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SCHOOL OF GRADUATE STUDIES

ADDIS ABABA INSITUTE OF TECHNOLOGY

DEPARTMENT OF CHEMICAL ENGINEERING

Biodiesel production from vernonia galamensis oil using ethanol with alkali catalyst

By, Enkuahone Abebe Alamineh

Advisor, Eng. Gizachew Shiferaw

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Acronyms and Notations

A	Catalyst weight
AB	Catalyst weight and Temperature
ABC	Catalyst, Temperature, and Alcohol: oil
AC	Catalyst weight and Alcohol: oil
ANOVA	Analysis of Variance
ASTM	American Standards Tests and Materials
AV	Acid Value
B	Temperature
BC	Temperature and Alcohol: oil
BLTV	Blank Level Titration Volume
C	Alcohol: oil
Cm	Concentration of Mass
EN	European Normalization (European Standards)
FFA	Free Fatty Acid
Mm	Molecular Mass
Ms	Mass of Sample
N	Normality
SV	Saponification Value
RF	Reagent factor
TF	Titration Factor
TV	Titration Volume
V/V	Volume per Volume
V/W	Volume per Weight
W/W	Weight per Weight
CCD	Central Composite Design
FAME	Fatty acid methyl esters
Rpm	Revolution per minute
X_1	Reaction Temperature
X_2	Ethanol to Oil ratio
X_3	Weight of Catalyst

Abstract

This work was done with the aim of producing biodiesel from vernonia galamensis oil by using ethanol with alkali catalyst, sodium hydroxide. Additionally it was investigated the effects of catalyst amount from 0.25 %(w/w) to 2 %(w/w) of weight of oil, molar ratio of ethanol to oil from 6:1 to 12:1 and reaction temperature from 35 ^{o}C to 75 ^{o}C on biodiesel yield. Vernonia galamensis oil was extracted using solvent extraction and mechanical pressing. The extracted oil was purified through degumming, neutralization, washing and drying sequentially. Acid value, amount of free fatty acid, saponification value and flash point of the extracted oil were determined. Biodiesel was produced from vernonia galamensis oil using anhydrous ethanol 99.5% (w/w) and sodium hydroxide catalyst 97% (w/w). The experimental design was done by using the Design Expert 7.0.0 software three levels; three factor Central Composite Design with full type in the optimization study, requiring 20 experiments. To determine the effect of temperature, amount of catalyst and molar ratio of alcohol to oil experiments were done in the ranges of 35^{o}C to 75^{o}C, 0.25% to 2.0% (w/w) and 6:1 to 12:1 subsequently. The maximum biodiesel yield was 87 % (w/w) at 55^{o}C, 9:1 molar ratio of alcohol to oil and 1.125% (w/w) sodium hydroxide catalyst amount. In contrast, the minimum biodiesel yield was 52% (w/w) at 75^{o}C, 12:1 molar ratio and 2% (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. Based on the preliminary economic analysis evaluation, the suggested project is feasible.

1. Introduction

1.1. Background

Biodiesel is the name for a variety of ester based fuels (fatty ester) generally defined as monoalkyl ester made from renewable biological resources such as vegetable oils (both edible and non edible), recycled waste vegetable oil and animal fats. This renewable source is as efficient as petroleum diesel in powering unmodified diesel engine. Today's diesel engines require a clean burning, stable fuel operating under a variety of conditions. Using biodiesel not only helps maintaining our environment, it also helps in keeping the people around us healthy. Biodiesel is miscible with petrodiesel in all ratios. In many countries, this has led to the use of blends of biodiesel with petrodiesel instead of neat biodiesel [1].

There are different types of feed stocks that are used for the production of biodiesel. These includes linseed oil, palm seed oil ,waste cooked vegetable oil, sunflower seed oil, cotton seed oil, jatropha seed oil, vernonia galamensis seed oil and animal fats. Oilseed plants are used for the production of biodiesel through the process called transesterification reaction which is a process by which alcohol reacts with vegetable oil in the presence of catalyst.

Triglycerides are major components of vegetable oils and animal fats. Chemically, triglycerides are esters of fatty acids with glycerol. Fatty acid ethyl esters are mostly involved because ethanol is the cheapest alcohol, but other alcohols, namely methanol, may be employed as well.

In this way, highly viscous triglycerides are converted in long chain monoesters presenting much lower viscosity and better combustion properties to enhance the burning. Homogeneous or heterogeneous catalysis are used to enhance the reaction rate.

Since different fatty acid has different physical and chemical properties, the fatty acid content is the most important parameter influencing the corresponding properties of a vegetable oil or animal fat [4].

Vernonia galamensis is a new potential industrial oilseed crop with origin in East Africa. The seed oil has unique chemical and physical properties that will permit its use in the formulation of reactive diluents, products to serve as solvents that become part of the dry paint surface and do not evaporate to pollute the air. Vernonia galamensis is one of the feed stocks which are rich in a useful epoxy fatty acid called vernolic acid. It has the largest oil content, up to 42%; and the extracted oil can contain vernolic acid (78-80%), linoleic acid (12-14%), oleic acid (2-3%) palmic acid (2-3%) and a trace amount of arachidic acid (2-3%), and used in paint formulations, coatings, plasticizers, and as a reagent for many industrial chemicals [2]. Vernonia galamensis, which is thrown as weed can provide us less dense biodiesel that can be used as diesel for air plane, and found in Easter and Western Gondar, Somali, Kefa, Borena, Arba Minch, Harar, Easter and Western Gojjam.

1.2. Statement of Problem

At present, due to industrial revolution 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 and biodiesel has recently attracted much attention all over the world because of its availability, renewability, non toxicity, better gas emissions and its biodegradability. Hence, assessing sustainable and renewable energy alternatives is indispensable at present, due not only to combat the fuel supply uncertainty and price fluctuations, but also becoming global concern and each country's responsibility to seek for environmentally kindly energy sources that are advocating to the global activities to reduce greenhouse gases and air pollutions.

Currently vernonia galamensis is under investigation to be planted commercially in Ethiopia, specifically, in Adet Agricultural Research Center, which can also grow in arid, semi arid, tropical and sub tropical areas, in degraded soil that is slightly suited for agricultural product which is thrown as weed. Vernonia galamensis is not edible. However, currently biodiesel from vernonia galamensis oil is not introduced in the any markets; hence vernonia galamensis oil will be suitable to produce biodiesel.

Most of biodiesel productions in the world from different oil have been done using methanol alcohol although; methanol is expensive and, toxic relative to ethanol; in addition to local availability of ethanol. Also methanol is non renewable as 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. Due to these reasons ethanol is used for biodiesel production.

Catalysts are the major raw material for production of biodiesel. A base catalyst such as sodium hydroxide and potassium hydroxide are commonly used. Therefore sodium hydroxide which is produced in Ethiopia will be used for the production of the biodiesel; hence, this will help to produce biodiesel from locally available vernonia galamensis oil and sodium hydroxide.

Reaction of biodiesel production is affected by amount of alkali catalyst, reaction temperature, and molar ratio of alcohol to oil. Therefore, in order to get high yield of biodiesel from vernonia galamensis oil using ethanol with alkali catalyst, the production reaction needs determination of the effects of reaction temperature, amount of alkali catalyst and molar ratio of alcohol to oil required.

1.3. Objectives

1.3.1. General Objective

The General Objective of the research was production of biodiesel from vernonia galamensis oil by using ethanol with alkali catalyst, sodium hydroxide.

1.3.2. Specific Objectives

Specific Objectives of the research were the following:

1. To determine physical and chemical properties of biodiesel produced.
2. To identify the effect molar ratio of alcohol to oil on chemical reaction of biodiesel production.
3. To investigate the effects of amount of alkali catalyst and reaction temperature on biodiesel yield.
4. To determine the feasibility aspects of biodiesel produced from vernonia galamensis oil.

1.4. Significance of the study

This thesis has great significance in terms of assuring the production of an alternative form of energy from vernonia galamensis and in the determination of the potentials of the country in supplying balancing feedstock for biodiesel production. It also will be helpful to produce biodiesel from vernonia galamensis oil using ethanol and alkali catalyst, which is locally available, can be abundantly cultivated and grown, non edible and good for production of biodiesel. This helps to encourage rural communities to cultivate more vernonia galamensis plant to sustain their earnings. In addition, the study will be used as a reference material for vernonia galamensis plant cultivation owners who are interested to produce biodiesel from vernonia galamensis oil using ethanol with alkali catalyst at small scale.

2. Literature Review

2.1. Introduction

Biodiesel, a clean renewable fuel, has recently been chosen as the best candidate for a diesel fuel substitution because it can be used in any compression ignition engine without the need for modification [7].

Biodiesel is currently manufactured by the transesterification of triglycerides with light alcohols. The triglycerides are found in vegetable oils and animal fats, more generally known as lipids. The transesterification reaction takes place in the presence of a suitable catalyst, acid or base. The biodiesel is released simultaneously with the reformation of the OH group in glycerol [4].

Biodiesel, as an alternative fuel, has many advantages as it is derived from a renewable, domestic resource, thereby relieving dependence on petroleum fuel trade in. It is biodegradable and nontoxic when 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, thus 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. Engine wear and long engine life are advantages that can be provided by biodiesel as it does have lubricating properties. Therefore, use of biodiesel is being grown vividly during the last years [8].

The costs of raw materials for biodiesel production accounts for large percent of the direct biodiesel production costs required. Thus, one way of reducing the biodiesel production costs is to use the less expensive raw material containing fatty acids such as animal fats, non edible oils, and waste cooking oil and by products of the refining vegetables oils.

Vernonia galamensis one of the best raw material for producing biodiesel as it is non edible, thus does not matter on food scarcity; it can be cultivated around poor soil, especially around dry valleys of Ethiopia that the land useful; biodiesel produced from it is less dense [9].

2.2. Vernonia galamensis plant

Vernonia galamensis is a plant in the sunflower family, known for its use as an oilseed. This species, often called ironweed, is the largest source of vernonia oil, which is rich in a useful epoxy fatty acid called vernolic acid and is used to make plastics, rubbery coatings, and drying agents. Use of this oil as a replacement for traditional plasticizers and binders in the production of paints and shows promise as a method of reducing pollution [3].

It is grown in many parts of Ethiopia, especially around the city of Harar, with an average seed yield of 2 to 2.5 t/ha. It is reported that the Ethiopian strains of vernonia have the highest oil content, up to 41.9% with up to 80% vernolic acid [2].

Vernonia galamensis is like a daisy which is quite variable in appearance between individual plants. It produces a flower which may be blue or purple, with long petals surrounding a center made up of shorter petals called florets. The center is filled with seeds. Depending on environmental conditions the plant may be short and shrubby or extremely tall. It may send out few stems, each with one flower, or many stems with bunches of flowers.

When not found in cultivation, the plant may be found growing wild, often as a weed which invades disturbed areas and rangeland. A number of insects feed on the plant. Species of the moth genus indent are sometimes known as vernonia worms due to their preference for vernonia plants as food [5].

Table2. 1: Factors affecting Vernonia galamensis growth

Elements	**Suitable features**
Rain fall	300mm-1850mm
Topography	1800m-1900m above sea level
Soil	Porous, well drained soil and poorly drained soil

Figure2. 1: Vernonia galamensis plant

2.2.1. Vernonia galamensis oil applications

Epoxy oil is important in industry for the manufacture of plastic formulations, protective coatings, lubricants, plastics and additives. A potential market use is as a drying agent for resin paints and other products. The low viscosity and polymerizing characteristics of this oil make it especially valuable as a solvent in industrial coatings and paints, for environments where fumes from traditional solvents are hazardous or polluting. Some of the products that are being developed from vernonia oil are degradable lubricants and lubricant additives, epoxy resins, adhesives, insecticides and insect repellants, crop oil concentrates, and the formulation of carriers for slow release pesticides [6].

2.3. Vernonia galamensis oil extraction methods

Two methods of oil extraction processes are identified. These are solvent extraction and mechanical extraction which are discussed below [22].

2.3.1.1.Oil extraction using solvent

Solvent extraction with n-hexane can produce about high yield by weight of oil per kilogram of the vernonia galamensis seed. To extract oil using solvent, vernonia galamensis seeds are crushed at the required size. The crushed seeds and hexane at ratio of 1:5 (w/v) respectively are fed to soxhlet apparatus to extract oil. The extraction temperature is near to the boiling point of hexane.

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

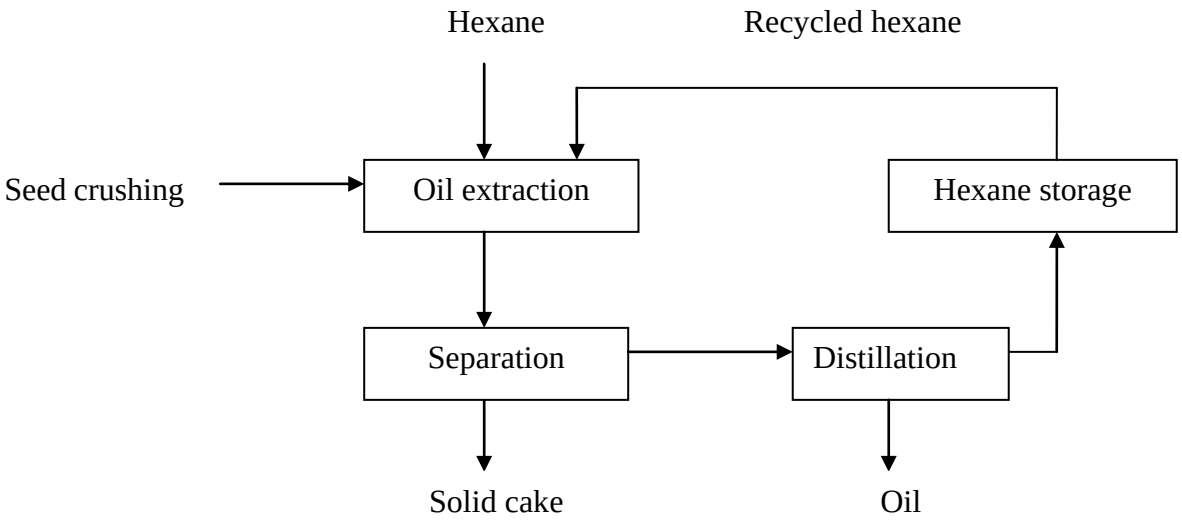


Figure2. 2: Oil extraction using hexane solvent

2.3.1.2.Mechanical pressing oil extraction

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

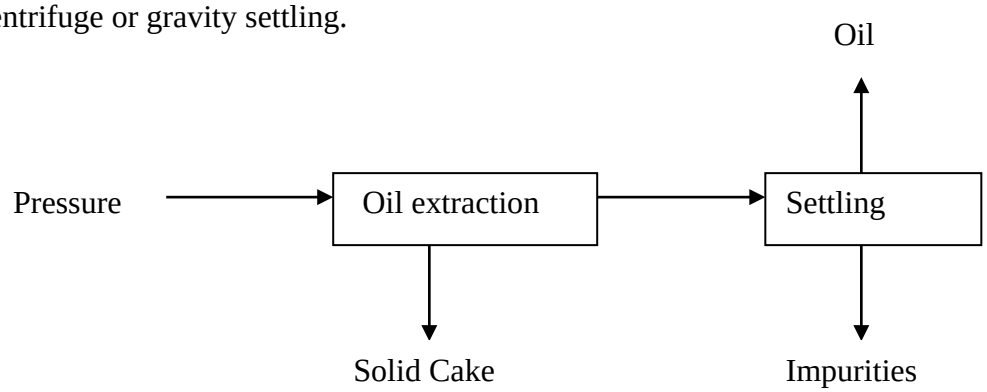


Figure2. 3: Mechanical press oil extraction

2.3.2. Fatty acid composition of vernonia galamensis oil

Table2. 2: Fatty acid composition of vernonia galamensis oil

Vernonia galamensis oil fatty acid types	Vernonia galamensis oil fatty acid composition (%)
Vernolic (18:1:1)	78-80%
Palmitic (16:0)	2-3%
Oleic(18:1)	2-3%
Linoleic acid (18:2)	12-14%
Average molecular weight of oil	926 g/mol

(Source: Perdue R.E. Jr. Carlson K.D. Gilbert MG)

2.4. Biodiesel Production Process Options

2.4.1. Batch process system

Vegetable oil is charged to transesterification in a batch reactor in the presence of an excess amount of ethanol, and catalyst. An excess of ethanol is necessary essentially to ensure full solubility of triglyceride and keep the viscosity of the reaction mixture low, but also for shifting the chemical equilibrium. The transesterification reaction may be considered finished when maximum conversion is achieved. However, the mixture composition should value the quality of biodiesel requirements. The excess ethanol is recovered for the next batch [7].

Remaining mixture is presented to the separation of esters from glycerol which can take place either by decantation or by centrifugation.

Hot water may be added to improve the phase split. The oil phase containing fatty esters is sent to finishing by neutralization with acid, followed by washing and drying. The ethanol recovery takes place by flash distillation or film evaporation. The batch process allows high flexibility with respect to the composition of the feedstock. However, the economic indices are on the lower side because of lower equipment productivity and higher operation costs, such as manpower and automation and less amount of mass and energy integration [20].

2.4.2. Continuous process system

Catalytic continuous process technology of biodiesel production is a conceptual scheme of a continuous process working at low pressure that is capable of processing a feedstock with a larger amount of free fatty acids, such as unrefined non edible vegetable oils, tallow fat and used cooking oil. For this reason in the first reactor the esterification of free fatty acids with ethanol is carried out. Then the transesterification reaction follows in the second reactor. A homogeneous catalyst is currently used, either as alkaline hydroxide or alkaline ethoxide. Ensuring high yield in monoester and minimum amounts of mono or di-triglycerides a minimum of two reactors in series with glycerol intermediate separation ought to be employed. The reaction mixture is then submitted to phase separation in crude ester and glycerol phase and separation can take place by decanting or centrifugation.

Glycerol phase is treated with acid for soap removal and recovery as free fatty acid. Then, the ethanol is recovered by evaporation and recycled then crude ester follows the route of ethanol separation. Material balance loop is closed by the recovery of excess ethanol from water solution by distillation [21].

Two reactors are employed with intermediate glycerol separation and excess ethanol is recovered by multistage flash distillation. Ester and glycerol can be separated by coalescence separation or centrifugation. In neutralization and washing steps ethanol can be recycled as vapor [7]. Remaining mixture is presented to the separation of esters from glycerol which can take place either by decantation or by centrifugation.

Water may be added to improve the phase split. The oil phase containing fatty esters is sent to finishing by neutralization with acid, followed by washing and drying. The ethanol recovery takes place by flash distillation or film evaporation. The batch process allows high flexibility with respect to the composition of the feedstock. However, the economic indices are on the lower side because of lower equipment productivity and higher operation costs, such as manpower and automation and less amount of mass and energy integration [20].

2.5. Biodiesel production processes

Biodiesel derived from biological resources is a renewable fuel, which has drawn more and more attention recently. A fatty acid methyl ester is the chemical composition of biodiesel. Transesterification is widely used for the transformation of triglyceride into fatty acid methyl ester [11].

The manufacturing process is based on the transesterification of triglycerides by alcohols to fatty acid methyl esters, with glycerol as a byproduct [12].

The base catalyzed production of biodiesel generally has the following process steps [10].

2.5.1. Mixing of alcohol and catalyst

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

2.5.2. Chemical reaction

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

2.5.3. Separation

After the reaction is completed, there exists glycerol and biodiesel formation. Both have a significant amount of the excess alcohol that was used in the reaction which is in need of being recovered. The reacted mixture is sometimes neutralized at this step if the basic media that is caused by alkali hydroxide is occurred. The glycerol phase is much denser than biodiesel phase, making biodiesel to be floated.

The two products can be separated by gravity using settling vessel. The glycerol is drawn off at the bottom of the settling vessel and biodiesel is drawn off at the top. In some cases, a centrifuge is used to separate the two materials faster by screening both phases.

2.5.4. Alcohol removal

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

2.5.5. Biodiesel washing

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

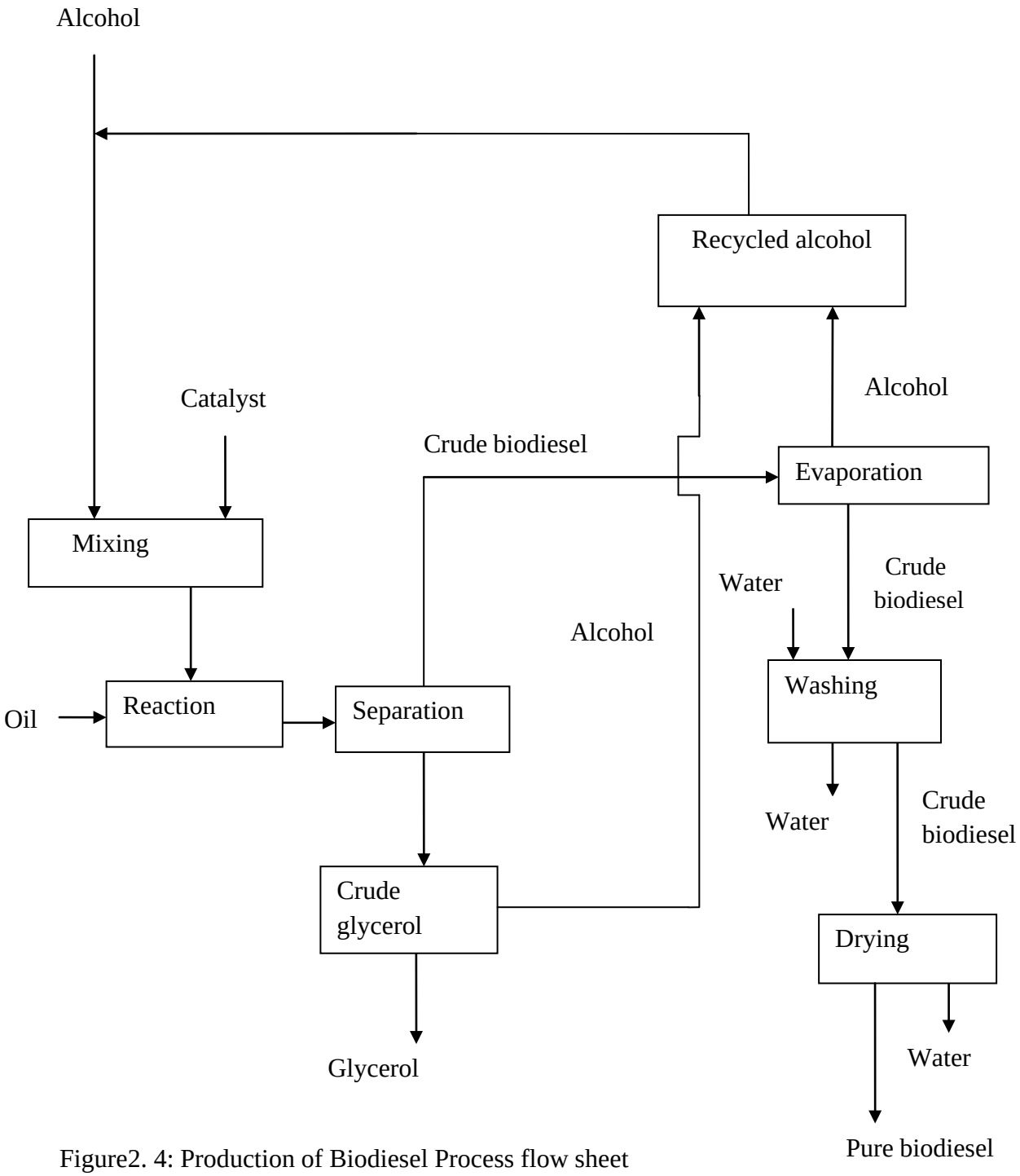


Figure2. 4: Production of Biodiesel Process flow sheet

2.6. Transesterification reaction

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 [10].

Among these, the transesterification is the key 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 [14, 24].

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 ethanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock and free fatty acids are converted to esters instead of soap, so a wide variety of feedstock can be used. Also the catalyst removal step is eliminated. As high temperature and pressure are required, cost energy production is higher [25].

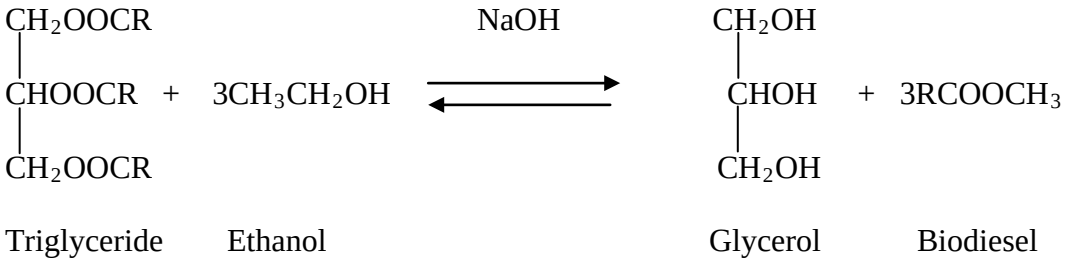
2.6.2. Lipase catalyzed transesterification

Using enzymes as a catalyst for the transesterification is verified by many researchers as good yield could be obtained from crude and used oils using lipases. The use of lipases makes the reaction less sensitive to high FFA content which is a problem with the standard biodiesel process. One problem with the lipase reaction is that ethanol cannot be used because it inactivates the lipase catalyst after one batch [24].

2.6.3. Transesterification reaction using alkali catalyst

Transesterification is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side [11].

Commercial biodiesel from plant oils are produced mostly by using very effective homogeneous catalysts such as alkali or acid. Sodium hydroxide and potassium hydroxide are more effective alkali catalysts. 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 as it prevents the formation of soap stock [12]. Conversely, the addition of an excessive amount of catalyst gives rise to the formation of an emulsion, which increases the viscosity and leads to the formation of gels. These hinder the glycerol separation process and, reduce the apparent ester yield.



2.7. Variables Affecting Alkali Catalyzed Transesterification Reaction

Transesterification reaction process is influenced by a variety of working factors. These are molar ratio of alcohol to oil, amount and catalyst type, reaction time, reaction temperature, stirring rate, presence of free fatty acids and moisture [13].

2.7.1. Stirring rate

Oils and alcohols are not totally miscible, thus reaction can only occur in the interfacial region between the liquids and transesterification reaction is a moderately slow process; for this reason dynamic mixing is required to increase the area of contact between the two immiscible phases. Alcoholysis process can be enhanced by the agitation intensity of the reactor. Mass transfer of biodiesel from the oil phase towards the alcohol-oil interface might be a vital step that limits rate of alcoholysis reaction because the reaction is heterogeneous mixture.

Reduced mass transfer between two phases in the initial phase of the reaction results in a sluggish reaction rate, the reaction being mass transfer controlled. Fast stirring accelerates transesterification reaction; therefore, variations in mixing strength are expected to change the kinetics of the transesterification reaction [13, 14].

2.7.2. Molar ratio of alcohol to oil

One of the most important parameters affecting the yield of biodiesel 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 methyl/ethyl esters and 1 mole of glycerol is used. Transesterification is an equilibrium controlled reaction in which excess of alcohol can be used to get complete conversion and alcohol is easily recoverable. Further, the conversion efficiency is remains the same, but to decrease the energy increment required for the recovery of alcohol, we should avoid increasing molar ratio of alcohol to oil. Additionally, 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. The molar ratio is associated with the type of catalyst used such as; alkali catalyzed transesterification reaction the alcohol to oil molar ratio is about 6:1 to 12:1 which 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 [14, 15, 16]. The molar ratio of alcohol to oil has no effect on acid value, saponification values and iodine values of esters.

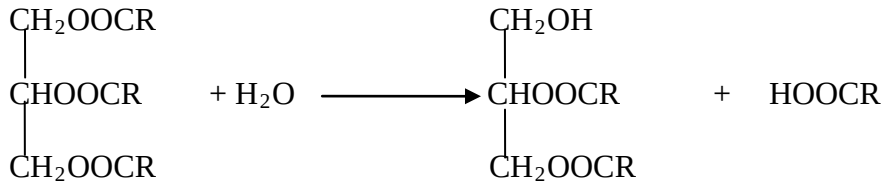
2.7.3. Free fatty acid and moisture content

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. To carry out this reaction to completion, less than 3% free fatty acid content in oils is needed [17]. 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.

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 the glycerol phase. The starting materials used for base catalyzed alcoholysis should meet certain specifications. The triglycerides should have lower acid value and all material should be substantially anhydrous.

The 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 [12, 13, 17]. The presence of water at high temperature resulted hydrolysis of triglycerides to diglyceride and form a free fatty acid as shown below.



Triglyceride Water Diglyceride Free fatty acid

Where:

1. R is the alkyl group of triglyceride components (vernolic, palmitic, stearic, oleic and linoleic)
2. Vernolic Acid: R = - (CH2)16– CH3, 18 carbons and 1 double bonds (18:1) and oxygen
3. Palmitic: R = - (CH2)14 – CH3, 16 carbons and 0 double bonds (16:0)

4. Stearic: R = - (CH2)16 – CH3, 18 carbons and 0 double bonds (18:0)
5. Linoleic: R = - (CH2)7 CH=CH-CH2-CH=CH (CH2)4CH3, 18 carbons and 2 double bonds (18:2)
6. Oleic: R = - (CH2)7 CH=CH (CH2)7CH3, 18 carbons and 1 double bond (18:1)

The presence of alkali catalyst and free fatty acid results to the formation of soap which is undesirable because the soap attaches the catalyst and making the catalyst inactive to accelerate the reaction.

Additionally disproportionate soap in the products can restrain later in processing of the biodiesel, glycerol separation and water washing. The reaction of free fatty acid and alkali catalyst is shown below.

$$HOOCR + NaOH \longrightarrow NaOOCR + H_2O$$

Free fatty acid Sodium hydroxide Sodium soap Water

So as to reduce the formation of soap as side reaction the oil as raw material should meet certain specifications when base catalyzed alcoholysis is used. Triglycerides ought to have lower acid value and all material should be substantially water free. Higher acidity can be avoided by adding more sodium hydroxide catalyst; however formed soap results in the formation of gels that hinders the reaction as well as with glycerol separation.

2.7.4. Alkali catalyst amount

A catalyst is needed to improve the transesterification reaction and amount of yield production. The alkaline catalysts such as sodium hydroxide and potassium hydroxide are most widely used. These catalysts increase the reaction rate several times faster than acid catalysts. Alkaline catalyst concentration in the range of 0.5 to 1.125% by weight yields 94 to 99% conversion efficiency. Further increase in catalyst concentration does not increase the yield, but it adds to the cost and makes the separation process more complicated [11].

2.7.5. Reaction time and temperature

The rate of the transesterification reaction is strongly influenced by the reaction temperature. Generally, the reaction is carried out close to the boiling point of ethanol (70-75°C) at atmospheric pressure.

With further increase in temperature there is more chance of loss of ethanol. 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 one hour [19]. Excess reaction time does not increase the conversion but favors the backward reaction (hydrolysis of esters) which results in a reduction of product yield.

2.8. Biodiesel Properties and Specification Standards

2.8.1. Biodiesel properties

1. Viscosity is the resistance to flow of a fluid under the influence of gravity. The kinematic viscosity is equal to the dynamic viscosity divided by density. The kinematic viscosity is a basic design specification for the fuel injectors used in diesel engines; moreover the high a viscosity implies the injectors fail to perform properly.
2. Density is defined as mass per unit volume of a substance at a specific temperature. The higher density of biofuel indicates presence of large mass in specific a volume, which is heavy biofuel.
3. Flash point 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.
4. Ash content is the residue remaining after a fuel sample has been burned. For biodiesel, this test is an indicator of the quantity of residual materials in the fuel that came from the catalyst used in the transesterification reaction and raw material used.
5. Acid number is an indication of the presence of free fatty acids in biodiesel. The free fatty acids can lead to corrosion and may be an indication of water in the fuel during manufacturing.
6. Iodine value indicates the level of saturation of the molecules which according to ASTM, the iodine number helps to indicate the oxidation stability of the biodiesel. The higher iodine number represents the lower oxidation stability.

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

8. Cloud point of the fuel is the temperature at which wax crystals first begin to be formed. Below the cloud temperature, filters will start to become blocked and potentially starve the engine of the fuel.
9. Water content is 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 period.
10. Cetane number is the measure of fuel's ignition and combustion quality. The higher cetane number biodiesel has lower ignition time delay, which means it, ignites immediately. 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 fuel specification defines and sets the quality standards for biodiesel which is based on the standard ASTM D6751.

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

The viscosity of biodiesel can be predicted ± 15 % using the esters composition determined. The viscosity has to be in a range of 1.9-6.0mm^2/s.

The acid number is "the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point''. The acid number is a direct measure of free fatty acids. The free fatty acids can lead to corrosion and may be a symptom of water in the fuel. Usually, for a base catalyzed process, the acid value after production will be low since the base catalyst will strip the available free fatty acids.

Nevertheless, the acid value may increase with time as the fuel degrades due to contact with air or water. The requirement is a maximum of 0.8 mg of KOH/goil [23]. The ASTM and EU biodiesel property specifications with the recommended test methods are given in Table 2.3.

Table2. 3: Standard Specifications of Biodiesel: USA and European

Property	Unit	USA	EU	
		ASTM D 6751	EN 14214	Recommended Test method
Density at 15^0C	Kg/m^3	-	860 – 900	ASTM D 4052
Kinematic viscosity at 40^oC	mm^2/s	1.9 -6.0	3.5 - 5.0	ASTM D 445
Flash point	^{o}C	≥ 120	≥ 130	ASTM D 93
Cloud point	^{o}C	-	-	ASTM D 2500
Sulfur content,100%	w%	≤ 0.05	≤ 0.01	ASTM D 5453
Sulphated Ash	wt%	≤ 0.02	≤ 0.02	ASTM D 874
Water content	mg/Kg	-	≤ 500	EN ISO 12937
Total contamination	mg/Kg	-	≤ 24	EN 12662
Water and sediment	% vol.	≤ 0.05		ASTM D 2709
Corrosion (Cu) at 50^oC	-	≤ No.3	class 1	ASTM D 130
Cetane number	-	≥ 47	≥ 51	ASTM D 613
Acid number	Mg KOH/g	≤ 0.8	≤ 0.5	ASTM D 664
Oxidation Stability ,110^oC	hours		≥ 6	EN14112
Ethanol content	wt%		≤ 0.2	EN 14110
Ester content	wt%		≥ 96.5	EN 14103
Carbon Residue,100%	wt%	0.05 max		ASTM D 4530
Triglycerides	wt%		≤ 0.20	EN 14105
Diglycerides	wt%		≤ 0.80	EN 14105
Monoglycerides	wt%			EN 14105
Free glycerol	wt%	≤ 0.02	≤ 0.02	ASTM D 6584
Total glycerol	wt%	≤ 0.24	≤ 0.25	ASTM D 6584
Iodine value	$gI_2/100g$		≤ 120	EN 14111
Phosphorus	mg/Kg	≤ 10	≤ 10	ASTM D 4951

Source: Adopted from Biodiesel industries, Australia 2003

3. Materials and Methodology

3.1. Materials

Materials which were used for biodiesel production were vernonia galamensis seeds oil, ethanol alcohol, sodium hydroxide catalyst, property test study chemicals as shown in Table 3.1. The vernonia galamensis seeds were brought from West Gojjam, Adet Agricultural Research Centre. Chemicals were bought from Neway Private Limited Company; in Addis Ababa.

Table3. 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	Phosphoric acid

3.2.Methodology

3.2.1. Experimental works

Experimental works were done in Chemical Engineering Department Laboratory class rooms. In addition, mechanical pressing of oil extraction was done in Dembecha in West Gojjam Wagaye Walelgn Private Limited Company.

3.2.1.1.Vernonia galamensis seeds sample preparation

For extracting the oil the samples of vernonia galamensis seeds were cleaned and prepared. Seeds were crushed by motor mill with 1.0 mm to 2.0 mm sieve size in Chemical Engineering Size Reduction Laboratory; then the sample was ready for oil extraction.

3.2.1.2.Vernonia galamensis oil extraction

The oil was extracted by solvent extraction and mechanical pressing extraction methods. Procedures of oil extraction using hexane solvent were based on [22].

3.2.1.2.1. Oil extraction using solvent

Seeds were crushed in a crushing mill with a particle size of 1.0 mm to 2.0 mm. Then, the crushed seeds and hexane solvent were placed in the extraction unit at a solvent to solid ratio of 5:1(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 reusing in extraction of oil. The oil was collected and stored to be filtered.

3.2.1.2.2. Oil extraction using mechanical pressing

Seeds were crushed using a crushing mill with a particle size of 1.0 mm to 2.0 mm. Next, the crushed seeds were tied by a cotton cloth and fed at the top of a presser.

At each batch 1kg of the crushed seed 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 place. 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.

3.2.1.3.Vernonia galamensis oil refining

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

1. **Settling**: It is crude oil separating from impurities by using a centrifuge at a speed of 800 rpm for 20 minutes.
2. **Degumming**: It is used to remove phosphorus compounds of crude oil using a phosphoric acid and a hot water. Distilled water 3% (v/v) of oil at 70^{o}C and 1.5% phosphoric acid (v/v) of oil were mixed with the oil which was heated at 70^{o}C. The mixtures were stirred at speed of 200 rpm for 1 hour at a temperature of 70^{o}C. The impurities were separated using a centrifuge at a speed of 800 rpm for 20 minutes.
3. **Neutralization**: After determining the free fatty acid (FFA) of oil, the free fatty acid was neutralized by 0.05N of NaOH. Neutralization was done by heating the oil 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

Saponification value and acid tests were done based on experimental procedures of [23, 27, 28].

3.2.1.4.1. Acid value of oil

For determining acid value, firstly, a titration solution of 0.1N of KOH in distilled water was prepared. Subsequently, 2g of oil was added to the 250ml conical flask and heated at 70^{o}C for 3 minutes. Then, 20ml of anhydrous ethanol (99.5%w/w) and 5 drops of phenolphthalein were added into the titration beaker with sample oil.

Then 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 (99.5%w/w) and 0.5mol/l hydrochloric acid solution in distilled water was prepared. Then, a 2 g sample was placed in a 250ml conical flask. Next, a 25ml of 0.5mol/l potassium hydroxide in ethanol solution was added. The flask was heated at a temperature of 70^{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. Kinematic viscosity of oil

Vibro-viscometer was used to determine the viscosity of oil, and the sample was kept in the water thermostat bath until it reaches the equilibrium temperature of 40^{o}C. After maintaining the equilibrium temperature, the vibro-viscometer tip was inserted to the sample and the reading was taken from the controller. The kinematic viscosity is then equal to the ratio of dynamic viscosity to density of the oil.

$$\nu = \mu/\rho \qquad (3.1)$$

Where:

ν =kinematic viscosity, mm^2/s

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

3.2.1.4.4. Moisture Content Determination

The empty dish was weighed with and without the amount of seed and dried in an oven at 105^{o}C for 7hr, weighing each 2hr till constant weight is obtained and finally the weight

was taken and compared with the initially recorded weight. The percentage weight in the seed was calculated using the formula:

$$\text{Moisture content\%(w/w)} = \frac{W_1 - W_2}{W_1} * 100 \quad (3.2)$$

Where:

W_1 = Original weight of the sample before drying

W_2 = Weight of the sample after drying

3.2.1.4.5. Determination of Specific Gravity

After the sample was filled into graduated cylinder (50 ml) and its temperature was recorded; Hydrometer was used to measure the specific gravity of the oil at 20 ^{o}C specified. Hence, the density of the oil is determined using the specific gravity.

3.2.1.4.6. Ash content of oil

Ash content of oil was determined using a furnace. A 20 g of oil was added in a burning cup. Then, the sample was placed in a furnace. A furnace was located at a temperature of 500^{o}C for 1 hour and after burning the residue sample was weighted and ash content was calculated.

3.2.1.5. *Feed Material Requirement for Biodiesel Production*

For every run 100ml of purified vernonia galamensis oil was used. Hence, the amount of ethanol and catalyst was calculated as follows using the process parameters. The amount of ethanol required when the molar ratio of ethanol to oil ratio 6:1;

$$\text{nEthanol}/\text{nOil} = 6 \quad (3.3)$$

Substituting mass for mole;

$$\frac{\text{Given mass of ethanol} / \text{Molecular mass of ethanol}}{\text{Given mass of oil} / \text{Molecular mass of oil}} = 6 \quad (3.4)$$

Where:

Molecular mass of ethanol is=56g/mol

Average molecular mass of vernonia galamensis oil=926g/mol; and for the experiment 100ml of vernonia galamensis oil is going to be used, and density of oil is 880kg/m^3.

Therefore given mass of oil is;

Given mass of oil=density of oil*volume of oil

Given mass of oil=880kg/m^3*100*$10^{-6}$$m^3$

Given mass of oil =88g, Substituting in equation 3.4;

$$\frac{\text{Given mass of ethanol} \,/_{56\text{g/mol}}}{88\text{g} \,/_{926\text{g/mol}}} = 6 \qquad (3.5)$$

Thus, given mass of oil ethanol=31.93g. To get the volume of ethanol used for 100ml of oil; given mass of ethanol=density of ethanol*volume of ethanol

Substituting;

31.93g=800g/l*volume of ethanol

Thus, volume of ethanol=39.91ml.

$$\frac{Mass\ of\ catalyst}{Mass\ of\ oil} = 1.125\% \qquad (3.6)$$

Substituting in to equation 3.6;

Thus, mass of catalyst=0.99g

3.3. Experimental work design

During this work the biodiesel was produced using purified vernonia galamensis oil and ethanol with a homogeneous catalyst of sodium hydroxide.

Experimental design was analyzed and done by the Design Expert 7.0.0 software application. Experimental design selected for this study is CCD and the output measured is biodiesel yield gained.

Process variables revised are reaction temperature, molar ratio of ethanol to oil and weight percentage of catalyst. To get maximum conversion; reaction period and rotation speed was set at 2 hours and 500 rpm respectively and at constant atmospheric pressure. The operating limits of the biodiesel production process conditions are reasons to choose levels of the variables.

Three level three factors CCD was made use of in the optimization study, needing 20 experiments to be done. Catalyst concentration, ethanol to oil molar ratio and reaction temperature were the independent variables selected to optimize the conditions for biodiesel production by using sodium hydroxide as main catalyst for performing transesterification reaction.

Twenty experiments were done and the data was statistically analyzed by the Design Expert 7.0.0 software and to get suitable model for the percentage of fatty acid methyl ester as a function of the independent variables.

Table3. 2: Complete experimental design matrix of CCD

Variables	Factor Coding	Unit	Levels		
			-1	0	+1
Reaction Temperature	x_1	^oC	35	55	75
ethanol to Oil ratio	x_2	-	6	9	12
Amount of Catalyst	x_3	g	0.22	0.99	1.76

Table 3.2 indicates the complete experimental design matrix of CCD for the factorial design. Order in which the runs were made was randomized to avoid errors which are caused by systematic.

Table3. 3: Experimental design matrix

Run	Coded Factors			Actual Factors			Actual Biodiesel yield %(w/w)
	X_1	X_2	X_3	Temperature (^{O}C)	Ethanol to oil	Catalyst (g)	
1	-1	+1	+1	35	12	1.76	
2	+1	+1	-1	75	12	0.22	
3	0	0	0	55	9	0.99	
4	-1	-1	-1	35	6	0.22	
5	0	0	0	55	9	0.99	
6	+1	-1	+1	75	6	1.76	
7	0	0	0	55	9	0.99	
8	-1	-1	+1	35	6	1.76	
9	+1	+1	+1	75	12	1.76	
10	0	0	0	55	9	0.99	
11	-1	+1	-1	35	12	0.22	
12	+1	-1	-1	75	6	0.22	
13	0	0	0	55	9	0.99	
14	0	+1	0	55	12	0.99	
15	0	0	-1	55	9	0.22	
16	-1	0	0	35	9	0.99	
17	0	0	+1	55	9	1.76	
18	0	-1	0	55	6	0.99	
19	+1	0	0	75	9	0.99	
20	0	0	0	55	9	0.99	

4. Results and Discussions

4.1.Extracted Oil

The oil was extracted using mechanical pressing and hexane solvent. The required amount of oil was extracted using mechanical pressing to reduce the cost; even though the extraction efficiency of mechanical pressing was poor as it results some residue and the oil is get rid of together with the cake. From 100 g of purified seed, 35 g oil was found, that shows 35 %(w/w) of oil was extracted in the seed by using hexane. And by using mechanical pressing, from 100 g of purified seed, 20 g oil was found, that shows 20 %(w/w) of oil was extracted in the seed.

4.2. Physicochemical Properties of the Oil

Saponification and acid value tests were done based on experimental procedures of [23, 27, 28].

4.2.1. Acid value of oil

For testing acid value, mixture was kept until it changed to pink after 1.60 ml of titration volume added.

Table4. 1: Determination of acid value of oil

Run Number	Titration volume, ml	Color change
1	1.60	Gray to pink
2	1.71	Gray to pink
3	1.55	Gray to pink
Average value	1.62≈1.60	

$$\text{Acid value, mgKOH/gOil} = \frac{M * Mm * Tv}{Ms} \quad (4.1)$$

Where:

Mm=56.1g/mol; Ms=2g; M of KOH =0.1mol/l and Tv =1.60ml

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

$$\text{Acid value,} \frac{\text{mgKOH}}{\text{gOil}} = \frac{\frac{0.1\text{mol}}{\text{l}} * \frac{56.1\text{g}}{\text{mol}} * 1.60 * 10^{-3}\text{l}}{2\text{g}}$$

Acid Value= 4.48 mgKOH/gOil

Therefore, the acid value was 4.48 mg KOH/g of oil.

And thus, the free fatty acid content of the oil is half of the acid value which is equal to 2.24 mg /g of oil.

4.2.2. Saponification value of oil

First the blank level changed from pink to colorless at 15ml titration volume. The color at which the saponification test changed from pink color to red color was 4.1ml of titration volume. Titration results for saponification test are illustrated in Table 4.2.

Table4. 2: Titration results for Saponification value test

Run number	Titration volume, ml	Color change
1	4.0	Pink to red
2	4.3	Pink to red
3	4.5	Pink to red
4	3.7	Pink to red
Average value	4.1	

The saponification value was calculated as follows;

$$Saponification\ Value, mgKOH/g = \frac{(BLTv - Tv) * RF * Cm}{Ms} \quad (4.2)$$

Where:

BLTV is the blank level titration volume=15ml

Cm is the mass concentration of KOH = 0.5mol/l×56g/mol=28gKOH/ml

Ms is the mass of sample =2g

RF is the reagent factor of HCl =1.006

Tv is the titration volume=4.1 ml

Substituting the values in equation (4.2):

$$Saponification\ Value = \frac{(15ml - 4.1ml) * 1.006 * 28gKOH/ml}{2g}$$

Thus, the saponification value of the oil was about 153.52mgKOH/gOil.

4.2.3. Density of oil

The specific gravity of oil was measured by hydrometer to be 0.880; and after multiplying the specific gravity of oil by density of water, the density of oil was gained as follows.

$$\text{Density of oil} = \text{Specific Gravity of oil} * \text{Density of water} \quad (4.3)$$

Substituting 1000kg/m^3 for water density and 0.88 for oil specific gravity of oil density in equation 4.3, density of oil was gained as 880kg/m^3.Therefore the density of oil was 880kg/m^3.

4.2.4. Kinematic viscosity of oil

The dynamic viscosity of oil was determined to be 11.3m.Pa.s at temperature of 40^{o}C by using Vibro viscometer.

$$\text{Kinematic Viscosity of oil} = \frac{\text{Dynamic viscosity of oil}}{\text{Density of oil}} \quad (4.4)$$

Inserting the value of 880 kg/m^3 for density of oil, and the value of 11.3m.Pa.s for dynamic viscosity of oil in equation (4.4) gives kinematic viscosity of oil.

Dynamic viscosity of oil=11.3mpa.s=11.3*10^{-3}*kg/m.s

$$\text{Kinematic Viscosity of oil} = \frac{11.3 * 10^{-3} * \frac{\text{kg}}{\text{m. s}}}{880\text{kg/m}^3}$$

Thus, the kinematic viscosity of oil was 12.84mm^2/s.

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

4.2.5.1.Flash point

For determining the flash point of oil open cup method test was used, thus flash point of the oil was 205^{o}C. The temperature shows that the oil is appropriate for using and storing since its high flash point that opposes spontaneous combustion.

4.2.5.2.*Moisture content of oil*

By using equation (3.2) moisture content of oil was determined.

$$\text{Moisture content\%} \left(\frac{w}{w}\right) = \frac{W_1 - W_2}{W_1} * 100\% \quad (4.5)$$

Initial mass of oil=40.00g

Final mass of oil=39.85g

Inserting the above values in equation (4.3);

$$\text{Moisture content\%(w/w)} = \frac{40.00\text{g} - 39.85\text{g}}{40.00\text{g}} * 100\%$$

Thus, the moisture content of oil was 0.375% (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 of oil

$$\text{Ash content\% } (w/w) = \frac{\text{final mass of oil after burning} * 100\%}{\text{Initial mass of sample}} \quad (4.6)$$

Initial mass of sample=20g

Final mass of sample=0.0089g

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

$$\text{Ash content \%}(^{w}/_{w}) = \frac{0.008\text{g} * 100\%}{20\text{g}} = 0.04$$

It shows that the oil was refined and was suitable for biodiesel production as it is small.

Table4. 3: Physicochemical properties of the oil

Physicochemical properties	Units	Values
Density @ 20^{o}C	kg/m^{3}	880
Kinematics viscosity @ 40^{o}C	mm^{2}/s	12.84
Acid value	mgKOH/g	4.48
Free fatty acid	mg/g	2.24
Saponification value	mgKOH/g	153.52
Flash point	^{o}C	205
Moisture content	% (w/w)	0.375
Ash content	% (w/w)	0.04

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

4.3.1. Effect of reaction temperature on biodiesel production

Setting reaction time and mixing rate were 2 hours and 500 rpm, respectively for all the runs. The effect of temperature at 35^{o}C, 55^{o}C and 75^{o}C on biodiesel yield for 1.125% (w/w) catalyst, 100 ml oil feed and 9:1 ratio of alcohol to oil is indicated in Table 4.4.

Table4. 4: Effect of temperature on biodiesel yield

Run number	Temperature(^{O}C)	Biodiesel Yield%(w/w)
1	35	70
2	55	87
3	75	53

Biodiesel yield was directly proportional to temperature from 35^{O}C to 55^{o}C and inversely proportional from 55^{o}C to 75^{O}C. The yield obtained at 75^{o}C was as small as the formation emulsion was facilitated. Thus, the maximum and minimum yield was obtained at a temperature of 55^{o}C and 75^{o}C, correspondingly.

4.3.2. Effect of catalyst amount on biodiesel production

Setting reaction time and mixing rate were 2 hours and 500 rpm, respectively for all runs, the effect of catalyst at 0.25% (w/w), 1.125% (w/w) and 2.0 % (w/w) sodium hydroxide on biodiesel yield at 55^{o}C temperature, 100ml oil feed and 9:1 ratio of alcohol was indicated in Table 4.5.

Table4. 5: Effect catalyst amount on biodiesel yield

Run number	Catalyst %(w/w)	Biodiesel Yield%(w/w)
1	0.25	54
2	1.125	87
3	2.0	53.5

Biodiesel yield was directly proportional to catalyst amount from 0.25% (w/w) to 1.125% (w/w) and inversely proportional from 1.125%w/w to 2.0% (w/w).

As catalyst amount increases further above the optimum amount the yield reduced as a result of formation of the soap and emulsion. Thus, biodiesel yield was achieved maximum for a catalyst amount of 1.125% (w/w) while the minimum yield was obtained at 2.0% (w/w) catalyst amount.

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

Setting reaction time and mixing rate were 2 hours and 500 rpm, respectively for all runs, the effect of molar ratio of alcohol to oil of 6:1, 9:1and 12:1 for 1.125% (w/w) catalyst, 100ml oil feed and at a temperature of 55^{o}C on biodiesel production is shown in Table 4.6.

Table4. 6: Effect Molar ratio of alcohol to oil on biodiesel yield

Run number	Molar ratio of alcohol to oil	Biodiesel Yield%(w/w)
1	6:1	74
2	9:1	87
3	12:1	78

4.4. Analysis on Biodiesel Production

Transesterification reaction was carried out at reflux of ethanol, jacketed glass reactor which is equipped with a stirrer, condenser and thermostat. The statistical analysis of the biodiesel was discussed below.

4.4.1. Statistical Analysis on Factors Affecting Biodiesel Yield

Experimental design was selected for the statistical analysis of the study by selecting Central Composite Design (CCD) and the response measured is the yield of biodiesel or fatty acid methyl esters (FAME). The three transesterification process factors chosen to be studied were reaction temperature, ratio of ethanol to oil and weight of catalyst. Regression analysis and analysis of variance (ANOVA) was done by using Design Expert 7.0.0 program. The software program was used to generate surface plots, using the fitted equation obtained from the regression analysis, keeping one of the independent variables constant.

Response of the transesterification process was used to develop a mathematical model that correlates the yield of biodiesel to the transesterification process variables studied. Design Expert software version 7.0.0 was used for the regression analysis of the experimental data and also for evaluation of the statistical significance of the equation developed.

The central composite design results and responses, and the statistical analysis of the ANOVA are given in Tables 4.7 and 4.8, respectively. The actual yield of biodiesel produced at different process parameters. The model was tested for adequacy by analysis of variance.

$$\text{Biodiesel yield } \% \left(\frac{w}{w}\right) = \frac{\text{Mass of biodesel produced}}{\text{Mass of oil feed}} \quad (4.7)$$

Table4. 7: Experimental values of biodiesel yield

Run	Temp. (^{O}C)	Ethanol to oil	Catalyst (g)	Biodiesel (ml)	Density of biodiesel (kg/m^3)	Actual biodiesel yield %(w/w)	Predicted biodiesel yield %(w/w)	Residuals %(w/w)
1	35	12	1.76	65	842	62.2	60.4	1.8
2	75	12	0.22	64	841	59.2	55.84	3.36
3	55	9	0.99	88	840	84	84.51	-0.51
4	35	6	0.22	57	839	54	57.26	-3.26
5	55	9	0.99	89	840	84.9	84.51	.39
6	75	6	1.76	61	843	58.4	54.99	3.41
7	55	9	0.99	90	840	85.9	84.51	1.39
8	35	6	1.76	59	838	56.2	59.41	-3.21
9	75	12	1.76	50	841	52.0	54.99	-2.99
10	55	9	0.99	91	840	87.0	84.51	2.49
11	35	12	0.22	63	842	58.8	57.26	1.54
12	75	6	0.22	60	839	57.2	55.84	1.36
13	55	9	0.99	90	842	85.9	84.51	1.39
14	55	12	0.99	83.7	841	79.8	80.51	-0.71
15	55	9	0.22	68	843	65.2	66.70	-1.50
16	35	9	0.99	76	842	72.7	70.06	2.64
17	55	9	1.76	56	838	53.3	51.8	1.50
18	55	6	0.99	78	842	74.6	73.51	1.09
19	75	9	0.99	89	840	54.5	56.8	-2.30
20	55	9	0.99	91	840	87.0	85.51	1,49

From Table 4.7, the maximum yield was 87.0 % (w/w), at experiment number 20 and10, while the minimum yield was 52 % (w/w), at experiment number 9. Also from the table experiment numbers 3, 5, 7, 13, 14 and 19 were maximum amount of yield gained.
Therefore it was concluded that the maximum amount of biodiesel yield was gained at 1.125% (w/w) of catalyst, 9:1molar ratio of ethanol to oil and 55^{O}C. The minimum yield was obtained at a temperature of 75^{O}C, 2% (w/w) catalyst and 12:1 molar ratio of alcohol to oil, at experiment number 9.

4.4.1.1.Development of Regression Model Equation

The model equation that correlates the response yield of vernonia galamensis oil to biodiesel to the transesterification process variables in terms of actual value after excluding the insignificant terms was given below in equation 4.8.
Final Equation in terms of coded factors:
Biodiesel yield = +82.51-2.21* B+1.08* A-14.66 * B^2-11.73* A^2 (4.8)

A= Weight of catalyst amount
B= Reaction temperature
C= Molar ratio of ethanol to oil
Table4. 8: ANOVA analysis of experimental result

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Model	3241.98	9	360.22	12.18	<0.0009	**
A- Weight of catalyst amount	0.00	1	0.00	0.00	1	
B- Reaction temperature	32.40	1	32.40	1.10	0.3258	*
C- Molar ratio of ethanol to oil	40.00	1	40.00	*1.35*	0.2783	*
AB	24.50	1	24.50	0.83	0.3893	*
AC	4.50	1	4.50	0.15	0.7066	*
BC	0.50	1	0.50	0.017	0.899	*
A^2	1207.06	1	1207.06	40.82	<0.0002	**
B^2	279.59	1	279.59	9.46	0.0152	**
C^2	1.69	1	1.69	0.057	0.0169	*
Residual	236.56	8	29.57			
Lack of Fit	235.06	5	47.01	94.02	<0.0017	**
Pure error	1.50	3	3	0.66604	0.50	**
Cor Total	3744.95	19				

Where * significant, ** highly significant

The Model F-value of 12.18 implies the model is significant. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A^2, B^2 and C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

4.4.1.2.Effect of Interaction between Process Variables

The process variables were found to have significant interaction effects. Figure 4.1, 4.3 and 4.5 shows the interaction between catalyst weight and reaction temperature, Weight of catalyst and ethanol to oil molar ratio and reaction temperature to ethanol to oil molar ratio, respectively, on the yield of biodiesel yield. Generally, an increase in reaction temperature is found to increase the yield of biodiesel up to some optimal value in all three cases.

Additionally it was observed that at lower range of reaction temperature, higher weight of catalyst and higher molar ratio of ethanol to oil, always resulted in higher yield than when using lower weight of catalyst and lower ratio of ethanol to oil.

Reactions which were carried out using lower ratio of ethanol to oil and lower weight of catalyst is found to have higher yield as compared to reactions using lower reaction temperature, higher molar ratio of ethanol to oil and higher weight of catalyst.

However, at higher range of reaction temperature, the observations showed that using a combination of both, higher reaction temperature and higher molar ratio of ethanol to oil or higher weight of catalyst used is not beneficial in increasing the yield of biodiesel. This is probably because at these conditions, the higher reaction temperature is already sufficient to push the reaction forward. This phenomenon is further supported by the fact that reaction temperature is the most significant process variable that affects the yield of the biodiesel as indicated by graphs.

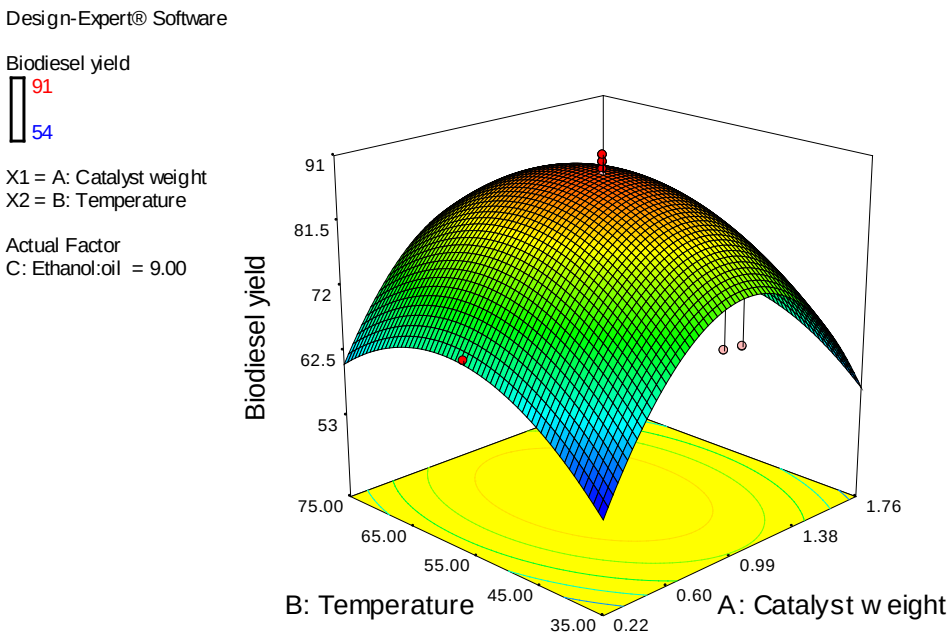


Figure4. 1: Surface plot of the interaction effect of temperature and catalyst weight versus biodiesel yield

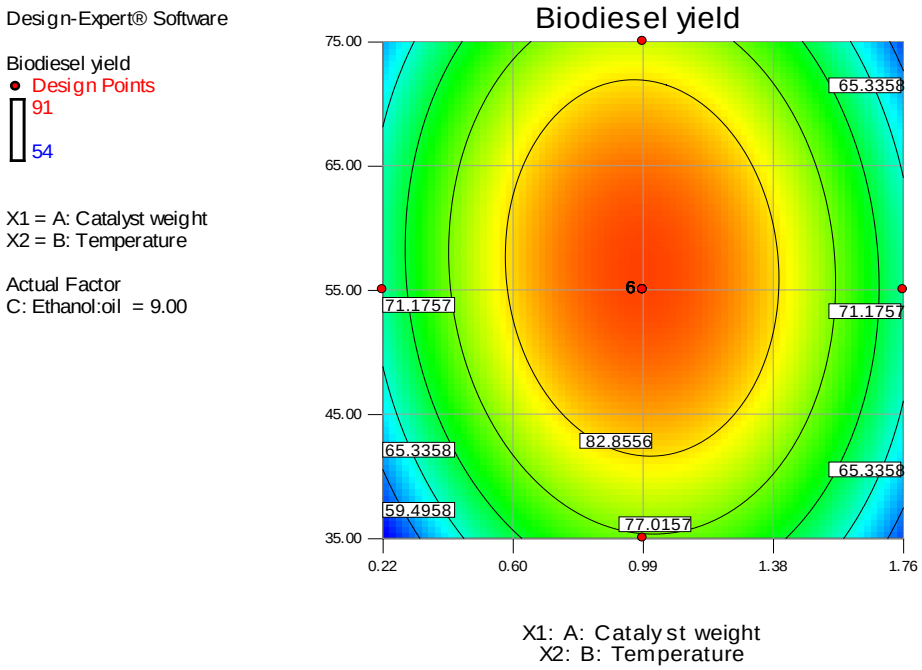


Figure4. 2: Contour plot of the interaction effect of temperature and catalyst weight versus yield

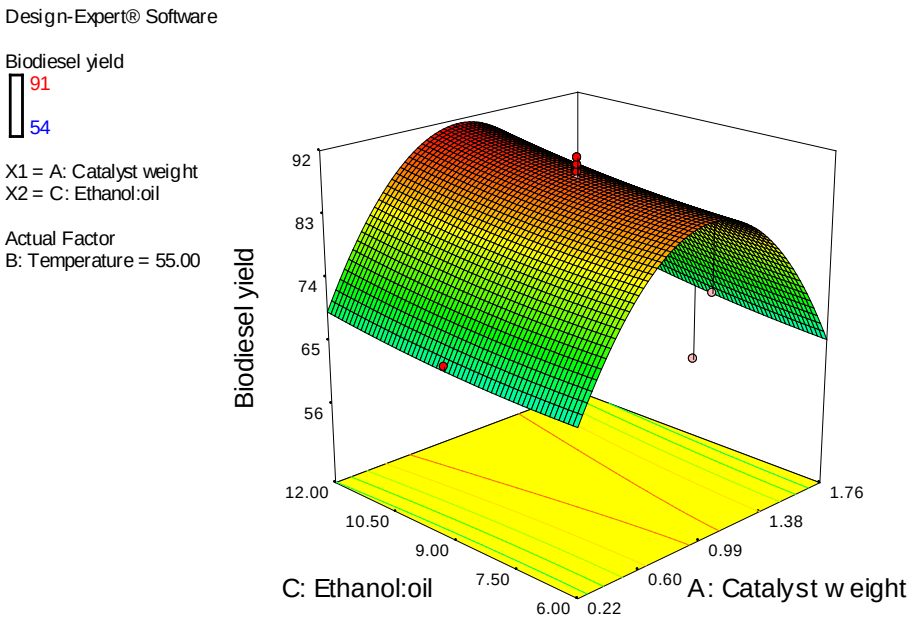


Figure4. 3: Surface plot of the interaction effect of catalyst weight and ethanol to oil molar ratio versus biodiesel yield

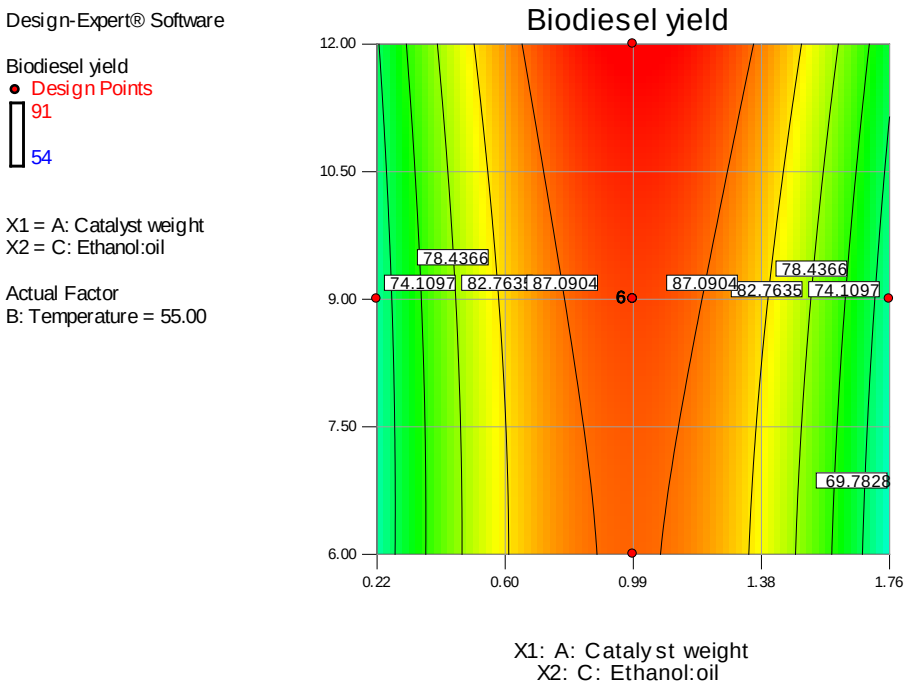


Figure4. 4: Contour plot of the interaction effect of catalyst weight and ethanol to oil molar ratio versus biodiesel yield.

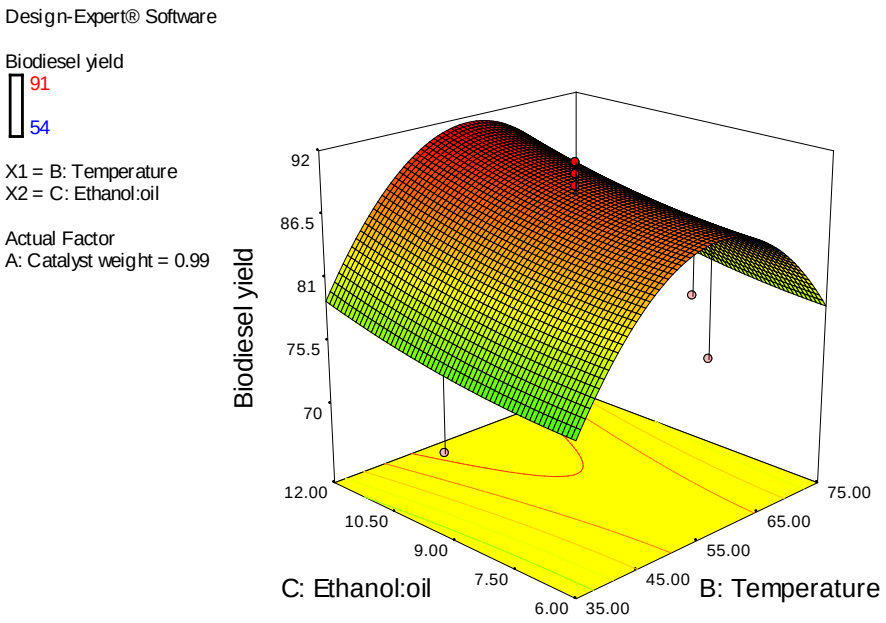


Figure4. 5: Surface plot of the interaction effect of temperature and ethanol to oil molar ratio versus on biodiesel yield.

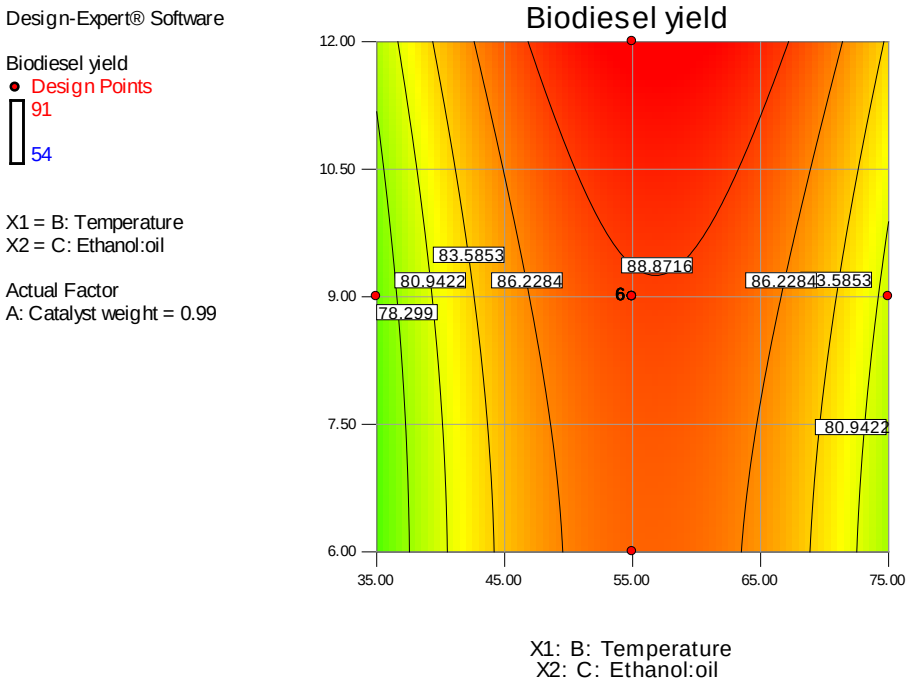


Figure4. 6: Contour plot of the interaction effect of temperature and ethanol to oil molar ratio versus on biodiesel yield

Figure 4.5 show the interaction between ethanol to oil molar ratio and weight of catalyst used, respectively on the yield of biodiesel. From Figure 4.3, the percentage of biodiesel amount increased with increasing catalyst concentration at a low ethanol to oil molar ratio. From Figure 4.1, the percentage of biodiesel amount increased with the increasing ethanol to oil molar ratio for a low reaction temperature.

4.4.1.3.Optimization of Process Variables

The above results have shown that the three transesterification process variables and their interactions among the variables affecting the yield of biodiesel. Using the optimization function in Design Expert 7.0.0, it was predicted that at the following conditions; 55^{o}C of reaction temperature, ethanol to vernonia galamensis oil ratio of 9:1 and catalyst weight 1.125% (w/w) of oil, an optimum biodiesel yield of 87% was obtained.

The optimization result showed that the same result as the ANOVA output. The ANOVA output shows that the transesterification process is highly and significantly affected by the temperature, catalyst weight and the interaction between the temperature and the catalyst.

4.4.2. Analysis of the parameters standardized effect on biodiesel yield

Analysis methods of parameters standardized effects were depended on procedures given in [29]. Biodiesel yield and analysis method are shown in Table 4.9.

4.5.Biodiesel Physicochemical Properties

Physicochemical properties analysis is conducted based on ten experimental numbers. These experiment numbers are 1, 2, 3, 4, 5, 6, 7, 13, 14 and 20 as shown in Table 4.9.

Table4. 9: Biodiesel yield used for physicochemical property analysis

Run	Temperature (^{O}C)	Ethanol to oil	Catalyst (g)	Biodiesel (ml)	Density of biodiesel (kg/m^3)	Biodiesel yield %(w/w)
1	35	12	1.76	65	842	62.2
2	75	12	0.22	64	841	59.2
3	55	9	0.99	88	840	84
4	35	6	0.22	57	839	54
5	55	9	0.99	89	840	84.9
6	75	6	1.76	61	843	58.4
7	55	9	0.99	90	840	85.9
13	55	9	0.99	90	842	85.9
14	55	12	0.99	83.7	841	79.8
20	55	9	0.99	92	840	87.0

4.5.1. Acid value of biodiesel

Titration method was used to determine the acid value of biodiesel. Experimental procedures were the same to those used in the oil acid value in Section 3.2.1.4.1. The acid value of biodiesel for each experiment number is given in Table 4.10.

$$\text{Acid value, mgKOH/gOil} = \frac{N * Mm * TV}{Ms} \quad (4.9)$$

Where:

Mm=56.1g/mol

Ms=2g

N of KOH =0.1mol/l

Tv Titration volume, ml

Table4. 90: Biodiesel acid values

Run	Temperature (^{O}C)	Ethanol to oil	Catalyst (g)	Biodiesel (ml)	Titration volume (ml)	Acid value, mgKOH/goil
1	35	12	1.76	65	0.24	0.68
2	75	12	0.22	64	0.26	0.73
3	55	9	0.99	88	0.28	0.78
4	35	6	0.22	57	0.30	0.84
5	55	9	0.99	89	0.31	0.87
6	75	6	1.76	61	0.32	0.89
7	55	9	0.99	90	0.30	0.84
13	55	9	0.99	90	0.29	0.81
14	55	12	0.99	83.7	0.31	0.87
20	55	9	0.99	92	0.29	0.81

Acid value of the biodiesel varied from 0.68mgKOH/g to 0.89mgKOH/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 determined by a titration procedure. The method was the same as for oil saponification determination in Section 3.2.1.4.2. Saponification values of the biodiesel are indicated in Table 4.11

$$Saponification\ Value, mgKOH/g = \frac{(BLTV - TV) * RF * Cm}{Ms} \quad (4.10)$$

BLTV is the blank level titration volume = 20 ml

Cm =28.05g/L

Ms=2g biodiesel sample

RF=1.006

T_V is the titration volume, ml; inserting the values in to the above equation;

Table4. 11: Saponification values of the biodiesel

Run	Temperature (^{O}C)	Ethanol to oil	Catalyst (g)	Biodiesel (ml)	T_V (ml)	BLTV (ml)	Saponification value (mgKOH/g)
1	35	12	1.76	65	12.5	20	105.82
2	75	12	0.22	64	12.8	20	101.6
3	55	9	0.99	88	12.5	20	105.82
4	35	6	0.22	57	12.8	20	101.6
5	55	9	0.99	89	12.9	20	100.2
6	75	6	1.76	61	12.2	20	110.05
7	55	9	0.99	90	12.8	20	101.6
13	55	9	0.99	90	12.7	20	103.0
14	55	12	0.99	83.7	12.1	20	111.5
20	55	9	0.99	92	12.8	20	101.6

Saponification value of the biodiesel was from 100.1mgKOH/g to 111.5 mgKOH/g. Saponification value shows the amount of biodiesel that changes to soap by KOH in the at high temperature in presence of water. Lower saponification value of the result is higher in quality of the product.

For determining the amount of residual soap in the biodiesel during the separation, the sample mixture was kept until it changed from gray to colorless where 16.7 ml of HCl titration volume (T_V) was added.

$$\text{Residual soap\%}\left(\frac{w}{w}\right)=\frac{TV*N\ of\ HCl*Mm*100\%}{1000*Mm} \quad (4.11)$$

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

Mw is mass of sample waste water=20g

N is the normality of HCl=0.1mol/l

TV=10.2ml

$$\text{Residual soap\%}\left(\frac{w}{w}\right) = \frac{10.2 * 0.1 * 304.4 * 100\%}{1000 * 20} = 1.6$$

Thus, the residual soap is about 1.6%, and the waste water was taken at the first to get the maximum amount of waste in terms of soap during glycerol separation when biodiesel was being washed.

4.5.3. Density and kinematic viscosity of biodiesel

Viscosity and density of biodiesel determining procedures are the same as oil density and viscosity measuring procedures that were explained in Sections 3.2.1.4.3 and 3.2.1.4.4. The density and viscosity of biodiesel are given in Table 4.12.

$$\text{Kinematic viscosity of oil} = \frac{\text{Dynamic viscosity of biodiesel}}{\text{Density of biodiesel}} \quad (4.12)$$

Where; 1m.Pa.s=1×10^{-3}g/mm.s

Table4. 10: Viscosity and density of the biodiesel

Run	Temperature (^{O}C)	Ethanol to oil	Catalyst (g)	FAME (ml)	Dynamic viscosity @40^{O}C (m.Pa.s)	Average density (kg/m^3)	Kinematic viscosity (mm^2/s)
1	35	12	1.76	65	3.9	842	4.63
2	75	12	0.22	64	4.5	841	5.35
3	55	9	0.99	88	2.97	840	3.54
4	35	6	0.22	57	3.2	839	3.82
5	55	9	0.99	89	2.98	840	3.55
6	75	6	1.76	61	3.01	843	3.57
7	55	9	0.99	90	2.90	840	3.52
13	55	9	0.99	90	3.08	842	3.66
14	55	12	0.99	83.7	2.95	841	3.51
20	55	9	0.99	92	3.12	840	3.71

Density of the biodiesel was from 839kg/m^3 to 843kg/m^3. Kinematic viscosity of biodiesel was from 2.90mm^2/s to 4.5mm^2/s. Thus, transesterification reaction reduced density and kinematic viscosity.

4.5.4. Flash point values of biodiesel

Flash point was determined by using an opened cup method. Measuring techniques are the same as those used for the oil flash point determination in Section 3.2.1.4.5. The biodiesel flash point values are shown in Table 4.13.

Table4. 13: Biodiesel flash point values

Run	Temperature (^{O}C)	Ethanol to oil	Catalyst(g)	Biodiesel(ml)	Flash point(^{O}C)
1	35	12	1.76	65	144
2	75	12	0.22	64	143
3	55	9	0.99	88	134
4	35	6	0.22	57	150
5	55	9	0.99	89	139
6	75	6	1.76	61	140
7	55	9	0.99	90	138
13	55	9	0.99	90	136
14	55	12	0.99	83.7	134
20	55	9	0.99	92	132

Flash point of the biodiesel was between 132^{o}C to 150^{o}C. Flash point shows the first temperature where biodiesel is going up in to flames. From Table 4.13, 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 contents of biodiesel

Determination of moisture contents of biodiesel was done in similar manner with that of oil in Sections 3.2.1.4.6 and 3.2.1.4.7, respectively. Moisture contents of the biodiesel are shown in Table 4.14.

$$\text{Moisture content}\%\left(\frac{w}{w}\right) = \frac{W_1 - W_2}{W_1} * 100\% \quad (4.13)$$

Table4. 114: Moisture content of biodiesel

Run	Temperature (^{O}C)	Ethanol to oil	Catalyst(g)	Biodiesel (ml)	Moisture content %(w/w)
1	35	12	1.76	65	0.013
2	75	12	0.22	64	0.015
3	55	9	0.99	88	0.017
4	35	6	0.22	57	0.014
5	55	9	0.99	89	0.011
6	75	6	1.76	61	0.019
7	55	9	0.99	90	0.019
13	55	9	0.99	90	0.015
14	55	12	0.99	83.7	0.014
20	55	9	0.99	92	0.016

Moisture content was determined to be from 0.011% (w/w) to 0.019% (w/w) in the biodiesel. If there is high moisture content in the biodiesel, it 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, such as poor drying [23]. Thus, the moisture content was obtained in the biodiesel was very small in amount as the biodiesel was dried in an oven for longer period of time at 105^{O}C.

4.5.6. Ash contents of biodiesel

Determination of ash contents of biodiesel was done in similar manner with that of oil in Sections 3.2.1.4.6 and 3.2.1.4.7, respectively. Ash contents of the biodiesel are shown in Table 4.15.

$$\text{Ash content } \% \left(\frac{w}{w}\right) = \frac{\text{Final mass of biodiesel after burning} * 100\%}{\text{Initial mass of sample}} \qquad (4.14)$$

Table4.15: Ash contents of the biodiesel

Run	Temperature (^{O}C)	Ethanol to oil	Catalyst (g)	Biodiesel(ml)	Moisture content % (w/w)
1	35	12	1.76	65	0.021
2	75	12	0.22	64	0.022
3	55	9	0.99	88	0.019
4	35	6	0.22	57	0.029
5	55	9	0.99	89	0.023
6	75	6	1.76	61	0.024
7	55	9	0.99	90	0.022
13	55	9	0.99	90	0.027
14	55	12	0.99	83.7	0.020
20	55	9	0.99	92	0.021

The ash content of biodiesel was from 0.019% (w/w) to 0.029% (w/w). If high ash content is present, it shows that the biodiesel has solid materials that are resulted from catalysts during transesterification reaction or seed cake during oil extraction process [23]. But the feed oil was refined and the biodiesel was washed with warm water and distilled water, with better mixing, low ash content was gained.

4.6.Comparison of Biodiesel Physicochemical Properties against Standards

Comparisons of biodiesel physicochemical properties against standard specifications are given in Table 4.18.

Table4. 12: Comparison of biodiesel physicochemical properties against standards

Biodiesel properties	Measured values	ASTM Standard
Density @ 20^{o}C (kg/m^{3})	839-843	875-900
Kinematic viscosity @40^{o}C (mm^{2}/s)	2.90 -4.50	1.9-6.0
Flash point (^{o}C)	132 – 150	$\geq$130
Acid value (mgKOH/g)	0.68 -0.89	$\leq$0.8
Saponification value (mgKOH/g)	115.5-124.5	-
Moisture content % (w/w)	0.011 -0.019	< 0.03
Ash content% (w/w)	0.019 -0.029	< 0.02
Iodine value (I_2g/100g)	-	$\leq$120
Cetane number	-	$\geq$47

Properties of biodiesel were under standard specification of ASTM. Iodine value and cetane number were not done due to lack of reagent chemicals and equipment. 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 [23].

5. Economic Evaluation

5.1.1. Process description and technology selection for biodiesel production from vernonia galamensis

The extracted oil is neutralized with sodium hydroxide after the oil free fatty acid (FFA) is determined at a temperature of 70^{o}C. The mixture of oil and NaOH solution is recommended to stir at 200 rpm for 1 hour. The mixture should be washed with a hot distilled water to remove a trace NaOH and produced soap. Finally, trace water is removed in an oven drying at a temperature of 105^{o}C for 6 hours. Then ethanol and sodium hydroxide are mixed in the mixer with standard agitator to facilitate the mixing. Alkali hydroxide is dissolved in the alcohol to produce alkoxide solution. Ethanol and sodium hydroxide mixture is then charged into a closed reaction vessel and the oil is added for 2 hour transesterification reaction at 500 rpm. It is recommended to have the catalyst amount as 1.125% of the weight of oil and the ethanol: oil to be 9:1 molar ratio. The reaction system is totally closed to the atmosphere to prevent the loss of ethanol, since it is easily vaporizable. The reaction mixture is kept at 55 ^{O}C which results the optimum amount of biodiesel.

After the reaction is completed, there exists glycerol and biodiesel formation. Both have a significant amount of the excess alcohol that was used in the reaction which is in need of being recovered. The 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. Then excess alcohol in each phase is removed with a flash evaporation process or by distillation commonly.

Finally the Biodiesel is separated from the glycerol, it is sometimes purified by washing gently with warm water to remove residual catalyst, alcohol or soaps to make more pure. The washed biodiesel needs drying in order to remove trace impurities at 105^{O}C for more than 6 hours.

Basic Operating Methods

After discussing the basic production process of biodiesel, the next judgment concerns how the plant will actually be worked. Three basic alternatives: batch, continuous or batch-continuous processes [32].

Batch Operation: One batch of feedstock is done without depending on the next for all processes such as pretreatment, reaction, separation and purification. Batch operations can easily be established and stopped, are good for facilities that do not function for 24 hours a day.

Continuous Operation: The process is an unending flow of feed stocks, reactions and purification. These operations are typically of the largest and most efficient ways of integrating energy and mass units. These operations are dependent upon a consistent feedstock, typically single sourced, and are sensitive to process conditions.

Batch-Continuous Operation: This operation endeavors to obtain the advantages of both of batch and continuous operations. It is based on reactors that feed the feedstock at once and continuously discharging the product or continuously adding the feedstock and discharging the product at once, a continuous separation and purification process. It used to control the reaction process and change feed stocks more rapidly than the continuous and batch operations. Table 5.1 compares characteristics of the batch with the continuous operations.

Table5. 1: Comparisons of batch and continuous operations

Characteristics	Batch	Continuous
Typical capital cost	Less	Greater
Economy of scale	< 10 million gallons per year	> 10 million gallons per year
Feedstock flexibility	Greater flexibility	Less flexibility
Consumption of input	Greater	Less
Operating cost per gallon	Greater	Less
Product yield	Less	Greater
Typical plant size	Smaller	Larger

(Source: Frazier Barnes & Associates, Memphis, TN)

From the alternatives given in Table 5.1, a continuous process is selected to be well matched with current production capacity for producing biodiesel from vernonia galamensis plant commercially.

5.2.Material balance on major unit operations

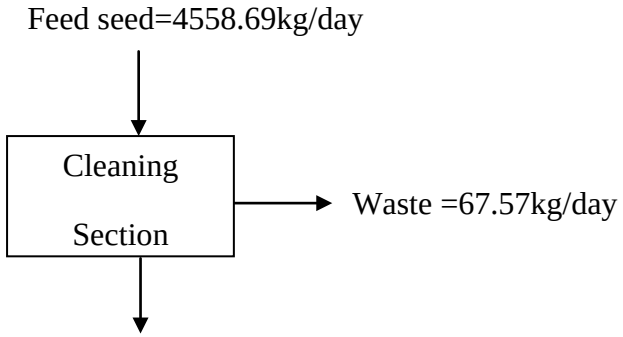
Capacity:

- Production capacity of the biodiesel plant will be 1000kg per day.
- There will be a need of 1257.57kg/day cleaned oil as 80% (w/w) of biodiesel is gained. Because 87% cannot be directly used as optimization number since the efficiency of production cannot achieve.
- There will be a need of 4491.32kg/day cleaned vernonia galamensis seed as 35 % (w/w) of the seed will be oil. .

1. Cleaning Section

Let's assume 1.482% of the total feed is rejected as a waste.

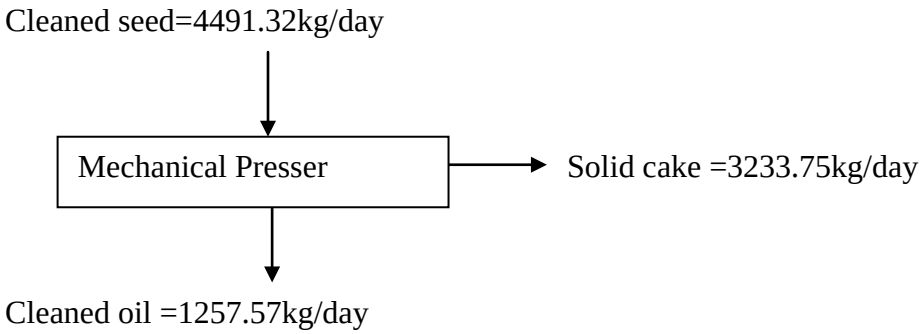
Waste =0.01482*4558.69kg/day=67.57kg/day



2. Mechanical Presser

Mechanical presser is 80% efficient and only 35% (w/w) of seed will be oil.

Cleaned seed=1257.57kg / (0.8*0.35) = 4491.32kg/day

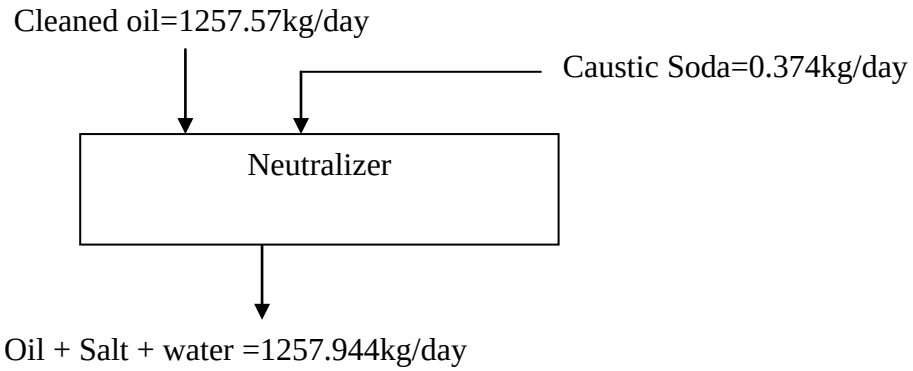


3. Neutralizer

The amount of caustic soda needed for neutralization was 0.374kg/day. Calculation is clearly done in the annex1.

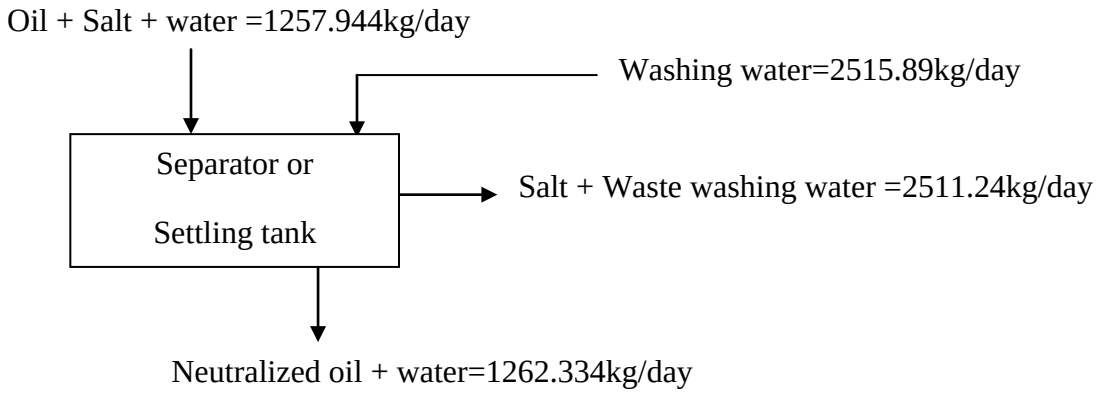
$$HOOCR + NaOH \longrightarrow NaOOCR + H_2O$$

Free fatty acid Sodium hydroxide Sodium soap Water



4. Separator (Settling Tank)

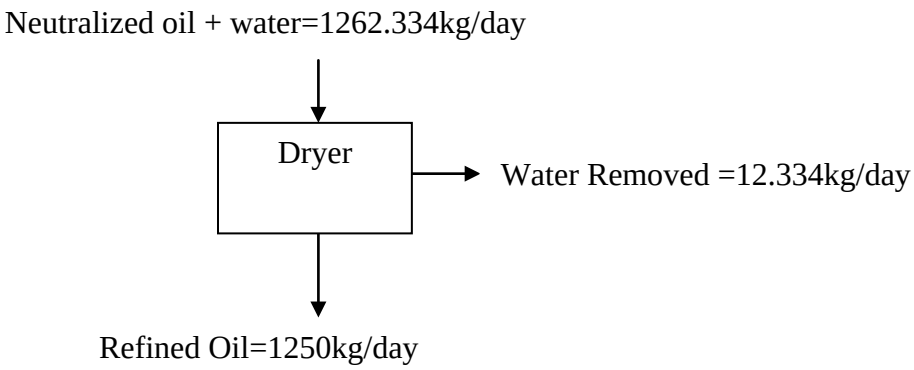
The water and soap stock formed is assumed to be removed together with NaOH when washing is applied. And the washing water is twice that of the mixture and one percent of the mixture is water to be dried.



5. Dryer

From the oil about 99.02% (w/w) of water is removed in the drier as it has been checked in laboratory works.

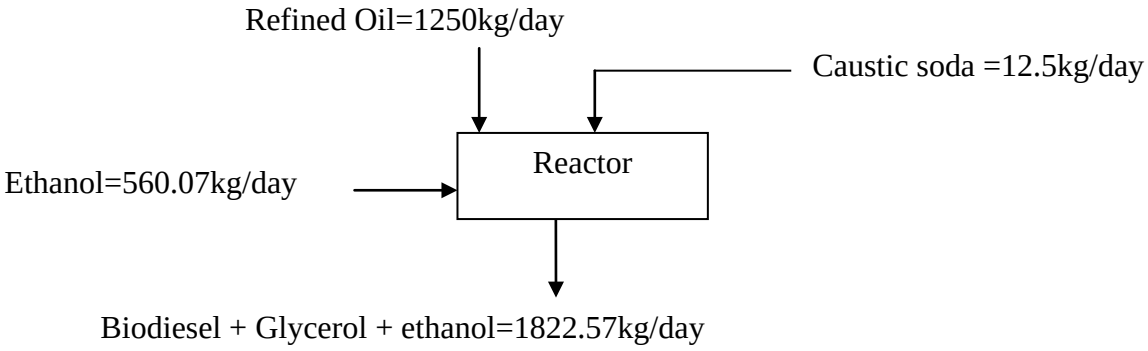
Water Removed = (1-0.9902)*1262.334kg/day=12.334kg/day



6. Reactor

For optimum biodiesel yield the ethanol to oil ratio is 9:1 and the catalyst amount is 1.125% (w/w) of oil. Therefore for 1250kg/day oil 560.07kg/day ethanol is used, and there will be a need of 12.5kg/day caustic soda.

Caustic soda=0.01*1250kg/day=12.5kg/day



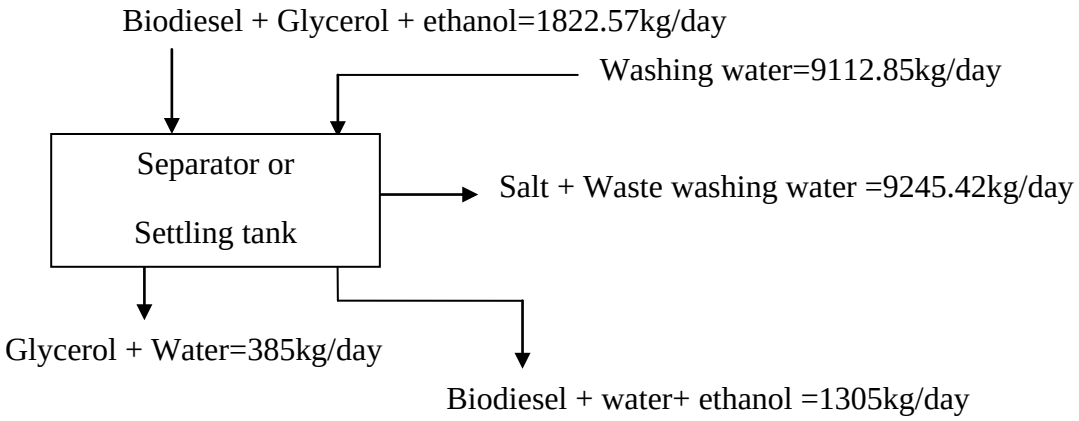
7. Separator (Settling Tank)

The glycerol formed is assumed to be removed together with NaOH when washing is applied. And the washing water is five times that of the mixture and one percent of the mixture is water to be dried. The transesterification reaction is taking place in the presence of a suitable catalyst such as alkali or acid and glycerol is the only byproduct produced. Approximately 100 kg of oil reacts with 40 kg of ethanol to produce 100 kg of biodiesel and 40 kg of glycerol [30]. Therefore approximately 30 % of weight of oil will be converted in to glycerol. Thus, 375kg/day of glycerol can be collected. As the glycerol is very difficult to separate adding 10 kg of hot distilled water before settling is proper

before washing for ease of collecting the glycerol. And ethanol and water in the washed biodiesel approximately were 0.5% (w/w) and 30% (w/w) of the purified biodiesel.

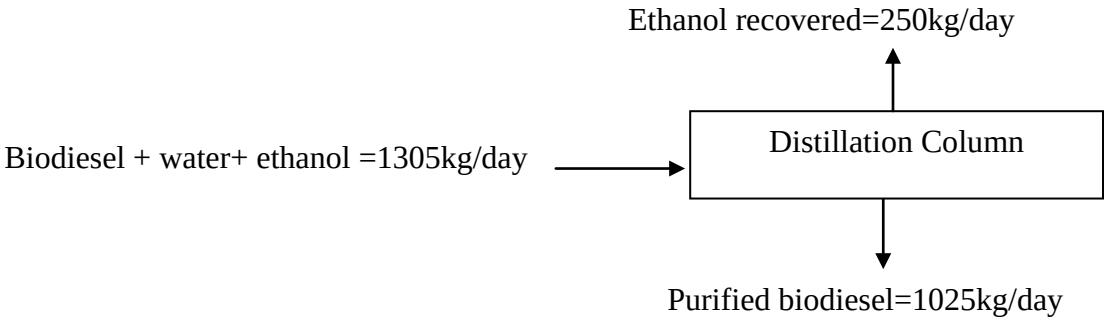
Glycerol + Water=0.3*1250kg/day+10kg/day=485kg/day

Washing water=5*1822.57kg/day=9112.85kg/day



8. Balance on distillation column

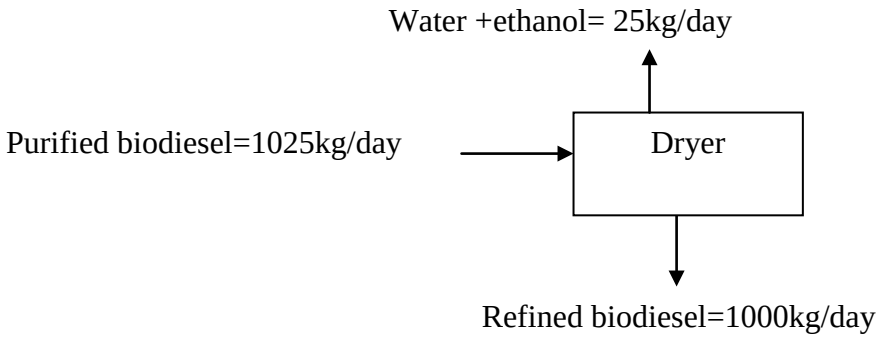
In the distillation column there is only a recovery of 250kg ethanol from 300kg ethanol.



9. Dryer

In the drier about 2.439% (w/w) purified biodiesel is removed as water and ethanol.

Water +ethanol= 0.02439*1025kg/day=25kg/day



5.3.Energy balance on major unit operations

1. Balance on Neutralizer

To achieve full neutralization in one hour of mixing the temperature had to be 70^0C. The amount of caustic soda added for neutralization was 0.0297 %(w/w) of the cleaned oil.

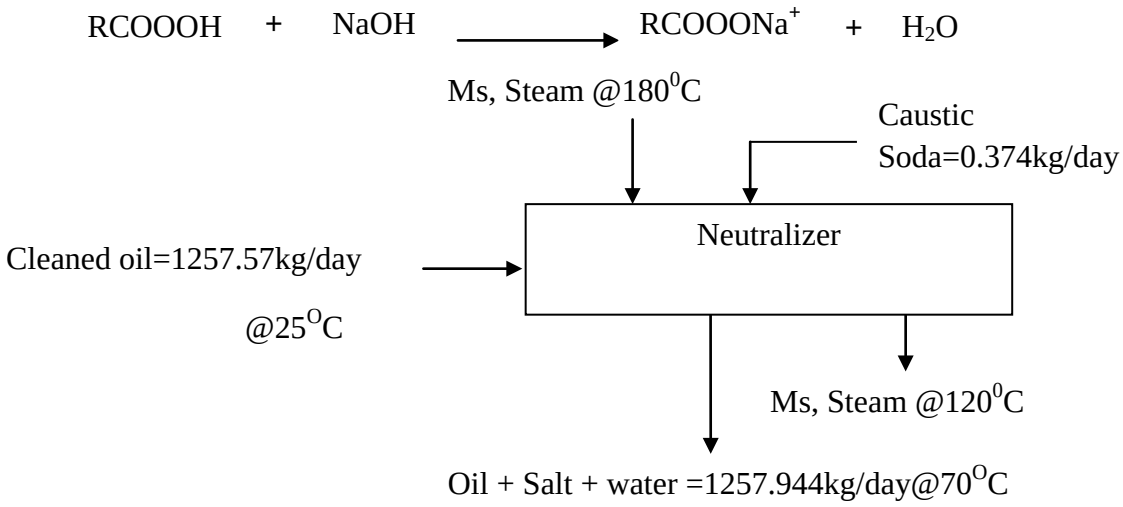
Assumption:

Specific heat is constant (little change in temperature rise)

Steam is available at 180^0C and given out at 120^0C (for later use in the heater)

Heat of reaction is not significant.

Reference temperature=25^0C



Component	Specific heat (kJ/kg ^{0}C)
Vernonia galamensis oil	2.18
NaOH	0.781
Purified vernonia galamensis oil	2.21

Total balance:

Input +generated –consumed –output=0;

Assumption: Heat generated =0; Heat consumed=0

Input=Output
Where:
Ls= Latent heat of steam
Ls @180^{o}C =2800kJ/kg

Ls @120^{o}C =2500 kJ/kg

Q_{VG} + Q $_{NaOH}$ + Q $_{VG}$ in=Q purified $_{VG}$ + Q steam, out; Where; VG=Vernonia galamensis

MVG*Cp*ΔT + M NaOH*Cp *ΔT+Ms*Ls, in =M purified $_{VG}$*Cp*ΔT + Ms*Ls, out

1257.57kg/day*2.18*kJ/kg ^{O}C*(25 ^{O}C -25 ^{O}C) +0.781*0.374kg/day* (25^{O}C-25^{O}C) +2800kJ/kg*Ms=1257.944kg/day*2.21kJ/kg *(70^{O}C-25^{O}C) +M_S*2500kJ/kg

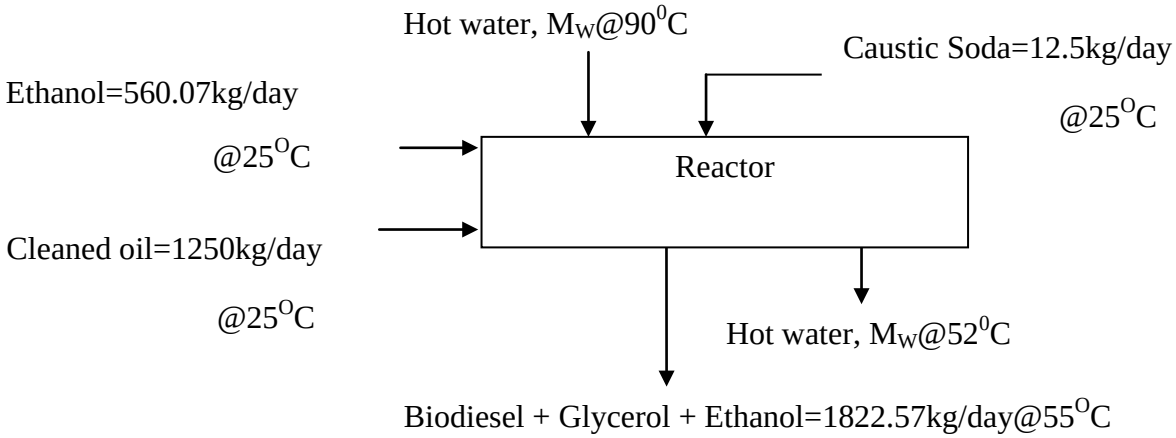
2800kJ/kg*M_S-2500kJ/kg*M_S=125102.53kJ/kg day

300kJ/kg*M_S=125102.53kJ/kg day

M_S=417.01kg/day

2. Balance on Reactor

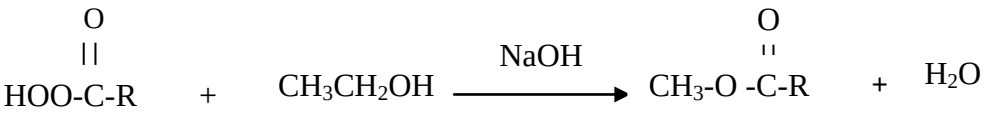
For producing an optimum amount of biodiesel yield the temperature inside the reactor should be maintained at 55^{0}C. This temperature is assumed to be achieved by supplying hot water at 90^{O}C and this temperature is assumed to fall to 52^{0}C so that the temperature inside the reactor is adjusted to the required value after charging the needed alcohol and catalyst at reference temperature.



Assumption:

The specific heat is constant for a given liquids for small change of temperature.

The major component of free fatty acid in the vernonia galamensis oil is vernolic acid. Where; R= $(CH_2)13\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3$,



Heat of reaction (Hrx) = [(2 mol *O-C +1mol *C=O + 2mol*H-O + 9mol* C-C + 2mol* C=C + 32mol* C-H) – (2mol*O-C +1mol *C=O + 2mol*H-O + 9mol* C-C + 2mol* C=C + 32mol* C-H)] =0

Therefore, input = output;

$Q_{Ethanol} + Q_{Hot\ Water} + Q_{Cleaned\ oil} + Q_{Caustic\ Soda} = Q_{Biodiesel + Glycerol + ethanol} + Q_{Hot\ Water}$

$M_{Ethanol}*Cp_{Ethanol}*\Delta T + M_{Hot\ Water}*Cp_{Hot\ Water}*\Delta T + M_{Cleaned\ oil}*Cp_{Cleaned\ oil}*\Delta T + M_{Caustic\ Soda}*Cp_{Caustic\ Soda}*\Delta T = Q_{Biodiesel + Glycerol + ethanol} + Q_{Hot\ Water}$

$0 + M_{Hot\ Water} + 4.18*(90-55) + 0 + 0 = M_{Biodiesel + Glycerol + ethanol} * 1.99*(55-25)$

$146.3* M_{Hot\ Water} = 1822.57*59.7$

$M_{Hot\ Water} = 743.73 kg/day$

3. Balance on distillation column

Assumptions:

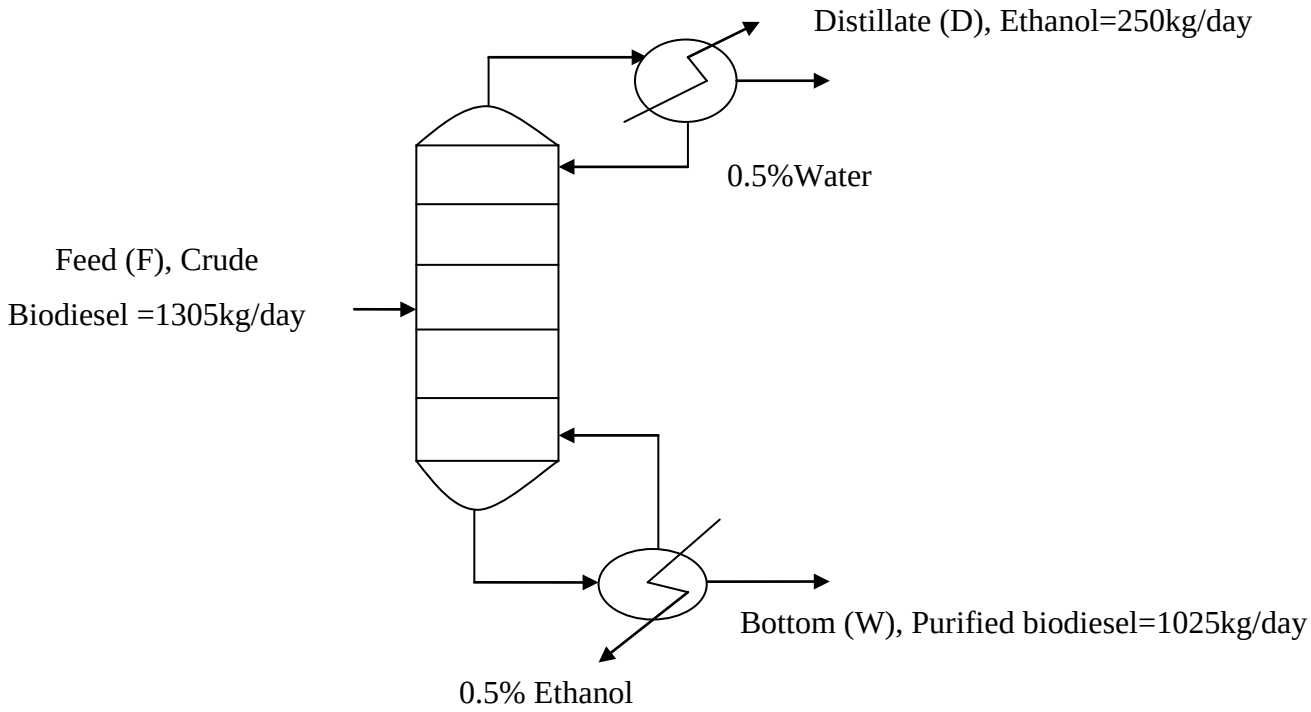
The balance is with no chemical reaction and used to determine the mass of cooling water and steam required for the distillation column operation.

Steam is available at 180^0C and 1 bar.

The rise in cooling water temperature is limited to 30^0C.

Distillation column operates at 1 bar.

The distillate contains 0.5% water and the bottom contains 0.5% ethanol.



Potential and kinetic energy of the process stream will be small and ignored. The energy balance can be done on the condenser and Re-boiler.

Inputs: Re-boiler Heat, Q_B + feed sensible heat H_F.

Outputs**:** Condenser Cooling Q_C + top and bottom product sensible heats ($H_D + H_W$).

To minimize heat losses from the system the column and exchangers are properly covered and will be neglected.

In the column the residence time is 2 hours at 25^0C.

Heat capacity data were taken from Coulson and Richardson, 2005 (V-1) that is average values.

Ethanol @ 20 ^{0}C to 60 ^{0}C, 2.47kJ/kg^{0}C

Crude biodiesel: 1.99kJ/kg^{0}C, Heat capacities can be taken as additive

Basis: 25^0C, 1 residence time for 2 hours in the column

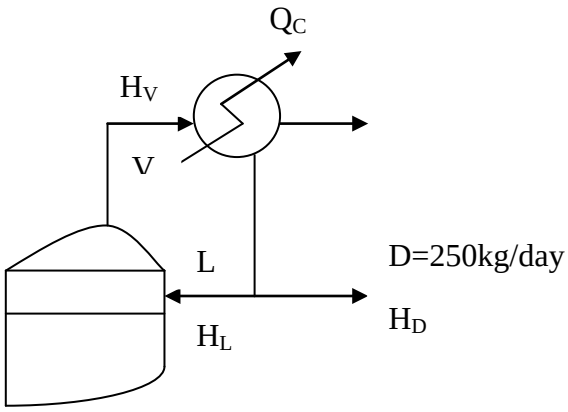
Water: 25^0C to 100^0C, 4.21kJ/kg^{0}C and it is assumed constant in the range

Feed = 0.836* 2.41 + 0.164* 1.12 = 2.28kJ/kg^{0}C

Tops, 99.5 percent ethanol = 0.995 *2.47 + 0.005 * 4.21 = 2.48kJ/kg^{0}C

Bottoms, 99.5 percent biodiesel and 0.5 percent water; Cp=0.995*2.34+0.005* 4.21 kJ/kg^{0}C= 2.48 kJ/kg^{0}C

Q_C must be determined by taking a balance round the condenser



Where:

V=Vapor flow

L=Reflux flow

H=Enthalpy

R=L/ D=0.58 (This value is taken from optimal value of design)

L= 0.58*250kg/day = 145 kg/day

V = L+D = 145 kg/day + 250kg/day=395kg/day

Boiling point of 99 percent ethanol/water = 78^0C

At steady state:

Input = output

$H_V = H_D + H_L + Q_C$

Hence; $Q_C = H_V - H_D - H_L$

Assume complete condensation is taking place

Enthalpy of vapor H_V = Latent heat + Sensible heat

Latent heat of ethanol at 78 ^{0}C =2430 kJ/kg

Latent heat of water at 78 ^{0}C=3330 kJ/kg

Taking latent heats as additive

H_V = 250 *[(0.005*2430 + 0.995*3330) + (78-25) *2.41)] =863,307.7 kJ/hr.

The enthalpy of the top product and reflux are zero, because they are at the reference temperature. Both are liquid, and the reflux will be at the same temperature as the product. Therefore, $Q_C = H_V$ = 863,307.7 kJ/day; Q_B can be determined from a balance over entire system

Input=Output

$Q_B + H_F = QC + HD + HW$

HF=1305*1.99(25-25) =0

H_W= 1025*4.21*(80-25) = 280,491.25kJ/day; output temperature of the bottom product is taken to be 80 ^{O}C.

So; $Q_B = Q_C + H_W + H_D$

Q_B=863,307.7 kJ/day+280,491.25kJ/day

Q_B=1,143,798.95kg/day; Q_B is supplied by condensing steam.

Latent heat of steam =2835.7kJ/kg at 180^{0}C

Steam required =1,143,798.95/2835.7 = 403.36kg/day

Q_C is removed by cooling water with a temperature rise of 25 ^{0}C

Q_C =water flow * 25*4.21

Water flow= 863,307.7 kJ/day/105.25=8,202.45kg/day

5.4.Preliminary Equipment specifications and sizing

Storage tanks are sized depended on daily requirement; they can store and the assumption that the plant works for 2 shifts and 8 hour with 10% safety factor for the volume. And for the tanks it should be given 30 days allowance for storage and 80%for design safety.

Amount of ethanol = 1day*16hr/24hr*560.07kg/day=373.38 kg

Volume of tank = 373.38 kg /800.00 kg/m^3 =0.467m^3 and for the 10% safety factor;

Volume of tank=0.467m^3+0.1*0.467m^3=0.514m^3/day*30day=15.42m^3

By the similar approach,

Sodium hydroxide storage tank = 4.43*$10^{-3}$$m^3$/day*30day=0.133$m^3$

Oil storage tank= 1.048m^3/day*30day=31.44m^3

Glycerol storage tank = 0.348m^3/day*30day=10.44m^3

Biodiesel storage tank = 0.873m^3/day*30day=26.19m^3

Neutralization tank=0.66m^3/day*30day=19.8m^3

Transesterification reactor=0.298m^3 /0.8=0.3725m^3

Ethanol/catalyst mixer=0.095m^3/0.8=0.11m^3

Heater=0.546m^3/0.8=0.683m^3

Rough sizing of distillation column provides a height of 1.5 m and a diameter of 0.3 m.

5.5. Estimation of Total Capital Investment

Purchase equipment cost estimation

Purchased cost for some basic plant equipments are estimated from the empirical relations provided by [31] and www.Matche/Equipcost/index.com.

The cost (C^0_R) of the jacketed, agitated, well-mixed reactors is calculated based on the following equation [31].

$$C^0_R = 15000\ V^{0.55} \quad (5.1)$$

Where V is the volume of reactor in m^3 and applies for materials constructed from stainless steel and reactor volumes between 0.1 m^3 and 20 m^3.

The Costs (C^0_V) of mixing and pH adjustment tanks can be calculated using the following equation [31].

$$C^0_V = 12080 + V^{0.525} \quad (5.2)$$

Where V is the volume of reactor in m^3 and applies for materials constructed from stainless steel and reactor volumes between 0.1 m^3 and 70 m^3.

The cost of field erected, stainless steel storage tanks that are smallest and can be calculated using the following equation [31].

$$C^0_{ST} = 65000 + 158.7V \quad (5.3)$$

Where V is the storage tank volume in m^3 and applies for construction from stainless steel.

Table5. 2: Purchased Equipment Cost estimation

Equipment	Amount	Size(m^3)	Unit Cost ($)	Total Cost ($)
Storage tanks				
Ethanol	1	15.42	900.00	900.00
Sodium hydroxide	1	0.133	800.00	800.00
Biodiesel	1	26.19	1,000.00	1,000.00
Glycerol	1	10.44	4,000.00	4,000.00
Process equipments				
Ethanol/catalyst mixer	1	0.118	8,700.00	8,700.00
Pump	20	-	9000.00	18,000.00
Transesterification reactor	1	0.373	9,000.00	9,000.00
Dryer	1	-	5,000.00	5,000.00
Neutralization tank	1	0.19.8	8,700.00	8,700.00
Mechanical presser	1	-	4,500.00	4,500.00
Distillation column	1	-	6,000.00	6,000.00
Settling tank(Separator)	1	-	4,000.00	5,000.00
Heater	1	0.683	9,500.00	9,500.00
Conveyer	3	-	600.00	1,800.00
			Total cost in ($)	**87,400.00**
			Total cost in(Birr)	**1,573,200.00**

Estimation of Fixed Capital Investment

Table5. 3: Estimation of Fixed Capital Investment

	Components	Factors	Cost(birr)
1.Direct cost	Purchased equipment cost (PEC)	PEC	1,573,200.00
	Equipment erection	0.05PEC	78,660.00
	Piping	0.02 PEC	31,464.00
	Electricity	0.01 PEC	15,732.00
	Building	0.05 PEC	78,660.00
	Utilities	0.025 PEC	39,330.00
	Storage	0.025 PEC	39,330.00
	Total Direct Cost		**1,856,376.00**
2.Indirect cost	Design and Engineering	0.02 PEC	31,464.00
	Contractors fee	0.05 PEC	78,660.00
	Contingency	0.01 PEC	15,732.00
	Total Indirect Cost		**125,856.00**
3.Fixed Capital Investment	**FCI =Direct Cost + Indirect Cost=1,982,232.00Birr**		
4.Working Capital (WC)	0.05FCI		**99,111.6.00Birr**
5.Total Capital Investment	FCI+WC		**2,081,343.60Birr**

5.6. Estimation of Total Production Cost

Cost of raw materials

The cost of each raw material per year is estimated by multiplying the raw material required per day by 200 working days per year and 16 working hours per day, and then multiplying by raw material unit price.

Table5. 4: Cost of raw materials

Raw material	Quantity per annum (kg/year)	Unit price (birr/kg)	Total cost (birr)
Vernonia galamensis	911,738.00	0.300	273,521.40
Ethanol	62,014.00	10.00	620,140.00
Sulfuric acid	200	12.00	2400.00
Sodium hydroxide	2,574.8	16.0	41,196.80
		Total	**937,258.20**

Annual utility cost estimation

Annual utility cost estimation can be determined from energy balance by calculating the total amount of steam, water and electricity cost.

Current price one tonne of steam=650.00 Birr/tonne

Total amount of steam required per year =83.402 tonne/yr

Cost of steam =54,211.13Birr/yr

Current price of electricity=0.46cents/kWh

Total power used annually = 40,000kWh/yr

Cost of current = birr 18,400Birr/yr

Water: current price = 0.26 birr per 20 liter

Total amount of water required per year = 247,449.00kg/yr

Cost of water = 3,217.9birr/yr

Total utility cost = 75,829.03 birr/yr

Table5. 5: Operating labor cost estimation

Work specification	No. Required	Monthly salary (birr)	Yearly salary (birr)
Manager	1	4,500.00	54,000.00
Production head	1	2,000.00	24,000.00
Quality head	1	2,600.00	31,200.00
Purchasing and sales head	1	2,300.00	27,600.00
Accountant	1	1,500.00	18,000.00
Secretary	1	1,100.00	13,200.00
Laboratory technician	1	1,500.00	18,000.00
Mechanics	1	1100.00	13,200.00
Production line worker	4	700.00	33,600.00
Raw material storage area workers	1	600.00	7,200.00
Final product storage area workers	1	600.00	72,000.00
Drivers	1	800.00	9,600.00
Security guard	2	600.00	14,400.00
Cleaners	2	600.00	14,400.00
Total	**19**	**415,200.00**	**415,200.00**

Table5. 6: Estimation of Total Product Cost

	Components	Factors	Cost (birr)
1.**Manufacturing cost**	**A. Direct production cost**		
	1.Raw material cost	Calculated	937,258.20
	2.Operating Labor (OL)	Calculated	415,200.00
	3.Direct supervision	10%OL	41,520.00
	4. Utilities	Calculated	75,829.03
	5. Maintenance and repair	0.4% FCI	7,928.93
	6. Laboratory charges	1%OL	4,152.00
	Direct production cost		**1,483,688.20**
	B. Fixed charges		
	1.Depreciation	8%FCI	158,578.56
	2.Capital charge	1%FCI	19,822.32
	3.Insurance	1%FCI	19,822.32
	Fixed charges		198,223.20
	C. plant overhead	5%OL	**20,760.00**
	A+B+C=manufacturing cost		**1,702,671.40**
2.General expenses	1.Adminstrative cost	2%TPC	32,960.52
	2.Distribution and selling cost	2%TPC	32,960.52
	3. R&D	2%TPC	32,960.52

Total production cost (TPC) = Manufacturing cost + General expenses

TPC = 1,702,671.40+ 6%TPC

TPC-0.06TPC=1,702,671.40

TPC = 1,811,352.60 birr/year

Unit cost of biodiesel=10.00birr/liter

Annually earning of biodiesel= 2,811,352.60birr/yr

Unit cost of solid cake=1.00birr/kg

Annually earning of solid cake = 646,750kg/yr* 1.00birr/kg=646,750.00birr/yr

Unit cost of glycerol=2.00birr/kg

Annually earning of glycerol = 75,000.00kg/yr* 2.00birr/kg=150,000.00birr/yr

Therefore total annual earning=3,180,203.40birr/yr

Table5. 7: Projected cash flow of the plant

Year	0	1	2	3	4	5	6	7
Capacity utilization%	-	70	80	100	100	100	100	100
I. Cash inflow(birr)	-	2,226,142.38	2,544,162.72	3,180,203.40	3,180,203.40	3,180,203.40	3,180,203.40	3,180,203.40
Income(birr)	-	2,226,142.38	2,544,162.72	3,180,203.40	3,180,203.40	3,180,203.40	3,180,203.40	3,180,203.40
Salvage value(birr)		-	-	-	-	-	-	-
II. Cash outflow(birr)	2,081,343.60	1,309,256.68	1,496,293.34	1,870,366.68	1,870,366.68	1,870,366.68	1,870,366.68	1,870,366.68
Investment (birr)	2,081,343.60	-	-	-	-	-	-	-
RM &others(birr)	-	1,113,857.34	1,272,979.82	1,591,224.77	1,591,224.77	1,591,224.77	1,591,224.77	1,591,224.77
Utilities(birr)	-	53,080.32	60,663.22	75,829.03	75,829.03	75,829.03	75,829.03	75,829.03
Factory overheads (birr)	-	14,532.00	16,608.00	20,760.00	20,760.00	20,760.00	20,760.00	20,760.00
Depreciation(birr)	-	111,004.99	126,862.85	158,578.56	158,578.56	158,578.56	158,578.56	158,578.56
Capital charges(birr)	-	19,179.46	19,179.46	23,974.32	23,974.32	23,974.32	23,974.32	23,974.32
Interest (20%)	-							
Gross Profit(birr) (I-II)	-2,081,343.60	916,887.70	1,047,869.38	1,309,836.72	1,309,836.72	1,309,836.72	1,309,836.72	1,309,836.72
Net profit(birr)	-2,081,343.60	916,887.70	1,047,869.38	1,309,836.72	1,309,836.72	261,967.34	261,967.34	261,967.34

Year	Cumulative cash flow	Yearly cash flow
	-2,081,343.60	
1st year	-1,164,455.90	916,887.70
2nd year	-102,085.50	1,047,869.38
3rd year	945,783.88	1,309,836.72

Payback period= 2 years+$\frac{102,085.50}{1,047,869.38}$

Payback period=2.1years

6. Conclusions and Recommendations

6.1. Conclusions

Biodiesel was produced using sodium hydroxide and ethanol alcohol catalyst at constant reaction time of 2 hours, mixing rate of 500 rpm and at atmospheric pressure. Production of biodiesel was performed by batch process system. The effects of amount of sodium hydroxide catalyst, reaction temperature and molar ratio of alcohol to oil on biodiesel yield were determined. By using Design Expert 7.0.0 soft ware three levels; three factor Central Composite Design with full type, when reaction temperature, catalyst amount and molar ratio of alcohol to oil were increased, the biodiesel yield increased until the optimal amount. However, further addition of these working variables during transesterification reaction results in reduction of biodiesel yield due to formation of emulsion which made difficulty in the separation of biodiesel from glycerol.

Additionally, it was observed that the biodiesel yield has a quadratic response with temperature and catalyst weight and linear response with alcohol to oil ratio. From these three parameters and their interaction effects, the highest effect on biodiesel yield was observed due to molar ratio of alcohol to oil with both catalyst weight and temperature while the effect of temperature and catalyst weight was small relatively. The interaction effect of the three operating parameters was significantly detected on biodiesel yield.

The maximum biodiesel yield was attained at a temperature of 55^{o}C, 1.125% (w/w) NaOH catalyst amount and for 9:1 molar ratio of alcohol to oil. In contrast, the average minimum biodiesel yield was at 75^{o}C, 12:1 molar ratio and 2% (w/w) catalyst amount. The physicochemical properties of the biodiesel were determined, within ASTM standard values. Hence, the produced biodiesel can be used as an engine fuel.

Based on an existing production process and using current best values for reagent, equipment, and supply costs an economic analysis it is suggested that the production cost of vernonia galamensis biodiesel would be approximately Birr 10.00birr/l. Thus, the preliminary economic analysis evaluation suggested that the project is feasible. Therefore, vernonia galamensis can be used as a less expensive supplementary feedstock for biodiesel production by curing the environment and increasing the agricultural earning.

6.2. Recommendations

The oil was extracted using both solvent extraction and mechanical pressing; though, solvent extraction was difficult because of high cost of hexane. For this reason, mechanical pressing must be used in better accuracy. Biodiesel was produced using ethanol alcohol and non edible vernonia galamensis oil which are available locally. Consequently, consideration must be given to produce biodiesel as substitute of diesel fuel.

Biodiesel was produced using an alkali catalyzed transesterification reaction that results large amount of washing water as waste. Although, production of biodiesel using ethanol and acid catalyzed, enzymatic catalyzed or heterogeneous catalyzed transesterification reaction should be explored. Biodiesel production was done in batch process system; but, production should be conducted in continuous process system.

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. Even though, there was loss of yield with the glycerol. In consequence, Efficiency of separation process should be improved.

Rotary evaporator and distillation were conducted at atmospheric pressure and recovery of ethanol alcohol using a rotary evaporator or a distillation was used at high temperature that is boiling point of alcohol. During alcohol recovery using a rotary evaporator or a distillation, the catalyst should be neutralized before evaporation of alcohol to reduce further unwanted reaction due to higher temperature; instead vacuum flash evaporation should be used.

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

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Annexes

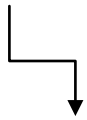
Annex1. Molecular Mass of Triglyceride Calculation

1. R is the alkyl group of triglyceride components (vernolic, palmitic, stearic, oleic and linoleic)
2. Vernolic Acid: R = - (CH2)16– CH_3, 18 carbons and 1 double bonds (18:1) and oxygen
3. Palmitic: R = - (CH2)14 – CH3, 16 carbons and 0 double bonds (16:0)
4. Stearic: R = - (CH2)16 – CH3, 18 carbons and 0 double bonds (18:0)
5. Linoleic: R = - (CH2)7 CH=CH-CH2-CH=CH (CH2)4CH3, 18 carbons and 2 double bonds (18:2)
6. Oleic: R = - (CH2)7 CH=CH (CH2)7CH3, 18 carbons and 1 double bond (18:1)

Table0. 1: Percentage composition of free fatty acid

Vernonia galamensis oil fatty acid types	Vernonia galamensis oil fatty acid composition (%)
Vernolic (18:1:1)	78-80%
Palmitic (16:0)	2-3%
Oleic(18:1)	2-3%
Linoleic acid (18:2)	10-12%
Stearic acid(18:0)	0-2%
Average molecular weight	926 g/mol

RCH_2OOC



Molecular mass of CH_2OOH=58g/mol

Molecular mass of Triglyceride=Molecular mass of vernolic acid + Molecular mass Palmitic Acid + Molecular mass Stearic Acid +Linoleic Acid +Oleic Acid

Molecular mass of Triglyceride= [14*16+15+58]*0.8+ [14*14+15+58]*0.03+ [17*16+15+58]*0.02+ [17*16+31+58]*0.12+ [17*16+33+58]*0.03

Molecular mass of Triglyceride= [297]*0.8+ [269]*0.03+ [345]*0.02+ [361]*0.12+ [363]*0.03

Molecular mass of Triglyceride=306.78g/mol

FFA% (w/w) =0.224% (w/w) of oil and Degumming does not reduce the total amount of oil. In one gram of oil, $0.224*10^{-}2=2.24*10^{-}3$gFFA was existed and $2.973*10^{-}4$g NaOH /g oil of was required to neutralize.

Annex 2. Equipments Used for Experimental Works

Equipments that were used in laboratory session are measuring cylinder, analytical balance, agitator, mill grinder, oil presser, rotary evaporator, condenser, heater, vibro viscometer, hydrometer, jacketed reactor, thermometer, pH meter, separator funnel, vacuum filter, centrifuge, flask, beaker, furnace and oven dryer were used for biodiesel production and its property analysis in the experimental works.

Annex 3. Saponification value calculation

The saponification number was determined by using titration. The solution was prepared with the required concentration. Since the exact concentration was not known, we have to standardize the solution. Thus, primary and secondary standardization was used.

Mass of KOH = N * equivalent weight * Volume of solution in liter =0.5mol/lit *56.1g/mol*1lit= 28.055gm

Mass of HCL= N*equivalent weight*Volume of solution in liter=0.5*36.5*1 =18.25gm

V HCL=m/ρ=18.25/1.16 =15.73ml and 0.2 gm of sodium hydroxide was dilute in 100ml distilled water was used as a primary standard with a known concentration which is 0.1 normality.

25ml solution of sodium hydroxide was taken and titrated with HCL solution to determine the concentration using 3 drops of methyl orange as indicator. The Volume was noted as the end point appears.

$V_1N_1=V_2N_2$

$N_2= (V_1N_1)/V_2$ =25*0.1/5.4 =0.46

Another experiment was done to validate the concentration;

N_2=25*0.1/5.5=0.4545

N_3=25*0.1/5.4 =0.46

Then the average concentration becomes;

NHCL=0.46

Similarly, HCL is used to standardize the ethanolic alcohol solution. Then 25ml of ethanolic KOH was titrated against HCL using 3 drop methyl orange as indicator to determine the exact concentration of ethanolic KOH. The volume of HCL was noted.

$N_{31}= (V_2N_2)/V_3$ =34.7*0.46/25 =0.634

N_{32}= (33.9*0.46)/ 25=0.619

N_{33}= (33.8*0.46) /25 =0.623

N KOH=0.625

5gm of oil was dissolved in ethanolic KOH and titrated with HCL. Blank titration was done titrating ethanolic KOH against HCL. In both cases, the volume of HCL was recorded.

Annex 4. Effect of variables on biodiesel yield

Effect of temperature on biodiesel yield

As the temperature was increased from 35^{o}C to 55^{o}C, the yield increased. The yield had inverse relation with reaction temperature between 55^{o}C and 75^{o}C. The effect of temperature on biodiesel yield is a quadratic response as shown in Figure 0.1.

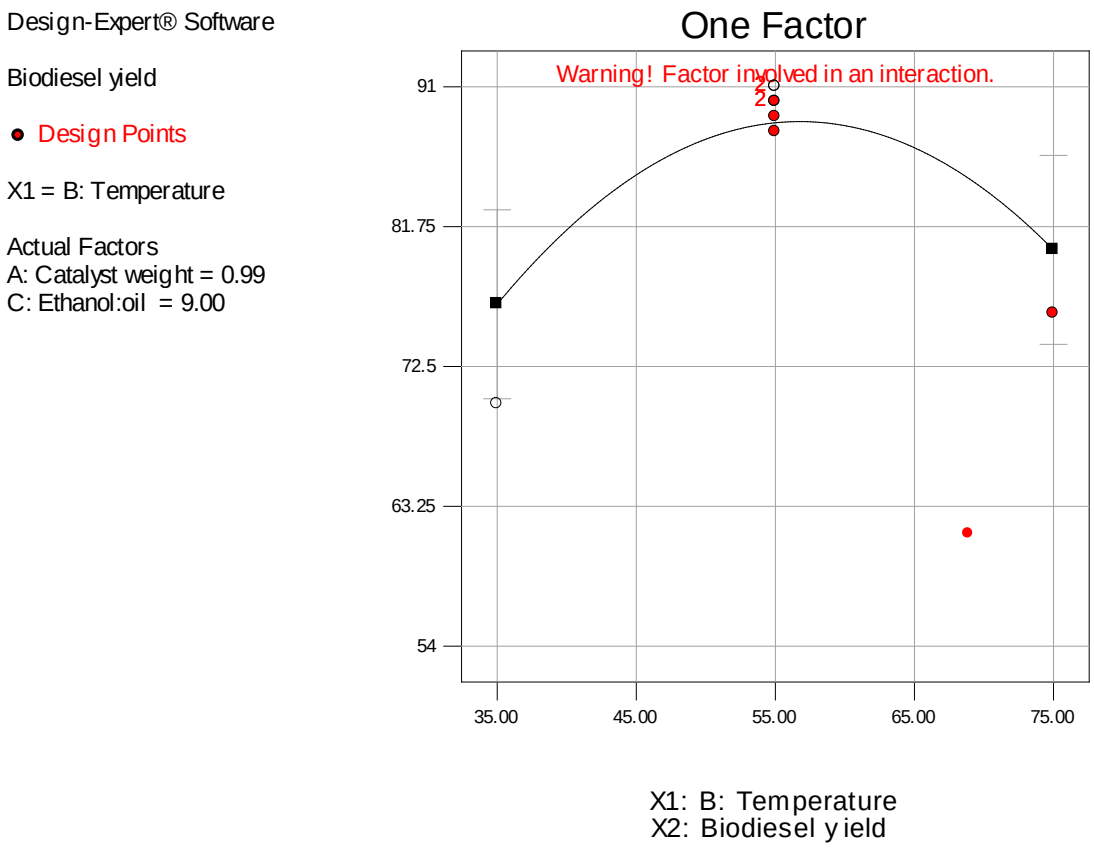


Figure0.1: Effect of temperature on biodiesel

Effect of NaOH catalyst weight on biodiesel yield

When the amount of catalyst was increased from 0.25 %(w/w) to 1.125 %(w/w), the yield increased. Biodiesel yield had direct relation with the catalyst amount between 0.25% (w/w) and 1.125% (w/w). The effect of amount of NaOH catalyst alone on yield is a quadratic response shown in Figure 0.2.

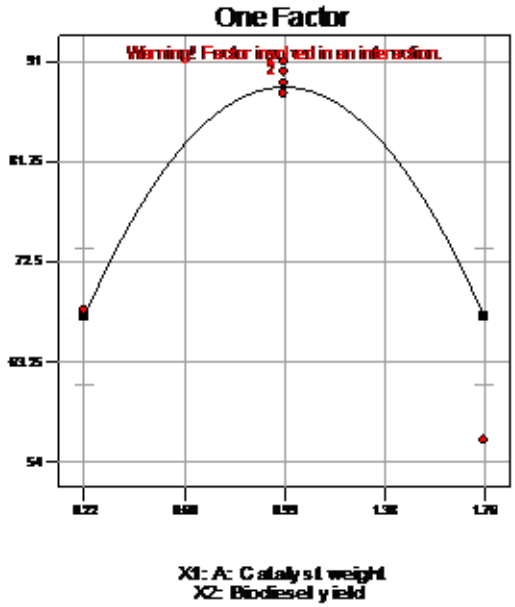


Figure0. 2: Effect of catalyst on biodiesel yield

Effect of alcohol on biodiesel yield

When the amount of alcohol to oil molar ratio was increased from 6:1 to 9:1, the yield of biodiesel increased. The yield of biodiesel had direct relation with alcohol to oil molar ratio between 6:1 and 9:1 and the effect of alcohol alone on yield is a linear response as shown in Figure 0.3.

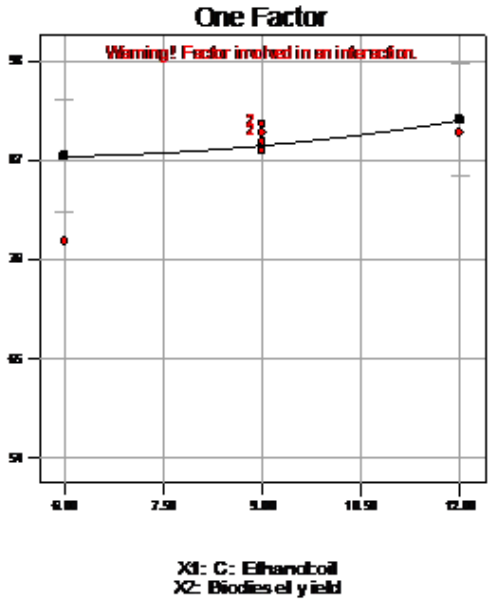


Figure0. 3: Effect of alcohol on biodiesel yield

Annex 5. Laboratory work images

Figure0. 4: Separation of biodiesel from glycerol phase

Figure0. 5: Purified biodiesel

Declaration

I, the under signed, declare that this thesis is my own work and that all sources of material used for the thesis have been accordingly acknowledged.

_____ _____

Enkuahone Abebe Date

This is to certify that the above declaration made by the candidate is correct to the best of my Knowledge.

_____ _____

Advisor, Gizachew Shiferaw (Eng.) Date