	C (ml)	Y, %(w/w)
2	-1	+1	+1	-1	-1	+1	-1	55	0.64	34	83.6
4	+1	-1	-1	-1	-1	+1	+1	65	0.32	25	64.9
5	+1	+1	+1	+1	+1	+1	+1	65	0.64	34	75.6
8	-1	-1	-1	+1	+1	+1	-1	55	0.32	25	70.2
10	+1	+1	-1	+1	-1	-1	-1	65	0.64	25	68.7
11	+1	-1	+1	-1	+1	-1	-1	65	0.32	34	72.0
14	-1	+1	-1	-1	+1	-1	+1	55	0.64	25	69.6
15	-1	-1	+1	+1	-1	-1	+1	55	0.32	34	71.0

where:

+1 and -1 are the higher and lower levels, respectively

A, B and C are the temperature, catalyst and alcohol, respectively

AB is the interaction of reaction temperature and catalyst amount

ABC is the interaction of temperature, catalyst amount and alcohol

AC is the interaction of reaction temperature and ethanol alcohol

BC is the interaction of catalyst amount and ethanol alcohol

Σ is the Summation

Y is the biodiesel yield for actual experiment

Y_r is the biodiesel yield obtained from regression equation

4.4.1.1. Analysis of each parameter and their interaction effects

"X" is the factor parameter represents A, B, C, AB, AC, BC and ABC. The number of factors "k" is 3. The standardized effect of each factor and their interaction were determined.

Substituting the yield values from Table 4.8 and equation (3.2) gives the standardized effect of each factor and their interaction during transesterification reaction.

$$\text{Effect of X} = \frac{\Sigma \text{Y at} X^{+} - \Sigma \text{Y at } X^{-}}{2^{k-1}}$$

$$\text{Effect of A} = \frac{\Sigma \text{Y at} A^{+} - \Sigma \text{Y at} A^{-}}{2^{k-1}}$$

$$\text{Effect of A} = \frac{(64.9 + 75.6 + 68.7 + 72) - (83.6 + 70.2 + 69.6 + 71)}{2^{3-1}} = -3.3$$

$$\text{Effect of B} = \frac{\Sigma \text{Y at} B^{+} - \Sigma \text{Y at} B^{-}}{2^{k-1}}$$

$$\text{Effect of B} = \frac{(83.6 + 75.6 + 68.7 + 69.6) - (64.9 + 70.2 + 72 + 71)}{2^{3-1}} = 4.85$$

$$\text{Effect of C} = \frac{\Sigma \text{Y at } C^{+} - \Sigma \text{Y at} C^{-}}{2^{k-1}}$$

$$\text{Effect of C} = \frac{(83.6 + 75.6 + 72 + 71) - (64.9 + 70.2 + 68.7 + 69.6)}{2^{3-1}} = 7.2$$

$$\text{Effect of AB} = \frac{\Sigma \text{Y at} AB^{+} - \Sigma \text{Y at} AB^{-}}{2^{k-1}}$$

$$\text{Effect of AB} = \frac{(75.6 + 70.2 + 68.7 + 71) - (83.6 + 64.9 + 72 + 69.6)}{2^{3-1}} = -1.15$$

$$\text{Effect of AC} = \frac{\Sigma \text{Y at} AC^{+} - \Sigma \text{Y at} AC^{-}}{2^{k-1}}$$

$$\text{Effect of} AC = \frac{(75.6 + 70.2 + 72 + 69.6) - (83.6 + 64.9 + 68.7 + 71)}{2^{3-1}} = -0.2$$

$$\text{Effect of BC} = \frac{\Sigma \text{Y at BC}^{+} - \Sigma \text{Y at BC}^{-}}{2^{k-1}}$$

$$\text{Effect of BC} = \frac{(83.6 + 64.9 + 75.6 + 70.2) - (68.7 + 72 + 69.6 + 71)}{2^{3-1}} = 3.25$$

$$\text{Effect of ABC} = \frac{\Sigma \text{Y at} ABC^{+} - \Sigma \text{Y at} ABC^{-}}{2^{k-1}}$$

$$\text{Effect of} ABC = \frac{(64.9 + 75.6 + 69.6 + 71) - (83.6 + 70.2 + 68.7 + 72)}{2^{3-1}} = -3.35$$

The effects of each factor and their interaction are summarized in Table 4.9 and Figure 4.7.

Table 4.9: Summary of the three factors and their interaction effects.

Factors and their interactions	Standardized effects of the factors and their interaction
A	-3.3
B	4.85
C	7.2
AB	-1.15
AC	-0.2
BC	3.25
ABC	-3.35

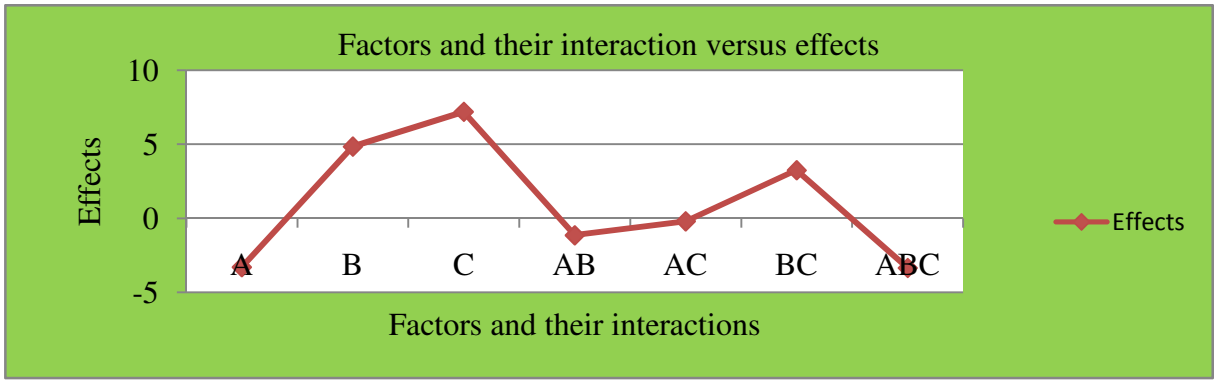


Figure 4.7: Effect of the factors and their interactions.

Among the three factors (A, B and C), the highest and the lowest effect on biodiesel yield was observed by alcohol (C) and reaction temperature (A) respectively. The negative values indicated that higher yield was obtained at lower level of factors value and their interactions whereas the positive values indicated that higher yield was obtained at higher levels of factors value and their interactions during transesterification reaction. Among factors interaction, the effect of interaction of temperature and alcohol (AC) was the lowest on yield although slightly higher yield was obtained at lower levels interaction. However, the effect of the three factors interaction (ABC) was the highest among interaction effects. Hence, highest effect was observed due alcohol and lowest effect was observed due to interaction of reaction temperature and alcohol.

4.4.1.2. Linear regression equation model

A linear regression was used to formulate equation to represent the factors effect on the biodiesel yield. The linear regression model equation was based on the coded variables. From equations (3.3-3.5), the linear regression equation coefficients and final regression equation was determined as follows.

$$Y_r = b_0 + b_1A + b_2B + b_3C + b_{12}AB + b_{13}AC + b_{23}BC + b_{123}AB$$

$$b_0 = \frac{\Sigma Y_{total}}{N}$$

$$b_i = \frac{\text{Effect of X}}{2}$$

where:

i=1,2,3,12,13,23 and 123

b_0, b_1, b_2, b_3, b_{12}, b_{13}, b_{23} and b_{123} are the linear regression coefficients.

From Table 4.9 and equations (3.2 – 3.5) the regression coefficients were calculated as follows;

$$b_1 = \frac{\text{Effect of A}}{2} = \frac{-3.3}{2} = -1.65$$

$$b_2 = \frac{\text{Effect of B}}{2} = \frac{4.85}{2} = 2.425$$

$$b_3 = \frac{\text{Effect of C}}{2} = \frac{7.2}{2} = 3.6$$

$$b_{12} = \frac{\text{Effect of AB}}{2} = \frac{-1.15}{2} = -0.575$$

$$b_{13} = \frac{\text{Effect of AC}}{2} = \frac{-0.2}{2} = -0.1$$

$$b_{23} = \frac{\text{Effect of BC}}{2} = \frac{3.25}{2} = 1.625$$

$$b_{123} = \frac{\text{Effect of ABC}}{2} = \frac{-3.35}{2} = -1.675$$

Therefore, from equation (4.7), the regression equation was written in the form of coded variables as follows;

$$Y_r = 71.95 - 1.65A + 2.245B + 3.6C - 0.575AB - 0.1AC + 1.625BC - 1.675ABC$$

The linear regression equation in terms of actual factors is given in Annex 4 analysis of variance software application. Thus, equation (3.3) become as follows;

Biodiesel yield=461.7-6.47×temperature-843.7×catalyst-
13.5×Alcohol+13.18×temperature
×catalyst+0.22×temperature×Alcohol+30.64×catalyst×Alcohol-
0.472×temperature×catalyst×Alcohol

The actual yield and yield from model equation are shown in Table 4.10.

Table 4.10: Actual yield and yield from model equation.

Experiment number	Actual biodiesel yield, Y % (w/w)	Yield from model equation, Y_r % (w/w)	Difference =Y-Y_r % (w/w)
2	83.6	83.42	0.18
4	64.9	65.08	-0.18
5	75.6	75.42	0.18
8	70.2	70.38	-0.18
10	68.7	68.52	0.18
11	72.0	72.18	-0.18
14	69.6	69.42	0.18
15	71.0	71.18	-0.18

The yield from a linear regression model equation fitted the data of actual yield since their difference was less than 0.2 % (w/w). The three factors alone had linear response on biodiesel yield between higher (+1) and lower (-1) levels and their interaction effects were surface response as shown in Annex 4 (Figure 0.1- 0.6). The regression model equation represented only the factors and interaction effects between higher and lower levels. Therefore, a linear regression model was appropriate to determine the three factors and their interaction effects on biodiesel yield between higher (+1) and lower levels (-1).

4.5. Biodiesel Physicochemical Properties

For physicochemical properties analysis eight experimental numbers from two levels full factorial design at average value were considered. The experiment numbers are 2,4,5,8,10,11,14 and15 as shown in Table 4.11.

Table 4.11: Biodiesel yield used for physicochemical property analysis.

Experiment number	Temperature (^{o}C)	Catalyst (g)	Alcohol (ml)	Average yield % (w/w)
2	55	0.64	34	83.6
4	65	0.32	25	64.9
5	65	0.64	34	75.6
8	55	0.32	25	70.2
10	65	0.64	25	68.7
11	65	0.32	34	72.0
14	55	0.64	25	69.6
15	55	0.32	34	71.0

4.5.1. Acid value of biodiesel

The acid value of biodiesel was determined by a titration method. The experimental procedures were identical to those used in the oil acid value in Section 3.2.1.4.1. The biodiesel acid value for each experiment number is given in Table 4.12.

From equation (2.1);

$$\text{Acid value(AV), mgKOH/g} = \frac{N \times M_m \times TV}{M_s}$$

Where:

M_m =56g/mol

M_s=2g

N= 0.1mol/L of KOH

TV is titration volume, ml

Substituting the values in equation (2.1) gives the acid value of biodiesel.

TV is titration volume, ml

Table 4.12: Biodiesel acid values.

Experiment number	Temperature (^{o}C)	Catalyst (g)	Alcohol (ml)	TV (ml)	Acid value (mgKOH/g)
2	55	0.64	34	0.24	0.67
4	65	0.32	25	0.26	0.74
5	65	0.64	34	0.27	0.76
8	55	0.32	25	0.20	0.56
10	65	0.64	25	0.25	0.70
11	65	0.32	34	0.20	0.56
14	55	0.64	25	0.25	0.70
15	55	0.32	34	0.26	0.72

The acid value of the biodiesel varied from 0.56 mgKOH/g to 0.76 mgKOH/g. The acid value is used to determine the amount of free fatty acid content in biodiesel. The lower acid value indicates that the quantity of free fatty acid in the biodiesel is also lower.

4.5.2. Saponification values of biodiesel

Saponification value of biodiesel was investigated by a titration. The procedures were the same as those for oil saponification determination in Section 3.2.1.4.2. The saponification values of the biodiesel are shown in Table 4.13.

From equation (2.2);

$$\text{Saponification value, mgKOH/g} = \frac{(\text{BLTV} - \text{TV}) \times \text{TF} \times \text{C}_\text{m}}{\text{M}_\text{s}}$$

where:

BLTV is the blank level titration volume = 22 ml

C_m =28g/L

M_s=2g biodiesel sample

TF=1.006

TV is the titration volume, ml

Substituting the above values in equation (2.2) gives the saponification values.

Table 4.13: Saponification values of the biodiesel.

Experiment number	Temperature (^oC)	Catalyst (g)	Alcohol (ml)	BLTV (ml)	TV (ml)	Saponification value (mgKOH/g)
2	55	0.64	34	22	13.6	118.2
4	65	0.32	25	22	13.2	123.6
5	65	0.64	34	22	13.7	116.2
8	55	0.32	25	22	13.5	119.4
10	65	0.64	25	22	13.3	122.6
11	65	0.32	34	22	13.2	124.5
14	55	0.64	25	22	13.4	121.6
15	55	0.32	34	22	13.8	115.5

The saponification value of the biodiesel was between 115.5 mgKOH/g and 124.5 mgKOH/g. Saponification value indicates that the quantity of biodiesel which changed to soap by KOH in the presence of water at high temperature. Higher saponification value of the product is lower in quality.

In addition to each saponification value test, the amount of residual soap in the biodiesel during the separation was also investigated. The sample mixture changed from gray to colorless where 15.2 ml of HCl titration volume (TV) was added.

$$\text{Residual soap } \%(\text{w/w}) = \frac{\text{TV} \times \text{N of HCl} \times \text{M}_\text{m} \times 100\%}{1000 \times \text{Mw}} \qquad (4.6)$$

where:

M_m is the molecular mass of sodium oleate=304.4g/mol

M_w is mass of sample waste water=26g

N is the normality of HCl=0.01mol/l

TV=15.2ml

Substituting the values in equation (4.10) gives the residual soap.

$$\text{Residual soap\% (w/w)} = \frac{15.2 \times 0.01 \times 304.4 \times 100\%}{1000 \times 26} = 0.18$$

Therefore, 0.18% (w/w) residual soap was left in the biodiesel during the glycerol separation which was determined only at maximum yield from its waste water which was collected when biodiesel was being washed.

4.5.3. Density and kinematic viscosity of biodiesel

Density and viscosity of biodiesel measuring procedures are the same as oil density and viscosity measuring procedures that were described in Sections 3.2.1.4.3 and 3.2.1.4.4.

The density and viscosity of biodiesel are given in Table 4.14.

$$\text{kinematics viscosity of oil} = \frac{\text{dynamic viscosity}}{\text{density}}$$

$1\text{m.Pa.s}=1\times10^{-3}\text{g/mm.s}$

where:

m.Pa.s: milli Pascal second

$1000\text{kg/m}^3=1\times10^{-3}\text{g/mm}^3$

$880\text{kg/m}^3=0.88\times10^{-3}\text{g/mm}^3$

Table 4.14: Density and viscosity of the biodiesel.

Experiment number	Temperature (^oC)	Catalyst (g)	Alcohol (ml)	Dynamic viscosity at 40^oC (m.Pa.s)	Average density (kg/m^3)	Kinematic viscosity (mm^2/s)
2	55	0.64	34	5.54	880	6.3
4	65	0.32	25	6.26	870	7.2
5	65	0.64	34	6.65	875	7.6
8	55	0.32	25	5.42	860	6.3
10	65	0.64	25	5.86	875	6.7
11	65	0.32	34	6.48	875	7.4
14	55	0.64	25	6.11	860	7.1
15	55	0.32	34	5.51	860	6.4

The measured density of the biodiesel was in between 860kg/m^3 and 880kg/m^3. The kinematic viscosity of biodiesel was between 6.3 mm^2/s and 7.6 mm^2/s. The density and kinematic viscosity of the oil was 910 kg/m^3 and 39.4 mm^2/s.

Thus, transesterification reaction reduced density and kinematic viscosity.

4.5.4. Flash point values of biodiesel

The flash point was measured using an opened cup method. The measuring procedures are the same as those used for the oil flash point in Section 3.2.1.4.5. The biodiesel flash point values are shown in Table 4.15**.**

Table 4.15: Biodiesel flash point values.

Experiment number	Temperature (^{o}C)	Catalyst (g)	Alcohol (ml)	Flash point (^{o}C)
2	55	0.64	34	145
4	65	0.32	25	153
5	65	0.64	34	165
8	55	0.32	25	163
10	65	0.64	25	165
11	65	0.32	34	158
14	55	0.64	25	168
15	55	0.32	34	175

The flash point of the biodiesel was from 145^{o}C to 175^{o}C. Flash point indicates the first temperature where biodiesel is ignited. Lower flash point fuels ignite spontaneously during handling, storage or transportation whereas higher flash fuels resist such problems [29]. From Table 4.15, high flash point values of the biodiesel were observed. Therefore, the flash point of the biodiesel is good for handling, storage or transportation.

4.5.5. Moisture and ash contents of biodiesel

The moisture and ash contents measuring experimental procedures for the biodiesel are the same as those used for the oil in Sections 3.2.1.4.6 and 3.2.1.4.7, respectively. The moisture and ash contents of the biodiesel are shown in Table 4.16.

From equations (4.3 and 4.4) the moisture and ash contents of the biodiesel were determined.

$$\text{Moisture content\% (w/w)} = \left(\frac{\text{initial mass} - \text{final mass}}{\text{initial mass}}\right) \times 100\%$$

$$\text{Ash content\% (w/w)} = \frac{\text{final mass of sample after burnt}}{\text{initial mass of sample}} \times 100\%$$

Table 4.16: Moisture and ash contents of the biodiesel.

Experiment numbers	Temperature (^oC)	Catalyst (g)	Alcohol (ml)	Moisture content %(w/w)	Ash content, %(w/w)
2	55	0.64	34	0.027	0.018
4	65	0.32	25	0.028	0.017
5	65	0.64	34	0.026	0.015
8	55	0.32	25	0.025	0.017
10	65	0.64	25	0.024	0.018
11	65	0.32	34	0.025	0.016
14	55	0.64	25	0.028	0.017
15	55	0.32	34	0.026	0.016

The moisture content of the biodiesel was from 0.024% (w/w) to 0.028% (w/w). Presence of high moisture content in the biodiesel causes further oxidation due to microbial growth during storage which reduces the shelf life and the product quality. The source of moisture in the biodiesel is highly related to wash water although there are other sources [29]. Here, the moisture content was obtained in the biodiesel as small quantity since biodiesel was dried in the oven at 105^oC for enough time.

Therefore, the biodiesel is suitable to keep the product quality and to store for long time.

The ash content of biodiesel was observed in the range of 0.015% (w/w) to 0.018% (w/w). Presence of high ash content indicates that the biodiesel has solid materials which came from catalysts during transesterification reaction or seed cake during oil extraction [29]. Since the feed oil was refined and the biodiesel was washed with gentle mixing, low ash content was obtained.

Therefore, the biodiesel was produced and washed in a suitable condition which was helped to reduce the ash content.

The physicochemical properties of produced biodiesel are summarized in Table 4.17.

Table 4.17: Physicochemical properties of the biodiesel.

Experiment numbers	2	4	5	8	10	11	14	15
Average biodiesel yield (%w/w)	83.6	64.9	75.6	70.2	68.7	72.0	69.6	71.0
Density (kg/m^3)	880	870	870	860	880	880	860	860
kinematics viscosity (mm^2/s)	6.3	7.2	7.6	6.3	6.7	7.4	7.1	6.4
Acid value (mgKOH/g)	0.67	0.74	0.76	0.56	0.70	0.56	0.70	0.72
Saponification value (mgKOH/g)	118.2	123.6	116.2	119.4	122.6	124.5	121.6	115.5
Flash point (^oC)	145	153	165	163	165	158	168	175
Moisture content %(w/w)	0.027	0.028	0.026	0.025	0.024	0.025	0.028	0.026
Ash content %(w/w)	0.018	0.017	0.015	0.017	0.018	0.016	0.017	0.016

At the maximum yield the density, kinematics viscosity, acid value, saponification value, flash point, moisture content and ash content were 880 kg/m^3, 6.3 mm^2/s, 0.67 mgKOH/g, 118.2 mgKOH/g, 145^oC, 0.027%(w/w) and 0.018%(w/w) whereas at the minimum yield the values were 870 kg/m^3, 7.2 mm^2/s, 0.74 mgKOH/g, 123.6 mgKOH/g 153^oC, 0.028% (w/w) and 0.018%(w/w), respectively.

The physical and chemical properties variations with experiments of the biodiesel are shown in Figure 4.8.

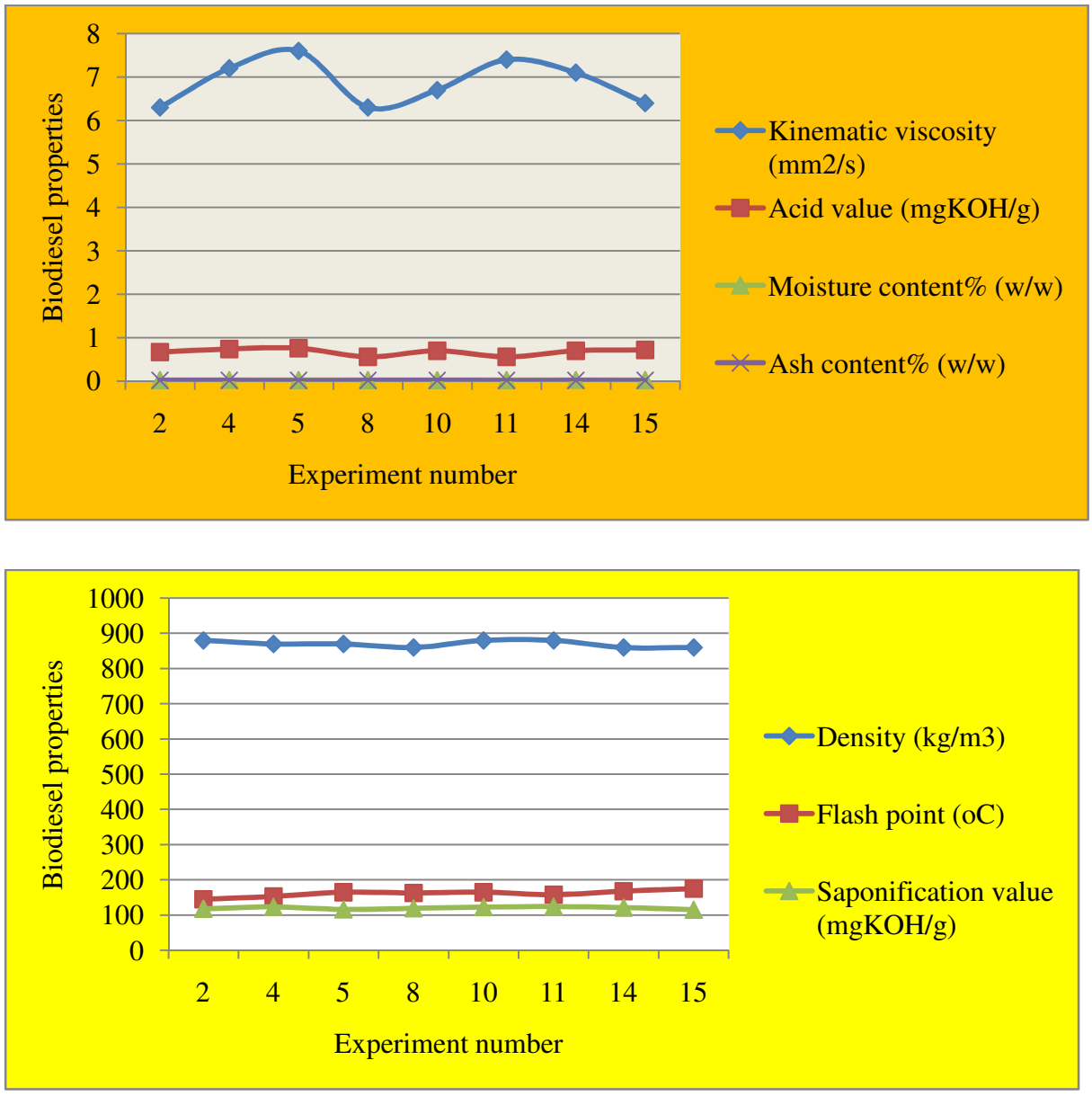


Figure 4.8: Biodiesel physicochemical properties variation with experiments.

Note: Experiment numbers corresponding operating parameters are given in Table 4.7. For example, experiment number 2 represents temperature of 55^{o}C, amount of catalyst1% (w/w) and 8:1 molar ratio of alcohol to oil.

4.6. Comparison of Biodiesel Physicochemical Properties against Standards

The comparisons of the biodiesel physicochemical properties against standard specifications are given in Table 4.18.

Table 4.18 : Comparison of biodiesel physicochemical properties against standards.

Biodiesel properties	Measured values	ASTM Standard
Density at 15^{o}C (kg/m^{3})	860-880	875-900
Kinematic viscosity at40^{o}C (mm^{2}/s)	6.3 - 7.6	1.9-6.0
Flash point (^{o}C)	145 – 175	≥130
Acid value (mgKOH/g)	0.56 - 0.76	≤0.8
Saponification value (mgKOH/g)	115.5-124.5	-
Moisture content % (w/w)	0.024 -0.028	<0.03
Ash content% (w/w)	0.015 - 0.018	<0.02
Iodine value (I_2g/100g)	-	≤120
Cetane number	-	≥47

The properties of biodiesel were under standard specification except kinematic viscosity which was slightly higher than the upper limit of ASTM. The iodine value and cetane number were not determined due to lack of reagent chemicals and equipment. This was the limitation of the work for comparison for these values against ASTM standards. The lower density fuel burns quickly and consumed immediately while higher density fuel burns for longer time. The lower flash point fuel is more favor for spontaneous ignition while it is transported or stored for longer time. However higher flash point fuel resists such problems [29]. Here, the flash point value of biodiesel was in the ASTM standard specification requirement. Therefore, the advantage of higher flash point of biodiesel like the ASTM standard value is suitable for handling, transportation and storage for longer time.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

Biodiesel was produced using ethanol alcohol and sodium hydroxide catalyst at constant reaction time of 2 hours, mixing rate of 300 rpm and at atmospheric pressure. The production of biodiesel was conducted by batch process system. The effects of a reaction temperature, amount of sodium hydroxide catalyst and molar ratio of alcohol to oil on biodiesel yield were determined.

From one factor and four levels experimental design results, when reaction temperature, catalyst amount and molar ratio of alcohol to oil were increased, the biodiesel yield increased until that reached at the maximum conditions. However, further addition of these operating factors during transesterification reaction, the yield was reduced due to formation of emulsion which complicated the separation process of biodiesel from glycerol.

In addition, from two level full factorial experimental design results, it was observed that the biodiesel yield has a linear response with temperature, catalyst and alcohol whereas the yield has a surface response with their interactions between higher (+1) and lower (-1) levels. Among the three parameters and their interactions, the highest effect on biodiesel yield was observed due to molar ratio of alcohol to oil whereas the effect of temperature and alcohol interaction was the lowest. The interaction of the three operating parameters effect was strongly observed on biodiesel yield.

The maximum biodiesel yield was obtained at a temperature of 55^{o}C, 1.0% (w/w) NaOH catalyst amount and for 8:1 molar ratio of alcohol to oil. However, the minimum biodiesel yield was obtained at a temperature of 65^{o}C, of 0.5% (w/w) NaOH catalyst amount and for 6:1 molar ratio of alcohol to oil. The average maximum biodiesel yield was 83.6% (w/w) whereas the average minimum yield was 64.9% (w/w) for two replicas.

The physicochemical properties of the biodiesel were within ASTM standard values except kinematic viscosity which was slightly higher than ASTM limit. Therefore, the produced biodiesel can be used as an engine fuel.

5.2. Recommendations

Oil was extracted using solvent extraction and mechanical pressing. However, solvent extraction was difficult due to high cost of hexane. Hence, mechanical pressing should be used.

Biodiesel was produced using ethanol alcohol and non-edible jatropha oil. These raw materials are available locally. Therefore, attention should be given to produce biodiesel which is used to substitute diesel fuel.

Biodiesel was produced using an alkali catalyzed transesterification reaction. However, production of biodiesel using ethanol and acid catalyzed, enzymatic catalyzed or heterogeneous catalyzed transesterification reaction should be investigated. In addition, biodiesel production was done in batch process system. However, production should be conducted in continuous process system.

The main processes for biodiesel production are chemical reaction of alcohol with oil and separation of the biodiesel from the glycerol. For ethanolysis reaction process, separation of the biodiesel from the glycerol using gravity settling only was difficult since some glycerol crystal was formed at room temperature. To separate the biodiesel before crystals was formed centrifuge and gravity settling was used in series while 0.01% (w/w) tannic acid was added to speed up separation. However, there was loss of product with the glycerol. Therefore, the separation process efficiency should be improved.

Since rotary evaporator and distillation were operated at atmospheric pressure, recovery of ethanol alcohol using a rotary evaporator or a distillation was used high temperature at boiling point of alcohol. During alcohol recovery using a rotary evaporator or a distillation the catalyst was neutralized before evaporation of alcohol otherwise further unwanted reaction was observed due to higher temperature over transesterification reaction. Therefore, to reduce the evaporation temperature vacuum flash evaporation should be used.

The glycerol property was not determined. However, glycerol has applications in cosmetics industry. Therefore, the property of glycerol should be investigated and purified for further applications.

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ANNEXES

Annex 1. Equipments Used for Experimental Works

Laboratory equipments such as analytical balance, mill grinder, oil presser, rotary evaporator, condenser, heater, measuring cylinder, viscometer, hydrometer, reactor, thermometer, pH meter, separator funnel, vacuum filter, centrifuge, flask, beaker, furnace and oven dryer were used for biodiesel production and its property analysis experimental works.

Annex 2. Chemicals Used for Property Tests

Reagent for acid value test

Molecular mass of KOH=39+16+1=56g/mol

0.1mol/l of potassium hydroxide in distilled water

Mass/l=0.1mol/l×56g/mole=5.6g/l

Reagents for Saponification Value Test

Molecular mass of KOH=39+16+1=56 g/mol

0.5mol/l of potassium hydroxide in ethanol

Mass/l=mole/l× molecular mass

Mass/l=0.5mole/l×56g/mole=28g/l

Molecular mass of HCl=1+35.5=36.5 g/mol

0.5mol/l of HCl in water

Mass/l=mol/l× molecular mass

Mass/l=0.5mol/l×36.5g/mol=18.25g/l

Tannic Acid Solution for Biodiesel Washing

Molecular mass of tannic acid ($C_{72}H_{52}O_{46}$) =12×72+1×52+16×46= 1652g/mole

0.0006M of tannic acid ($C_{72}H_{52}O_{46}$) solution in distilled water

Mass of tannic acid per liter of water = 0.0006mole/l×1652g/mole=1g/l

Annex 3. Experimental Design Arrangements

A. Part one: Experimental design for each factor independently

Table 0.1: Experimental design for each factor independently.

Temperature variation at constant catalyst amount and alcohol to oil ratio				
Experiment number	Temperature, ^{o}C	Catalyst, %w/w	Molar ratio of alcohol to oil	Oil feed, ml
1a	35	1.0	8:1	70
1b	55	1.0	8:1	70
1c	65	1.0	8:1	70
1d	75	1.0	8:1	70
Catalyst variation at constant temperature and alcohol to oil ratio				
Experimental numbers	Temperature, ^{o}C	Catalyst, %w/w	Molar ratio of alcohol to oil	Oil feed, ml
2a	55	0.25	8:1	70
2b	55	0.5	8:1	70
2c	55	1.0	8:1	70
2d	55	2.0	8:1	70
Alcohol to oil molar ratio variation at constant temperature and catalyst amount				
Experimental numbers	Temperature, ^{o}C	Catalyst, %w/w	Molar ratio of alcohol to oil	Oil feed, ml
3a	55	1.0	6:1	70
3b	55	1.0	8:1	70
3c	55	1.0	10:1	70
3d	55	1.0	12:1	70

B. Part two: Full factorial two level and two replicas experimental design for the three factors

Table 0.2 : Experimental design arrangement for three factors, two levels and two replicas.

Experiment number	Temperature (^{o}C)	Catalyst % (w/w)	Molar ratio of alcohol to oil	Oil feed (ml)
1	65	1.0	6:1	70
2	55	1.0	8:1	70
3	55	0.5	8:1	70
4	65	0.5	6:1	70
5	65	1.0	8:1	70
6	55	1.0	6:1	70
7	65	0.5	8:1	70
8	55	0.5	6:1	70
9	55	1.0	8:1	70
10	65	1.0	6:1	70
11	65	0.5	8:1	70
12	55	0.5	6:1	70
13	65	1.0	8:1	70
14	55	1.0	6:	70
15	55	0.5	8:1	70
16	65	0.5	6:1	70

The quantities of alcohol and catalyst used for oil feed of 70 ml are shown in Table 0.3.

Table 0.3: Alcohol and catalyst used for experimental design.

Ethanol alcohol		**NaOH catalyst**	
Molar ratio of alcohol to oil	volume, ml	%w/w	mass, g
6:1	25	0.25	0.16
8:1	34	0.5	0.32
10:1	42	1.0	0.64
12:1	50	2.0	1.28

Annex 4. Software Application for Two Levels Experimental Design Analysis

Analysis of variance

Analysis of variance is used to determine the factors effect in sum of square method, the regression coefficients and regression model equation. The resulting regression equation is obtained both in terms of coded variables and actual factors. Analysis of variance is given in Table 0.4.

Table 0.4: Analysis of variance.

Source	Sum of Squares	Degree of freedom	Mean Square	F Value	Probablity value	
Block	0.01	1	0.01	30.54	< 0.0001	
Model	449.59	7	64.23	21.99	0.0022	significant
A-temperature	46.24	1	46.24	45.21	0.0003	
B-catalyst	95.06	1	95.06	100.67	< 0.0001	
C-Alcohol	211.70	1	211.70	2.74	0.1419	
AB	5.76	1	5.76	0.17	0.6914	
AC	0.36	1	0.36	21.03	0.0025	
BC	44.22	1	44.22	21.99	0.0022	
ABC	46.24	1	46.24	-	-	
Residual	14.72	7	2.10	-	-	
sum Total	464.32	15	-	-	-	

Values of probability less than 0.0500 indicate model terms are significant. In this case A, B, C, BC and ABC are significant model terms. Values of model greater than 0.1000 indicate the model terms are not significant.

The regression equations in terms of coded variable and actual parameters are obtained from the analysis of variance software application as follows.

Final equation in terms of coded factors:

$$\text{Biodiesel yield} = +71.96 - 1.65 \times A + 2.425 \times B + 3.6 \times C - 0.575 \times AB - 0.1 \times AC + 1.625 \times BC - 1.675 \times ABC$$

Final equation in terms of actual factors:

$$\text{Biodiesel yield} = 461.7 - 6.47 \times \text{temperature} - 843.72 \times \text{catalyst} - 13.5 \times \text{Alcohol} + 13.18 \times \text{temperature} \times \text{catalyst} + 0.22 \times \text{temperature} \times \text{Alcohol} + 30.64 \times \text{catalyst} \times \text{Alcohol} - 0.47 \times \text{temperature} \times \text{catalyst} \times \text{Alcohol}$$

Effect of temperature on biodiesel yield

As the temperature was increased from 55°C to 65°C, the yield reduced. The yield had inverse relation with reaction temperature between 55°C and 65°C. The effect temperature on biodiesel yield is a linear response as shown in Figure 0.1.

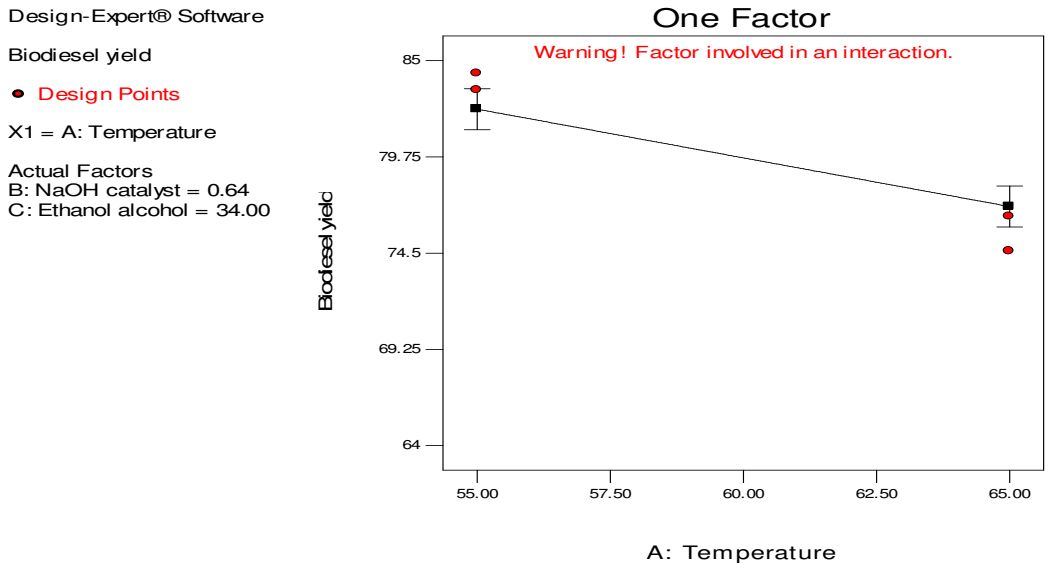

Figure 0.1: Effect of temperature on biodiesel.

Effect of NaOH catalyst on biodiesel yield

When the amount of catalyst was increased from 0.5% to 1%, the yield increased. Biodiesel yield had direct relation with the catalyst amount between 0.5% and 1%. The effect of amount of NaOH catalyst alone on yield is a linear response shown in Figure 0.2.

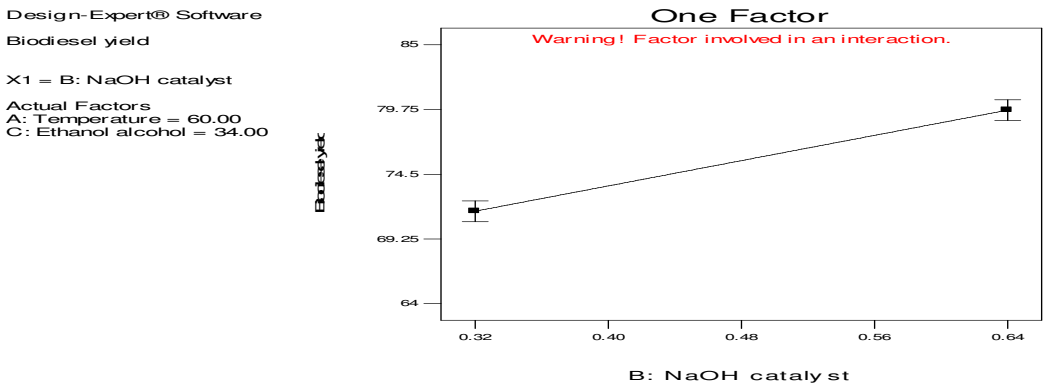

Figure 0.2: Effect of catalyst on biodiesel yield.

Effect of alcohol on biodiesel yield

When the amount of alcohol to oil molar ratio was increased from 6:1 to 8:1, the yield of biodiesel increased. The yield of biodiesel had direct relation with alcohol to oil molar ratio between 6:1 and 8:1. The effect of alcohol alone on yield is a linear response shown in Figure 0.3.

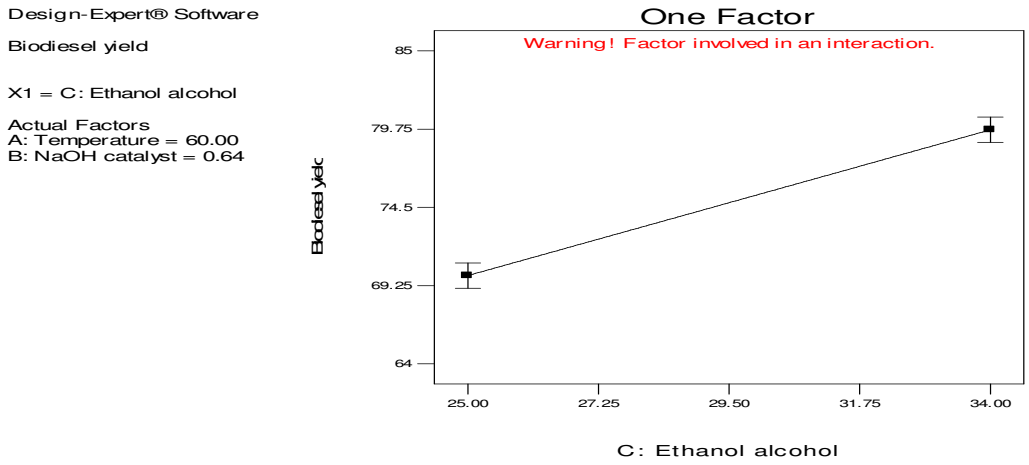

Figure 0.3: Effect of ethanol alcohol on yield.

Interaction of temperature and catalyst

The effect of temperature and catalyst interaction on biodiesel yield is a surface response as shown in Figure 0.4.

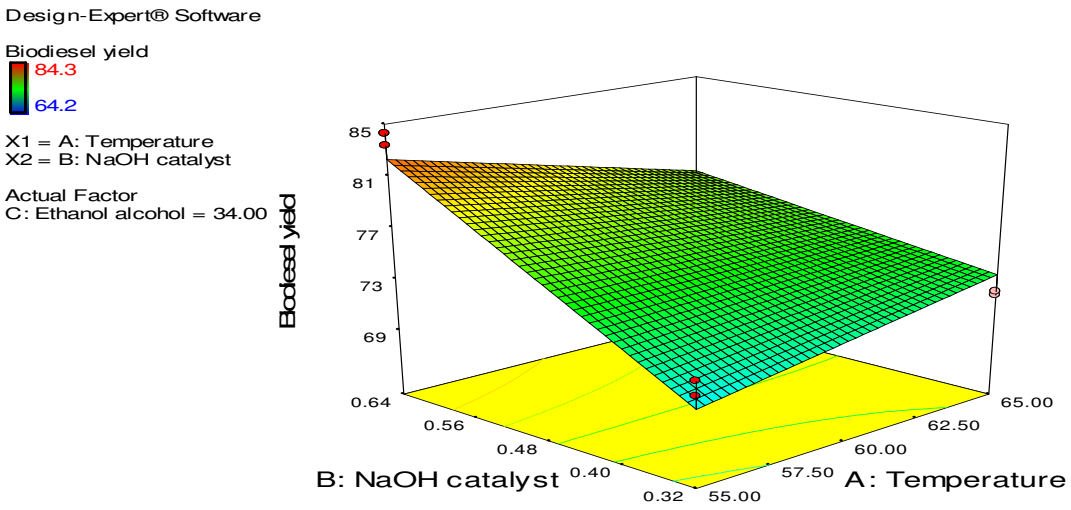

Figure 0.4: Effect of Temperature and NaOH catalyst interaction.

Interaction of temperature and alcohol

The effect of temperature and alcohol interaction on biodiesel yield is a surface response as shown below in Figure 0.5.

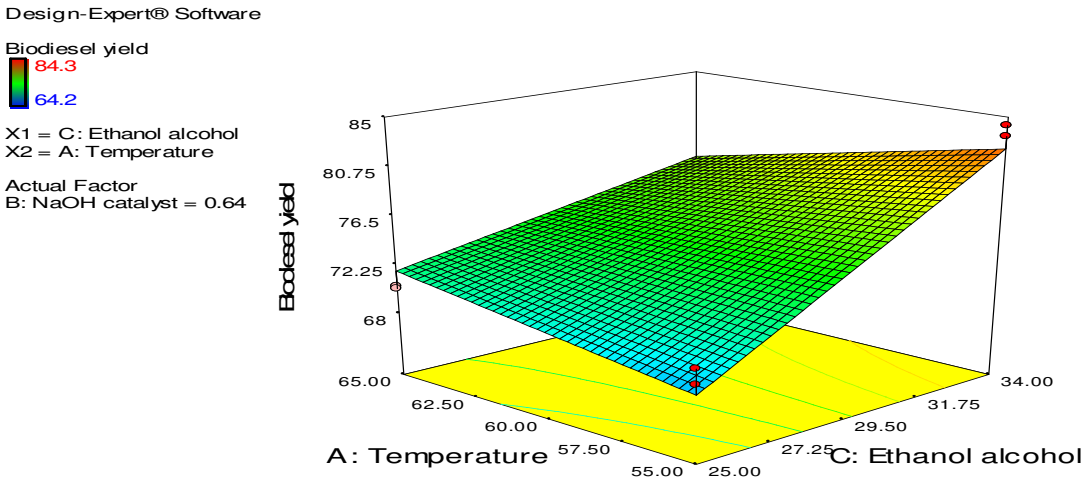

Figure 0.5: Effect of temperature and ethanol alcohol on yield.

Interaction of catalyst and alcohol

The effect of catalyst and alcohol interaction on biodiesel yield is a surface response as shown in Figure 0.6.

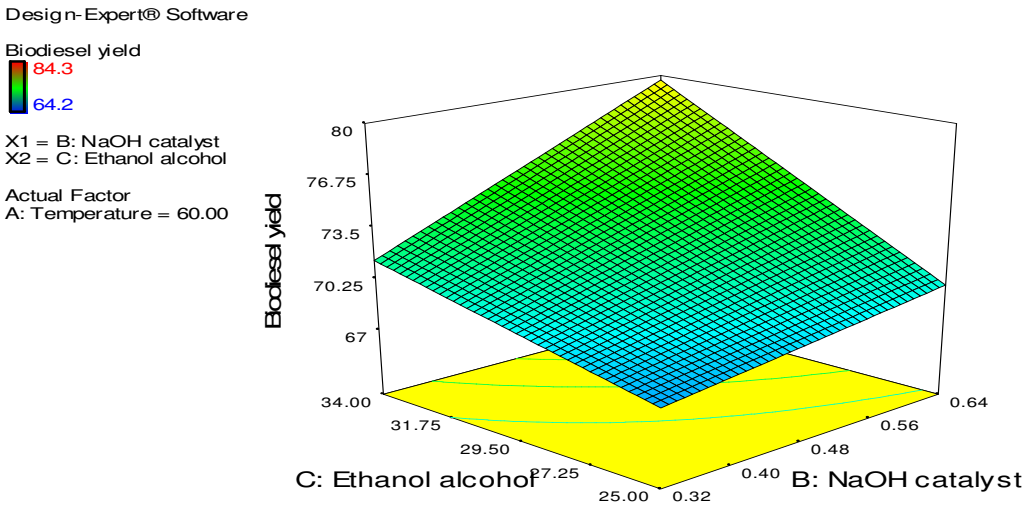

Figure 0.6: Effect of NaOH catalyst and ethanol alcohol interaction on yield.

Interaction of temperature, catalyst and ethanol alcohol

Since the interacting factors were three, three dimensional surface representation was impossible. Therefore, to determine their interaction effect graphically cube representation was used. The interaction effect of all the three factors together is shown in Figure 0.7.

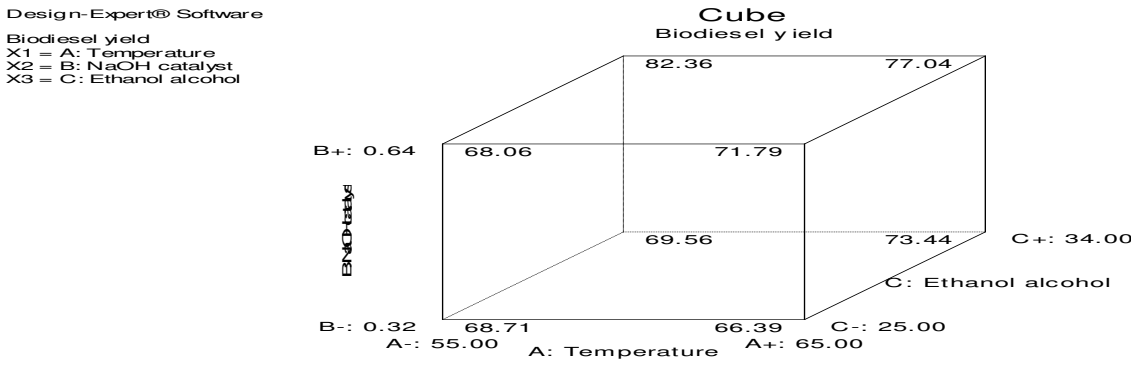

Figure 0.7: Effect of temperature, NaOH catalyst and ethanol alcohol interaction on yield.